The influence of second phases on the microstructural evolution and the mechanical properties of geological materials.

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Part I: The influence of a pore second phase on the microstructural evolution of halite during grain growth

2. Relevant background on grain growth and second phases

2.1. Normal grain growth
   2.1.1. The stages of grain growth
   2.1.2. Behaviour up to the onset of grain growth
   2.1.3. Characteristics of normal grain growth
      2.1.3.1. Driving forces and theoretical analysis
      2.1.3.2. Observed kinetics
      2.1.3.3. Grain size distributions
   2.1.4. Factors leading to the cessation of growth

2.2. Abnormal grain growth

2.3. Second phase influence on grain growth
   2.3.1. Mineral second phases
   2.3.2. Solute impurities
   2.3.3. Pores as second phases

2.4. Quantifying second phase effects
   2.4.1. Zener parameter
   2.4.2. Zener plot
   2.4.3. Refinements of the Zener parameter

2.5. Previous work on halite boundary migration and diffusion kinetics
   2.5.1. Past work on halite grain boundary migration
   2.5.2. Past work on halite diffusion kinetics

3. Experimental strategy for the 200 MPa confining pressure tests

3.1. Starting material
3.2. Experimental apparatus 75
  3.2.1. Nimonic 1 75
    3.2.1.1. The central section 80
    3.2.1.2. Top closure section and sealing units 80
    3.2.1.3. Bottom closure section 83
    3.2.1.4. Maintenance during the project 85
  3.2.2. Thermal profile calibration 85

3.3. Experimental procedure 88
  3.3.1. Sample fabrication and assembly 88
  3.3.2. Pressurising and heating procedure 91
  3.3.3. Data logging and end test procedures 91
  3.3.4. Thin-section preparation 92

3.4. Data acquisition 94
  3.4.1. Grain size data 94
  3.4.2. Grain size distribution data 95
  3.4.3. Electron microscope imaging 98
    3.4.3.1. Electron microscope operating conditions 98
    3.4.3.2. Pore analysis procedures 99

3.5. Data analysis 102
  3.5.1. Establishing grain growth start time and starting grain size 102
  3.5.2. Evaluation of the grain growth exponent 104
  3.5.3. Evaluation of the rate term in the growth equation 105
  3.5.4. Complications introduced by anomalous samples 105
  3.5.5. Fitting grain size distributions 106
    3.5.5.1. Fitting the log normal distribution 106
    3.5.5.2. Fitting the Weibull distribution 109
  3.5.6. Analysis of porosity using Zener plots 109

3.6. Confidence in the grain and pore size measurements, pore volume fraction determination, and kinetic value determination 112

4. Experimental results I: 200 MPa confining pressure tests 117

4.1. Starting material characterization 117

4.2. Summary of experiments carried out 119

4.3. Survey of the datasets obtained at 200 MPa confining pressure 119
  4.3.1. 330 °C 119
  4.3.2. 380 °C 125
  4.3.3. 437 °C 130
  4.3.4. 480 °C 135
  4.3.5. 500 °C 140
  4.3.6. 511 °C 146
  4.3.7. 600 °C 152

4.4. Synthesis of the 200 MPa confining pressure results 158
  4.4.1. Normal grain growth start time and start grain size 158
  4.4.2. Normal grain growth kinetics 160
4.5. Summary of the 200 MPa confining pressure results 163

5. Experimental results II: Anomalous samples and the influence of porosity 167

5.1. Observations of abnormal grain growth 167

5.2. Experiments at different confining pressures 171

6. Experimental results III: Zener parameter analysis of porosity effects 175

6.1. 330 °C 176
  6.1.1. HL24 176
  6.1.2. HL21 182
  6.1.3. 330 °C comparison 188

6.2. 380 °C 190
  6.2.1. HL17 190

6.3. 437 °C 196
  6.3.1. HL9 196

6.4. 480 °C 202
  6.4.1. HL29 202

6.5. 500 °C 209
  6.5.1. HP14 209
  6.5.2. HP21 215
  6.5.3. 500 °C comparison 221

6.6. 511 °C 223
  6.6.1. HL7 223
  6.6.2. HL5 229
  6.6.3. 511 °C comparison 235

6.7. 600 °C 237
  6.7.1. HP37 237

7. Discussion of halite grain growth and the influence of second phase porosity 243

7.1. Microstructural observations 243

7.2. Normal grain growth kinetics 245
  7.2.1. Grain growth start time and starting grain size 245
  7.2.2. Grain size distributions 247
  7.2.3. Grain growth exponent 248
  7.2.4. Activation enthalpy for grain growth 249

7.3. The influence of porosity 253
  7.3.1. The influence of pore size 254
  7.3.2. The influence of pore volume fraction 255
7.3.3. The Zener parameter and the comparative influence of its constituents 256

7.4. Model of pore-influenced grain growth 258
    7.4.1. Pore elimination > pore accumulation 259
    7.4.2. Pore accumulation > pore elimination 260
    7.4.3. The effect of temperature 264

7.5. Comparison with previous grain growth studies 265

Part II: The influence of a calcite second phase on the mechanical behaviour of two phase calcite + halite aggregates 271

8. Relevant background to the calcite + halite neutron diffraction tests 271
    8.1. The strength of materials 271
        8.1.1. Contiguity 272
        8.1.2. Mean free path 274
        8.1.3. Yield strength, load transfer and their relation to contiguity and mean free path 274
        8.1.4. The Hall-Petch effect 277
    8.2. Calcite 278
        8.2.1. Calcite crystal structure 278
        8.2.2. Relevant mechanical characteristics of calcite 279
    8.3. Halite 280
        8.3.1. Crystal structure 280
        8.3.2. Relevant mechanical characteristics of halite 281

9. Experimental strategy for the calcite + halite neutron diffraction tests 283
    9.1. Principles of neutron diffraction experiments 283
        9.1.1. The ISIS facility at the Rutherford Appleton Laboratory 283
        9.1.2. The production of neutrons at ISIS 284
        9.1.3. The ENGIN-X beamline 285
            9.1.3.1. Experimental set up on ENGIN-X 288
        9.1.4. Sample fabrication 290
            9.1.4.1. Volume fraction determination 290
            9.1.4.2. Pressing 291
    9.2. Diffraction pattern analysis 294
        9.2.1. The General Structure Analysis System (GSAS) 294
        9.2.2. Whole pattern fitting 295
        9.2.3. Single peak fitting 299
    9.3. Porosity and volume fraction determination 306
    9.4. Stress and strain analysis 307
        9.4.1. Axial stress applied to the sample 307
        9.4.2. Calculation of strains 307
        9.4.3. Calculation of stresses 311
9.5. Microstructural analysis
9.5.1. Measuring calcite contiguity
9.5.2. Measuring halite mean free path
9.5.3. Confidence in the mean free path equation variables

10. Results from the calcite + halite neutron diffraction tests
10.1. Contiguity and mean free path results
10.1.1. Contiguity and mean free path as a result of calcite volume fraction
10.1.1.1. Microstructural observations
10.1.1.2. Calcite contiguity observations
10.1.1.3. Mean free path observations
10.1.2. Contiguity and mean free path as a function of calcite size
10.1.2.1. Microstructural observations
10.1.2.2. Contiguity observations
10.1.2.3. Mean free path observations

10.2. Mechanical results
10.2.1. General description of the deformation response
10.2.2. Variation of the mechanical response with calcite contiguity and mean free path
10.2.2.1. Correlation of yield stress with calcite contiguity and mean free path
10.2.2.2. Correlation of post-yield load transfer with calcite contiguity and mean free path

11. Discussion of the calcite + halite neutron diffraction tests
11.1. Summary of key findings
11.2. The effect of mean free path and calcite contiguity on halite yielding
11.3. The effect of mean free path and calcite contiguity on load transfer after halite yield

Part III: Summary

12. Conclusions and future work
12.1. Conclusions
12.2. Future work

13. References

14. Appendix – On disk
14.1. Plots used to determine the most appropriate growth exponent for each temperature set
14.2. List of experiments carried out during this study
14.3. Tracings used to determine grain size distributions
14.4. Grain boundary and pore tracings from SEM images used to determined the pore size distributions and the Zener parameter

14.5. Full tabulations and plots for ENGX tests

Word count from Introduction onwards: 69,020 words.
Fig. 2.1. Schematic graph displaying the four stages of grain growth. \( D_0 \) is the starting grain size, \( D \) is the grain size and \( D_f \) is the final maximum grain size. (Adapted from Covey-Crump and Rutter, 1989).

Fig. 2.2. Photomicrograph of calcite displaying characteristic equilibrium normal grain growth textures. (From Covey-Crump, 1997).

Fig. 2.3. Schematic diagram of grain boundary migration driven by surface energy in a recrystallizing aggregate. The starting microstructure is seen in the upper image. Note the starting shape of grains “s” and “b”. In this aggregate, grain “s” is shrinking, and grain “b” is growing. Grain boundary migration is shown by the arrows. Initially, triple junctions migrate to form dihedral angles of 120° which results in grain boundaries becoming curved. Grain boundary migration is towards the radius of curvature. This results in the small grains shrinking and the larger grains growing. Visually, growing grains have grain boundaries that are concave outwards while shrinking grains have convex outwards boundaries. (From Platt and Behr, 2011).

Fig. 2.4. Probability distribution plot comparing the Weibull distribution of Fayad et al. (1999) (dots) to the data of Rios (1999) (solid line). The dashed line is the classic quasi-stationary distribution of Hillert (1965). \( R \) is grain radius. (Adapted from Rios, 2000).

Fig. 2.5. Abnormal grain growth in nickel annealed at 0.9\( T_m \) for 30 seconds then at 0.5\( T_m \) for 30 minutes. Note the clear microstructural differences between the smaller matrix grains and the large abnormal grains. (From Lee et al., 2000b).

Fig. 2.6. Diagram of the effect that second phases have on the migrating boundary of a matrix grain depending on the relative strength of driving and pinning forces. (Adapted from Krabbendam et al., 2003).

Fig. 2.7. Schematic diagram of the differences between rigid (left) and deformable (right) second phases. The dihedral angle (\( \Psi \)) is more likely to approach equilibrium in the deformable particle and thus will result in a more efficient pinning regime. The dragging force exerted is dependent upon the deformability and boundary energies of each phase. Breakaway occurs if the migration force exceeds the pinning force. (Adapted from Evans et al., 2001).

Fig. 2.8. Diagram of the ideal pinning regimes found in natural rocks. (Adapted from Brodhag et al., 2011)

Fig. 2.9. Deformation mechanism map showing stress vs. grain size for olivine. Strain rate (dashed lines) in \( s^{-1} \). The map also includes the stress/recrystallized grain size curve for olivine (heavy line). The solid arrows represent the evolution of a rock undergoing recrystallization while deforming at constant strain-rate. Accompanying the reduction in grain size is a drop in strength. In a monomineralic system, grain growth would then take place, and the rock would proceed along the dashed arrow, the overall result being an increase in rock strength. If the system contains second phases it is possible that the rock would remain in a weaker, smaller grain state owing to the pinning force of the second phases. (Adapted from de Bresser et al., 2001).

Fig. 2.10. Schematic diagrams displaying the variation in the major terms in Eq. 2.13 and Eq. 2.14 with distance (x) across a planar grain boundary (vertical line). a) Chemical potential energy of the impurity. b) Interaction energy of the impurity and boundary. c) Solute impurity distribution for a stationary boundary (solid line) and a boundary migrating at low velocity (dashed line). Boundary migration is from left to right. \(-\alpha \) and \( +\alpha \) represent the potential boundary width. d) Diffusivity across the boundary. (Modified from Humphreys and Hatherly, 2004).

Fig. 2.11. Schematic graph of the hypothesized form of the grain boundary velocity curves as a function of the driving force at different boundary impurity concentrations (\( C_B \)) where \( C_B < C_{B1} < C_{B2} < C_{B3} \). Dashed lines represent the discontinuous transition from each regime. (Modified from Humphreys and Hatherly, 2004).

Fig. 2.12. Schematic diagram of the material transport mechanisms in operation during sintering and densification. The material sources are displayed in Tab. 2.2. (Adapted from Kang, 2005).
Fig. 2.13. Schematic diagrams displaying the effect of varying the Zener parameter. Black ellipses are second phases and the clear grains are the matrix phase. In rocks with smaller Z values, the growing matrix will interact with the second phases at a smaller grain size than in rocks with large Z values. This has the potential to keep the grain size smaller. (Adapted from Herwegh and Berger, 2004).

Fig. 2.14. Example Zener plot of calcite stable matrix grain size vs. Zener parameter. Note the clear discrimination between pore controlled and boundary controlled fields. Note that even through the slope of the data points in the “Weakly affected by second phase” region are horizontal, this is rarely the case. Typically a reduction in the slope occurs. (From Herwegh and Berger, 2004).

Fig. 2.15. Experimental data obtained by Brodtag and Herwegh (2010) for static grain growth tests using norcamphor and glass spheres. The graphs display the linear relationship, and hence dependence, of a) n and b) k on Z when growth is influenced by second phases. There is no change in n and k at larger values of Z, that is the original normal grain growth equation (Eq. 2.8) then applies (From Brodtag and Herwegh, 2010).

Fig. 3.1. Diagram of the Nimonic 1 triaxial deformation apparatus. The apparatus is top loading. It is capable of confining pressures of approximately 300 MPa and temperatures of approximately 700°C (Covey-Crump, 1992). (Diagram adapted from Mariani, 2002).

Fig. 3.2. Photograph of the Nimonic 1 apparatus showing the components above the support frame (see Fig. 3.1). The image displays the machine as it would look inside its protective cage during an experiment.

Fig. 3.3. Image of the Nimonic 1 apparatus with the thermal insulation removed in order to show the furnace configuration.

Fig. 3.4. Photograph of the upper piston sealing unit (shown upside down).

Fig. 3.5. Photograph displaying the tapered top edge of the stainless steel mitre block.

Fig. 3.6. Photograph of the split mitre ring section of the top sealing unit.

Fig. 3.7. Photograph of the internal load cell unit used in the Nimonic 1 apparatus emphasizing the sealing arrangement. When in the machine, the lower piston extension piece sits flush with the threaded end of the force gauge.

Fig. 3.8. Photograph displaying the universal axial load joint.

Fig. 3.9. Graph displaying the thermal profile of Nimonic 1 taken in January 2011. The grey rectangle and the black dot represent the sample and the position of the thermocouple respectively.

Fig. 3.10. Graph displaying the thermal profile of Nimonic 1 taken in January 2012. The grey rectangle and the black dot represent the sample and the position of the thermocouple respectively.

Fig. 3.11. Photograph of the one side of the split-die assembly. The main body of the split-die is 8 cm tall. The copper jacket is in the same position as it would be while fabricating the sample. Whilst tamping the staring material into the jacket, the two halves of the split-die were secured together via four bolts.

Fig. 3.12. Left: Schematic diagram of the sample assembly. Right: Photograph of the assembly. Scale applies to both images.

Fig. 3.13. Photograph of the Engis Kent Mark II rotating polisher. The machine polishes samples through rotation of the polishing plate and lateral movement of the arm that holds the thin-section. The thin-section holder itself is free to rotate thus improving polishing efficiency. 15 cm ruler for scale.

Fig. 3.14. Top: Photomicrograph of HP65 (500°C, 00d 08h 00m). Middle: Grain boundary tracing of the above photomicrograph completed using Adobe Illustrator. Bottom: Image produced after processing the tracing in ImageJ. Width of all three images is 1450 µm.

Fig. 3.15. Top: Scanning electron microscope image of HL7 (511°C, 00d 05h 00m). Middle: Grain boundary tracing image produced after being analysed by ImageJ. Bottom: Pore tracing image produced after being analysed by ImageJ. The width of all three images is 1555 µm.

Fig. 3.16. Graph displaying the 500°C data set. The data set has been fitted to the normal grain growth equation using values of $n$ (0.25), $d_0$ (45 µm) and $t_0$ (10 sec). Note that no obvious change in slope is visible.

Fig. 3.17. Graph displaying the grain growth data for the 500°C data after fitting to the normal grain growth equation using values of $n$ (0.25), $d_0$ (100 µm) and $t_0$ (48200 sec).

Fig. 3.18. Plot of 500°C tests fitted to the normal grain growth equation using values of $d_0$ (100 µm) and $t_0$ (48200 sec) and $n$ values of 0.25, 0.33 and 0.5. The slope of the line of best fit (m) is included for each $n$. 

10
value. The most appropriate value of $n$ is that with a best fit line closest to 1. In this case, $n = 0.25$
represents the best fit. The dashed line has a slope of 1.................................................................104

**Fig. 3.19.** Graph displaying the grain growth data for the 500 °C data set fitted to the normal grain growth equation using values of $n$ (0.25), $d_0$ (100 µm) and $t_0$ (48200 sec). The circled data points are interpreted as not reflecting normal grain growth. The line of best fit (solid), when the four circled points are excluded, is shown.................................................................106

**Fig. 3.20.** High magnification SEM images of the pores traces in this section of the study. Top) HL9 (437 °C, 68d 16h 36m). Bottom) HL5 (511 °C, 00d 15h 56m). Note that the majority of pores lie along grain boundaries with occasional pores occurring as inclusions within grains.................................................111

**Fig. 3.21.** Graph displaying the grain size and $Z$ value of every grain analysed in HL24 (330 °C, 01d 23h 08m). The blue lines are drawn from the origin through the 5% and 95% $Z$ grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free. Note that for the sake of preserving detail, a grain with a $Z$ value of 23078 (grain size = 91 µm) is omitted from this plot. Note that this graph is repeated in §6.1.1. (Fig. 6.4) for the convenience of the reader.................................................112

**Fig. 3.22.** Cumulative grain size plot for HL21 (330 °C, 107d 23h 36m). Each point represents the cumulative mean grain size at intervals of 10 grains.................................................................113

**Fig. 3.23.** Cumulative pore size plot for HL24 (330 °C, 01d 23h 08m). Each point represents the cumulative mean grain size at intervals of 100 pores.................................................................114

**Fig. 3.24.** Cumulative grain area plot for HL24 (330 °C, 01d 23h 08m). Each point represents the cumulative mean grain size at intervals of 50 grains.................................................................115

**Fig. 3.25.** Cumulative pore area plot for HL24 (330 °C, 01d 23h 08m). Each point represents the cumulative mean grain size at intervals of 100 grains.................................................................115

**Fig. 4.1.** Photomicrograph displaying the microstructure present after the application of 200 MPa confining pressure.................................................................117

**Fig. 4.2.** Photomicrograph displaying the typical microstructure present in HP30 (350 °C, 10 sec).................118

**Fig. 4.3.** Graph showing the grain size variation of the 330°C halite grain growth tests.................................................120

**Fig. 4.4.** Photomicrographs of the 330 °C halite grain growth experiments displaying the microstructural evolution of the data set. a) HL20, 21d 18h 10m. b) HL22, 37d 18h 07m. c) HL19, 73d 18h 37m. d) HL21, 107d 23h 36m.................................................................121

**Fig. 4.5.** Graph displaying the 330 °C halite grain growth tests that are interpreted to represent normal grain growth. The line of best fit (solid, with its slope, $m$, and the correlation coefficient, $R^2$, indicated) and a line with a slope of 1 (dashed) are shown.................................................................122

**Fig. 4.6.** Graph displaying the grain size distributions for the 330 °C grain growth tests.................................................123

**Fig. 4.7.** Graph displaying the statistical analysis of the log normal grain size distributions at 330 °C.................123

**Fig. 4.8.** Graph showing, for the 330 °C grain growth tests, the cumulative frequency (F) of grains larger than $d/\bar{d}$ plotted so that it should give a straight line if well described as a Weibull distribution.................................................124

**Fig. 4.9.** Graph showing, for the 330 °C grain growth tests, the cumulative frequency (F) of grains larger than $d/\bar{d}$ plotted so that it should give a straight line if well described as a log normal distribution.................................................124

**Fig. 4.10.** Graph showing the grain size variation of the 380 °C halite grain growth tests.................................................125

**Fig. 4.11.** Photomicrographs of the 380 °C halite grain growth experiments displaying the microstructural evolution of the data set. a) HL30, 03d 17h 19m. b) HL31, 06d 18h 22m. c) HL18, 19d 23h 59m. d) HL17, 35d 17h 22m.................................................................126

**Fig. 4.12.** Graph displaying the 380 °C halite grain growth tests that are interpreted to represent normal grain growth. The line of best fit (solid, with its slope, $m$, and the correlation coefficient, $R^2$, indicated) and a line with a slope of 1 (dashed) are shown.................................................................127

**Fig. 4.13.** Graph displaying the grain size distributions for the 380 °C grain growth tests.................................................128

**Fig. 4.14.** Graph displaying the statistical analysis of the log normal grain size distributions at 380 °C.................128

**Fig. 4.15.** Graph showing, for the 380 °C grain growth tests, the cumulative frequency (F) of grains larger than $d/\bar{d}$ plotted so that it should give a straight line if well described as a Weibull distribution.................................................129

**Fig. 4.16.** Graph showing, for the 380 °C grain growth tests, the cumulative frequency (F) of grains larger than $d/\bar{d}$ plotted so that it should give a straight line if well described as a log normal distribution.................................................129

**Fig. 4.17.** Graph showing the grain size variation of the 437 °C halite grain growth tests.................................................130
Fig. 4.18. Photomicrographs of the 437 °C halite grain growth experiments displaying the microstructural evolution of the data set. a) HL16, 03d 20h 44m. b) HL27, 06d 03h 58m. c) HL10, 39d 01h 33m. d) HL9, 68d 16h 36m............................131

Fig. 4.19. Graph displaying the 437 °C halite grain growth tests that are interpreted potentially to represent normal grain growth. The line of best fit (solid, with its slope, m, and the correlation coefficient, $R^2$, indicated). The fact that $m < 1$ implies $n < 0.25$, that is, the normal grain growth equation cannot be fitted to the data with a meaningful value of $n$.................................132

Fig. 4.20. Graph displaying the grain size distributions for the 437 °C grain growth tests........................133

Fig. 4.21. Graph displaying the statistical analysis of the log normal grain size distributions at 437 °C ......133

Fig. 4.22. Graph showing, for the 437 °C grain growth tests, the cumulative frequency (F) of grains larger than $d/\dot{d}$ plotted so that it should give a straight line if well described as a Weibull distribution.................134

Fig. 4.23. Graph showing, for the 437 °C grain growth tests, the cumulative frequency (F) of grains larger than $d/\dot{d}$ plotted so that it should give a straight line if well described as a log normal distribution.............134

Fig. 4.24. Graph showing the grain size variation of the 480 °C halite grain growth tests.....................135

Fig. 4.25. Photomicrographs of the 480 °C halite grain growth experiments displaying the microstructural evolution of the data set. a) HL33, 03d 18h 47m. b) HL29, 07d 23h 08m. c) HL12, 20d 02h 19m. d) HL13, 44d 01h 56m.................................136

Fig. 4.26. Graph displaying the 480 °C halite grain growth tests that are interpreted to represent normal grain growth. The line of best fit (solid, with its slope, m, and the correlation coefficient, $R^2$, indicated)....137

Fig. 4.27. Graph displaying the grain size distributions for the 480 °C grain growth tests....................138

Fig. 4.28. Graph displaying the statistical analysis of the log normal grain size distributions at 480 °C ......138

Fig. 4.29. Graph showing, for the 480 °C grain growth tests, the cumulative frequency (F) of grains larger than $d/\dot{d}$ plotted so that it should give a straight line if well described as a Weibull distribution.................139

Fig. 4.30. Graph showing, for the 480 °C grain growth tests, the cumulative frequency (F) of grains larger than $d/\dot{d}$ plotted so that it should give a straight line if well described as a log normal distribution.............139

Fig. 4.31. Graph showing the grain size variation of the 500 °C halite grain growth tests.....................141

Fig. 4.32. Photomicrographs of the 500 °C halite grain growth experiments displaying the microstructural evolution of the data set. a) HP24, 00d 00h 48m. b) HP26, 00d 04h 04m. c) HP23, 01d 01h 24m. d) HP65, 02d 00h 00m. e) HP18, 05d 00h 36m. f) HP20, 12d 23h 00m. Note that the scale on HP20 is different from the remaining five images.................................142

Fig. 4.33. Graph displaying the 500 °C halite grain growth tests that are interpreted to represent normal grain growth. The line of best fit (solid, with its slope, m, and the correlation coefficient, $R^2$, indicated)....143

Fig. 4.34. Graph displaying the grain size distributions for the 500 °C grain growth tests....................144

Fig. 4.35. Graph displaying the statistical analysis of the log normal grain size distributions at 500 °C ......145

Fig. 4.36. Graph showing, for the 500 °C grain growth tests, the cumulative frequency (F) of grains larger than $d/\dot{d}$ plotted so that it should give a straight line if well described as a Weibull distribution.................145

Fig. 4.37. Graph showing, for the 500 °C grain growth tests, the cumulative frequency (F) of grains larger than $d/\dot{d}$ plotted so that it should give a straight line if well described as a log normal distribution.............146

Fig. 4.38. Graph showing the grain size variation of the 511 °C halite grain growth tests.....................147

Fig. 4.39. Photomicrographs of the 511 °C halite grain growth experiments displaying the microstructural evolution of the data set. a) HL3, 00d 00h 10m. b) HL7, 00d 05h 17m. c) HL6, 03d 21h 43m. d) HL28, 06d 06h 32m.................................148

Fig. 4.40. Graph displaying the 511 °C halite grain growth tests that are interpreted to represent normal grain growth. The line of best fit (solid, with its slope, m, and the correlation coefficient, $R^2$, indicated)....149

Fig. 4.41. Graph displaying the grain size distributions for the 511 °C grain growth tests....................150

Fig. 4.42. Graph displaying the statistical analysis of the log normal grain size distributions at 511 °C ......150

Fig. 4.43. Graph showing, for the 511 °C grain growth tests, the cumulative frequency (F) of grains larger than $d/\dot{d}$ plotted so that it should give a straight line if well described as a Weibull distribution.................151

Fig. 4.44. Graph showing, for the 511 °C grain growth tests, the cumulative frequency (F) of grains larger than $d/\dot{d}$ plotted so that it should give a straight line if well described as a log normal distribution.............151

Fig. 4.45. Graph showing the grain size variation of the 600 °C halite grain growth tests.....................153
Fig. 4.46. Photomicrographs of the 600 °C halite grain growth experiments displaying the microstructural evolution of the data set. a) HP37, <5 mins. b) HP42, 00d 01h 00m. c) HP33, 01d 01h 18m. d) HP40, 01d 23h 35m. e) HP32, 04d 17h 26m. f) HP35, 05d 22h 57m.

Fig. 4.47. Graph displaying the 600 °C halite grain growth tests that are interpreted to represent normal grain growth. The line of best fit (solid, with its slope, m, and the correlation coefficient, R^2, indicated)...

Fig. 4.48. Graph displaying the log normal grain size distributions for the 600 °C grain growth tests.

Fig. 4.49. Graph displaying the statistical analysis of the log normal grain size distributions at 600 °C.

Fig. 4.50. Graph showing, for the 600 °C grain growth tests, the cumulative frequency (F) of grains larger than d/\bar{d} plotted so that it should give a straight line if well described as a Weibull distribution.

Fig. 4.51. Graph showing, for the 600 °C grain growth tests, the cumulative frequency (F) of grains larger than d/\bar{d} plotted so that it should give a straight line if well described as a log normal distribution.

Fig. 4.52. Graph displaying the relationship between the determined t_\text{v} values and 1000/T. The correlation coefficient, R^2, of the line of best fit is shown.

Fig. 4.53. Graph displaying the relationship between the determined d_\text{v} values and 1000/T. The correlation coefficient, R^2, of the line of best fit is shown.

Fig. 4.54. Graph used to calculate the activation enthalpy and growth constant values for normal grain growth in halite. The 330 °C to 511 °C data sets are used as these data sets are best described by n = 0.25. The line is a line of best fit for the data. Owing to the Arrhenius relationship for the normal grain growth equation, the displayed line is used to calculate the activation enthalpy and growth constant. The correlation coefficient, R^2, is also shown. One standard deviation error bars are also shown.

Fig. 4.55. Graph displaying all halite grain size data interpreted as representing normal grain growth using an n value of 0.25. The dashed lines represent the idealised positions of each data set based on the calculated kinetic values shown on the plot using the 330 ° to 511 °C data sets. The 600 °C data are shown plotted using n=0.25 for ease of comparison but are best described by n = 0.5.

Fig. 5.1. Photomicrograph of HP14 (500 °C, 01d 21h 30m). Note the high occurrence of large grains with lobate boundaries characteristic of abnormal grain growth. Patches of smaller grains displaying a texture typical of that seen in normal grain growth are also present.

Fig. 5.2. Photomicrograph of a patch of grains displaying normal grain growth texture (relatively straight grain boundaries, 120° triple junctions) in HP14 500 °C (01d 21h 30m) (Fig. 5.1). Note the presence of porosity along many of the grain boundaries. The highly spotted areas of the image are an artefact of the thin-section being too thick and as a result porosity can be seen along the entire boundary as it curves into the slide.

Fig. 5.3. Graph displaying halite grain size data interpreted as representing normal grain growth (dots) and those interpreted as representing abnormal grain growth (crosses) using an n value of 0.25. The dashed lines represent the idealised positions of each data set based on the calculated kinetic values shown on the plot using the 330 ° to 511 °C data sets. The 600 °C data are shown plotted using n=0.25 for ease of comparison but are best described by n = 0.5.

Fig. 5.4. Photomicrograph of HP21 (500 °C, 35d 00h 00m). A large range of grain sizes is present. The central area of the sample contains grains that display textures that suggest the occurrence of normal grain growth.

Fig. 5.5. Higher magnification photomicrograph of HP21 (500 °C, 35d 00h 00m) displaying grains exhibiting a characteristic normal grain growth texture. Note the high occurrence of porosity within the sample despite the long test duration.

Fig. 5.6. Plot displaying the grain size results for the variable confining pressure experiments. Temperature is at a constant 500 °C.

Fig. 5.7. Photomicrographs of the 500 °C, 48 hour variable confining pressure tests. a) HP63, 70 MPa. b) HP62, 100 MPa. c) HP65, 200 MPa. Note the constant presence of porosity in all samples.

Fig. 5.8. Photomicrographs of abnormal grain growth in the variable confining pressure tests. a) HP73, 70 MPa, 120 hours. b) HP71, 100 MPa, 72 hours. c) HP65, 200 MPa, 48 hours.

Fig. 6.1. a) Photomicrograph of Area 14 in HL24 (330 °C, 01d 23h 08m). b) Tracings of the grain boundaries. c) Tracings of the pores. The scale bar in a) applies to all three images.
Fig. 6.2. Pore size distributions for three areas in HL24 (330 °C, 01d 23h 08m) a) Log normal pore size distribution curves in which pore size ($d_p$) has been normalized by mean pore size ($\bar{d}_p$), b) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a log normal distribution.

Fig. 6.3. Z distribution for HL24 (330 °C, 01d 23h 08m).

Fig. 6.4. Graph displaying the grain size and Z value of every grain analysed in HL24 (330 °C, 01d 23h 08m). The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free. Note that for the sake of preserving detail, an individual grain with a Z value of 23079 (grain size = 91 µm) has been omitted from this plot. Note that this graph is the same as Fig. 3.21 (§3.5.6.) and is repeated here for the convenience of the reader.

Fig. 6.5. Graphs displaying the relationship between halite grain size and a) Z, b) pore size and c) pore volume fraction in three areas of HL24 (330 °C, 01d 23h 08m).

Fig. 6.6. a) Photomicrograph of Area 10 in HL21 (330 °C, 107d 23h 36m). b) Tracings of the grain boundaries. c) Tracings of the pores. The scale bar in a) applies to all three images.

Fig. 6.7. Pore size distributions for three areas in HL21 (330 °C, 107d 23h 36m) a) Log normal pore size distribution curves in which pore size ($d_p$) has been normalized by mean pore size ($\bar{d}_p$), b) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a log normal distribution.

Fig. 6.8. Z distribution for HL21 (330 °C, 107d 23h 36m).

Fig. 6.9. Graph displaying the grain size and Z value of every grain analysed in HL21 (330 °C, 107d 23h 36m). The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free.

Fig. 6.10. Graphs displaying the relationship between halite grain size and a) Z, b) pore size and c) pore volume fraction in three areas of HL21 (330 °C, 107d 23h 36m).

Fig. 6.11. Graphs displaying the relationship between grain size and a) average Z, b) average pore size and c) average porosity volume fraction in the 330 °C data set. Data obtained by collating and averaging data from the three areas examined in each sample.

Fig. 6.12. a) Photomicrograph of Area 8 in HL17 (380 °C, 35d 17h 22m). b) Tracings of the grain boundaries. c) Tracings of the pores. The scale bar in a) applies to all three images.

Fig. 6.13. Pore size distributions for three areas in HL17 (380 °C, 35d 17h 22m) a) Log normal pore size distribution curves in which pore size ($d_p$) has been normalized by mean pore size ($\bar{d}_p$), b) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a log normal distribution.

Fig. 6.14. Z distribution for HL17 (380 °C, 35d 17h 22m).

Fig. 6.15. Graph displaying the grain size and Z of every grain analysed in HL17 (380 °C, 35d 17h 22m). The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free.

Fig. 6.16. Graphs displaying the relationship between halite grain size and a) Z, b) pore size and c) pore volume fraction in three areas of HL17 (380 °C, 35d 17h 22m).

Fig. 6.17. a) Photomicrograph of Area 23 in HL9 (437 °C, 68d 16h 36m). b) Tracings of the grain boundaries. c) Tracings of the pores. The scale bar in a) applies to all three images.

Fig. 6.18. Pore size distributions for three areas in HL9 (437 °C, 68d 16h 36m) a) Log normal pore size distribution curves in which pore size ($d_p$) has been normalized by mean pore size ($\bar{d}_p$), b) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a log normal distribution.

Fig. 6.19. Z distribution for HL9 (437 °C, 68d 16h 36m).
Fig. 6.20. Graph displaying the grain size and Z value of every grain analysed in HL9 (437 °C, 68d 16h 36m). The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free..........................200

Fig. 6.21. Graphs displaying the relationship between halite grain size and a) Z, b) pore size and c) pore volume fraction in three areas of HL9 (437 °C, 68d 16h 36m). ..........................................................201

Fig. 6.22. a) Photomicrograph of Area 18 in LH29 (480 °C, 07d 23h 08m). b) Tracings of the grain boundaries. c) Tracings of the pores. The scale bar in a) applies to all three images. ..........................203

Fig. 6.23. a) Photomicrograph of Area 19 in LH29 (480 °C, 07d 23h 08m). b) Tracings of the grain boundaries. c) Tracings of the pores. The scale bar in a) applies to all three images. .............204

Fig. 6.24. Pore size distributions for four areas in LH29 (480 °C, 07d 23h 08m) a) Log normal pore size distribution curves in which pore size \( d_p \) has been normalized by mean pore size \( \bar{d}_p \), b) cumulative frequency \( F \) of pores larger than \( d_p / \bar{d}_p \) plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency \( F \) of pores larger than \( d_p / \bar{d}_p \) plotted so that it should give a straight line if well described as a log normal distribution. ..............................205

Fig. 6.25. Log normal Z distribution for LH29 (480 °C, 07d 23h 08m)..........................................................207

Fig. 6.26. Graph displaying the grain size and Z of every grain analysed in LH29 (480 °C, 07d 23h 08m). The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free...........207

Fig. 6.27. Graphs displaying the relationship between halite grain size and a) Z, b) pore size and c) pore volume fraction in three areas of LH29 (480 °C, 07d 23h 08m). ..........................................................208

Fig. 6.28. a) Photomicrograph of Area 17 in HP14 (500 °C, 01d 21h 30m). b) Tracings of the grain boundaries. c) Tracings of the pores. The scale bar in a) applies to all three images. Note the white space represents a single large abnormal grain. ..........................................................210

Fig. 6.29. Pore size distributions for three areas in HP14 (500 °C, 01d 21h 30m) a) Log normal pore size distribution curves in which pore size \( d_p \) has been normalized by mean pore size \( \bar{d}_p \), b) cumulative frequency \( F \) of pores larger than \( d_p / \bar{d}_p \) plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency \( F \) of pores larger than \( d_p / \bar{d}_p \) plotted so that it should give a straight line if well described as a log normal distribution. ........................................211

Fig. 6.30. Log normal Z distribution for HP14 (500 °C, 01d 21h 30m). ..........................................................213

Fig. 6.31. Graph displaying the grain size and Z of every grain analysed in HP14 (500 °C, 01d 21h 30m). The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free...........213

Fig. 6.32. Graphs displaying the relationship between halite grain size and a) Z, b) pore size and c) pore volume fraction in three areas of HP14 (500 °C, 01d 21h 30m). ..........................................................214

Fig. 6.33. a) Photomicrograph of Area 10 in HP21 (500 °C, 35d 00h 00m). b) Tracings of the grain boundaries. c) Tracings of the pores. The scale bar in a) applies to all three images. Note the white space represents an area in which tracing of the grain boundary challenging, hence no boundaries were traced.216

Fig. 6.34. Pore size distributions for three areas in HP21 (500 °C, 35d 00h 00m) a) Log normal pore size distribution curves in which pore size \( d_p \) has been normalized by mean pore size \( \bar{d}_p \), b) cumulative frequency \( F \) of pores larger than \( d_p / \bar{d}_p \) plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency \( F \) of pores larger than \( d_p / \bar{d}_p \) plotted so that it should give a straight line if well described as a log normal distribution. ........................................217

Fig. 6.35. Log normal Z distribution for HP21 (500 °C, 35d 00h 00m). ..........................................................219

Fig. 6.36. Graph displaying the grain size and Z of every grain analysed in HP21 (500 °C, 35d 00h 00m). The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free...........219

Fig. 6.37. Graphs displaying the relationship between halite grain size and a) Z, b) pore size and c) pore volume fraction in three areas of HP21 (500 °C, 35d 00h 00m). ..........................................................220

Fig. 6.38. Graphs displaying the relationship between grain size and a) average Z, b) average pore size and c) average porosity volume fraction in the 500 °C data set. Data obtained by collating and averaging data from the three areas examined in each sample. ..........................................................222
The relationship between the determined grain growth using the Weibull distribution and cumulative frequency (F) of pores larger than \( \frac{d_p}{\bar{d}_p} \) plotted so that it should give a straight line if well described as a log normal distribution.  

Fig. 6.40. Pore size distributions for three areas in HL7 (511 °C, 00d 05h 17m) a) Log normal pore size distribution curves in which pore size \( d_p \) has been normalized by mean pore size \( \bar{d}_p \), b) cumulative frequency (F) of pores larger than \( \frac{d_p}{\bar{d}_p} \) plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency (F) of pores larger than \( \frac{d_p}{\bar{d}_p} \) plotted so that it should give a straight line if well described as a log normal distribution.  

Fig. 6.41. Log normal Z distribution for HL7 (511 °C, 00d 05h 17m).  

Fig. 6.42. Graph displaying the grain size and Z of every grain analysed in HL7 (511 °C, 00d 05h 17m). The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free.  

Fig. 6.43. Graphs displaying the relationship between halite grain size and a) Z, b) pore size and c) pore volume fraction in three areas of HL7 (511 °C, 00d 05h 17m).  

Fig. 6.44. a) Photomicrograph of Area 12 in HL5 (511 °C, 00d 15h 56m).  b) Tracings of the grain boundaries.  c) Tracings of the pores.  The scale bar in a) applies to all three images.  

Fig. 6.45. Pore size distributions for three areas in HL5 (511 °C, 00d 15h 56m) a) Log normal pore size distribution curves in which pore size \( d_p \) has been normalized by mean pore size \( \bar{d}_p \), b) cumulative frequency (F) of pores larger than \( \frac{d_p}{\bar{d}_p} \) plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency (F) of pores larger than \( \frac{d_p}{\bar{d}_p} \) plotted so that it should give a straight line if well described as a log normal distribution.  

Fig. 6.46. Log normal Z distribution for HL5 (511 °C, 00d 15h 56m).  

Fig. 6.47. Graph displaying the grain size and Z of every grain analysed in HL5 (511 °C, 00d 15h 56m). The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free.  

Fig. 6.48. Graphs displaying the relationship between halite grain size and a) Z, b) pore size and c) pore volume fraction in three areas of HL5 (511 °C, 00d 15h 56m).  

Fig. 6.49. Graphs displaying the relationship between grain size and a) average Z, b) average pore size and c) average porosity volume fraction in the 511 °C data set. Data obtained by collating and averaging data from the three areas examined in each sample.  

Fig. 6.50. a) Photomicrograph of Area 4 in HP37 (600 °C, <5 min).  b) Tracings of the grain boundaries.  c) Tracings of the pores.  The scale bar in a) applies to all three images.  

Fig. 6.51. Pore size distributions for three areas in HP37 (600 °C, <5 min) a) Log normal pore size distribution curves in which pore size \( d_p \) has been normalized by mean pore size \( \bar{d}_p \), b) cumulative frequency (F) of pores larger than \( \frac{d_p}{\bar{d}_p} \) plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency (F) of pores larger than \( \frac{d_p}{\bar{d}_p} \) plotted so that it should give a straight line if well described as a log normal distribution.  

Fig. 6.52. Log normal Z distribution for HP37 (600 °C, <5 min).  

Fig. 6.53. Graph displaying the grain size and Z of every grain analysed in HP37 (600 °C, <5 min). The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free.  

Fig. 6.54. Graphs displaying the relationship between halite grain size and a) Z, b) pore size and c) pore volume fraction in three areas of HP37 (600 °C, <5 min).  

Fig. 7.1. Graph displaying the relationship between the determined \( t_0 \) values and 1000/T. The correlation co-efficient, \( R^2 \), of the line of best fit is shown.  

Fig. 7.2. Graph displaying the relationship between the determined \( d_q \) values and 1000/T. The correlation co-efficient, \( R^2 \), of the line of best fit is shown.  

Fig. 7.3. Graph displaying all halite grain size data interpreted as representing normal grain growth using an \( n \) value of 0.25. The dashed lines represent the ideal position of each data set based upon the kinetic values determined from the 3° to 511 °C data sets. The 600 °C data are shown plotted using \( n = 0.25 \) for ease of comparison but are best described by \( n = 0.5 \).
\textbf{Fig. 7.4.} Graph used to calculate the activation enthalpy and rate constant values for normal grain growth in halite. The 330 °-511 °C data sets are used as the grain growth mechanism is the same in all tests, and these data sets are all described by \( n = 0.25 \). Each data point represents the average \( \ln(d^{1/n} - d_0^{1/n}) - \ln(t - t_0) \) for each data set. The correlation co-efficient, \( R^2 \), is also shown.\( \text{........................................251} \)

\textbf{Fig. 7.5.} Schematic Zener plot of the proposed model of halite grain size and Z evolution in grains experiencing normal grain growth, i.e., pore elimination is greater than pore accumulation during grain boundary migration. Note that both halite grain size and Z are not to scale.\( \text{........................................260} \)

\textbf{Fig. 7.6.} Schematic Zener plot of the proposed model of halite grain size and Z evolution in grains experiencing early abnormal grain growth resulting in a reduced Zener parameter, i.e., pore accumulation is greater than pore elimination during grain boundary migration. Note that the upper section of the graph, i.e., the section in which the boundaries undergo a period of pore elimination, is highly speculative as no samples displayed this decrease in pore volume fraction after experiencing an initial increase at the largest grain sizes.\( \text{........................................261} \)

\textbf{Fig. 8.1.} Yield stress versus inverse square root mean free path of ferrite in pearlitic steel (ferrite and cementite). (Adapted from Takahashi and Nagumo, 1970).\( \text{........................................276} \)

\textbf{Fig. 8.2.} Two schematic diagrams of the calcite crystal structure viewed with the c-axis vertical (top) and the c-axis perpendicular to the page (bottom). Black dots represent C atoms, blue spheres are O atoms and green spheres are Ca atoms. The unit cell is shown in black. Structures drawn using ATOMS6.1. (Dowty, 2004).\( \text{........................................279} \)

\textbf{Fig. 8.3.} The crystal structure of halite. The green spheres represent Cl and orange dots Na⁺. The unit cell is drawn in black. Structure drawn using ATOMS6.1. (Dowty, 2004).\( \text{........................................281} \)

\textbf{Fig. 9.1.} Diagram of the ISIS facility showing the position of each beam line relative to Target Station 1 (top) and Target Station 2 (bottom) and the main synchrotron. ENGIN-X receives neutrons from Target Station 1, and lies between Target Stations 1 and 2. (STFC, 2013).\( \text{........................................284} \)

\textbf{Fig. 9.2.} Photograph of the ENGIN-X apparatus displaying the experimental set up. Note the 45° orientation of the Instron load frame to the beam aperture and the 90° angle between the beam aperture and the two detector banks.\( \text{........................................286} \)

\textbf{Fig. 9.3.} Top: Schematic diagram of the experimental set up. Bottom: More detailed diagram of the geometry of the sample demonstrating how the neutrons are diffracted to either the axial or radial detectors. Only grains containing lattice planes with scattering vectors parallel to the radial direction (A and B) will diffract neutrons towards the radial detector bank while those grains containing lattice planes with scattering vectors parallel to the axial direction (C and D) will diffract neutrons towards the axial detector bank. Note that if the orientation of the grains A and B, and likewise for grains C and D, are not the same, then the neutrons measured by the detectors will be from different lattice planes. (Adapted from Schofield et al., 2003).\( \text{........................................287} \)

\textbf{Fig. 9.4.} Photograph of the sample set up within the load frame on ENGIN-X.\( \text{........................................289} \)

\textbf{Fig. 9.5.} Photograph of the cold pressing set up used during the fabrication procedure of the calcite + halite samples.\( \text{........................................293} \)

\textbf{Fig. 9.6.} Example of a typical fit of the whole pattern diffraction data obtained from ENGIN-X. The axial diffraction pattern of the lowest load (2 MPa) in sample ENGX28 (calcite 0.61: halite 0.39, <38 μm Carrara marble) is shown. The blue points are the diffraction data, the black line is the fit to the diffraction data, the red line is the residual to the fit and the ticks represent the position of the diffraction peaks (light blue is halite and green is calcite). The peaks that correspond to these ticks are listed in Tab. 9.2.\( \text{............................296} \)

\textbf{Fig. 9.7.} Values of Chi-squared (\( \chi^2 \)) used as a measure of goodness of fit for ENGX26 (calcite 0.62: halite 0.38, 100 μm Carrara marble) axial data.\( \text{........................................298} \)

\textbf{Fig. 9.8.} Example single peak fit for the HL (220) peak at the lowest load (2 MPa) in ENGX28 (calcite 0.61: halite 0.39, <38 μm Carrara marble). Blue crosses are the diffraction data, the black line is the fit of the diffraction data, tick is the calculated position of the peak in Å-spacing and the red line is the residual. Note that the tick does not occur at the central position of the peak. This is because the peak shapes for neutron diffraction are not symmetrical.\( \text{........................................300} \)

\textbf{Fig. 9.9.} Example of peak overlap between the CC (21.1) and HL (222) peaks at the lowest load (2 MPa) in ENGX28 (calcite 0.61: halite 0.39, <38 μm Carrara marble). Blue crosses are the diffraction data, the black
line is the fit of the diffraction data, tick is the calculated position of the peak in d-spacing (blue for halite, green for calcite) and the red line is the residual.  .......................................................................................................................................................................................... 301

**Fig. 9.10.** Example of peak overlap between the CC (31.4) and HL (422) peaks at the lowest load (2 MPa) in ENGX28 (calcite 0.61: halite 0.39, ≪38 µm Carrara marble). Blue crosses are the diffraction data, the black line is the fit of the diffraction data, ticks are the calculated position of the peaks in d-spacing (blue for halite, green for calcite) and the red line is the residual.  .......................................................................................................................................................................................... 301

**Fig. 9.11.** Plots of aggregate stress versus d-spacing for single peaks in ENGX28 (calcite 0.61: halite 0.39, ≪38 µm Carrara marble). a) CC (10.4) and b) CC (11.6). Note that a) CC (10.4), is an extreme example where zero load lattice parameters, as indicated by the axial and radial detectors, differ. This primarily reflects residual stresses remaining after sample fabrication................................................................................................................................................................................................................ 303

**Fig. 9.12.** Sectors of equal angle stereograms (other sectors obtained from these by symmetry) showing the orientation of the single peaks analysed in this study (i.e., the orientation of the pole to the indicated lattice plane) for calcite (top left) and halite (bottom left). The variation in directional Young’s modulus with orientation is shown on an equal angle stereogram for calcite (top right) and against an orientation parameter \( r_\text{NL} = (h^2k^2 + h^2l^2 + k^2l^2) / (h^2 + k^2 + l^2) \) for halite (bottom right). For calcite, the directional Young’s modulus is obtained from the single crystal elastic stiffness tensor and so is equivalent to that obtained by a polycrystalline sample deforming under conditions of homogeneous stress. The real variation of directional Young’s modulus in an isotropic polycrystal of calcite has the same shape as this variation, but the variation is of smaller magnitude. For halite, the directional Young’s modulus is the self-consistent value for an isotropic polycrystal of halite as given by the equations of de Wit (1997). For further details, see §9.4.3 and note that the difference between the values determined by de Wit are slightly different (<<0.1 GPa) than those actually used in this study, which used Kröner’s self-consistent formulation. Plots constructed by Covey-Crump. .......................................................................................................................................................................................... 305

**Fig. 9.13.** Plots of aggregate stress vs. halite elastic strain and calcite elastic strain (top) and calcite elastic strain vs. halite elastic strain (bottom) for whole pattern data in ENGX28 (calcite 0.61: halite 0.39, ≪38 µm Carrara marble). In the top plot, plastic yielding of the halite is highlighted by a change in slope of the halite data at \( e_{\text{Y,hl}} = 780 \mu\text{e} \); the calcite remains linear elastic throughout. In the lower plot, it can be seen that the yielding in the halite leads to an increase in the rate at which elastic strain (and hence stress) accumulates in the calcite, that is, halite yield leads to enhanced load transfer from the halite to the calcite. On energetic grounds, the pre-yield data must lie between the homogeneous stress and homogeneous strain boundaries. The data should also lie within even tighter bounds based on minimizing potential energy and complementary potential energy (the Hashin and Shtrikman boundaries, HS+ and HS−; (Hashin and Shtrikman, 1963) Plots constructed by Covey-Crump. .......................................................................................................................................................................................... 309

**Fig. 9.14.** Example of the elastic strain vs. aggregate stress for the HL (200) peak (left) and the HL (311) peak (right) in ENGX28 (calcite 0.61: halite 0.39, ≪38 µm Carrara marble). Yielding of the halite is picked out very well by a change in slope of the axial data at 37 MPa. This is particularly the case in the HL (200) peak but less so in the HL (311). Plot constructed by Covey-Crump. .......................................................................................................................................................................................... 310

**Fig. 9.15.** Example of peak broadening as shown by halite elastic strain vs. halite normalized peak width in ENGX28 (calcite 0.61: halite 0.39, ≪38 µm Carrara marble). Derived from a whole pattern fit; the peak width parameter is normalized by the value of that parameter at the lowest load. Yielding of the halite is picked out in both axial and radial data by an increase in the rate of peak broadening with load. Plot constructed by Covey-Crump. .......................................................................................................................................................................................... 310

**Fig. 9.16.** Examples of the graphs used to display whole pattern stress data obtained from strain data for ENGX28 (calcite 0.61: halite 0.39, ≪38 µm Carrara marble). Top left: Axial and radial stresses in the calcite vs. axial stress applied to the sample. Top right: Axial and radial stresses in the halite vs. axial stress applied to the sample. Note that the stresses are well described using the uniaxial approximation (dashed lines (Eqs. 9.10-9.11)) up until the halite yields but that after yielding this approximation is less good. Bottom left: von Mises equivalent stresses in the calcite and halite vs. axial stress applied to the sample, clearly showing the yield point of halite. Bottom right: Calcite axial stress vs. halite axial stress, again clearly showing the yield point of halite, and the subsequent enhanced load transfer from halite to calcite. Plots constructed by Covey-Crump. .......................................................................................................................................................................................................................................................... 312
Fig. 9.17. Examples of the graphs used to display single peak stress values obtained from strain data for ENGX28 (calcite 61: halite 39, <38 µm Carrara marble). The position of the data below the 1:1 line on the right hand side plot indicates that the grains providing the data for CC (10.4) single peak are under less stress than the average calcite grain. Plots constructed by Covey-Crump ................................................314

Fig. 9.18. Photomicrograph of ENGX26 (calcite 0.62: halite 0.38, 100 µm Carrara marble) displaying the transients across which the mean free path and contiguity were calculated. The vertical red lines represent the boundaries between calcite (heavier relief phase) and halite (low relief phase) and were used to determine $P_{nl-cc}$. The loading direction is parallel to the transect lines. ........................................317

Fig. 9.19. Plot comparing the measured values of halite mean free path vs. values of halite mean free path calculated using the Underwood (Eq. 9.26) and Gurland (Eq. 9.27) definitions. ........................................319

Fig. 10.1. Photomicrographs of calcite + halite samples of different volume fractions. All volume fractions are calcite:halite. a) RUT34 (0.10:0.90). b) RUT39 (0.20:0.80). c) ENGX20 (0.37:0.63). d) RUT57 (0.50:0.50). e) RUT58 (0.70:0.30). f) RUT56 (0.80:0.20). g) RUT49 (0.90:0.10). Note that the scale in c) and g) is different to that of the remaining images. a), b) and c) are in plane polarized light, the remainder are in crossed-polarized light so as to provide a clear distinction between halite (isotropic) and calcite (anisotropic). The difference in colour between the images is because different cameras were used. ..................326

Fig. 10.2. Plot displaying the relationship between calcite volume fraction and calcite contiguity in constant calcite grain size (6 µm) tests. ........................................................................326

Fig. 10.3. Plot displaying the relationship between calcite volume fraction and halite mean free path in constant calcite grain size (6 µm) tests. .........................................................328

Fig. 10.4. Photomicrographs of calcite + halite samples of approximately the same composition (approximately 0.60:0.40 calcite:halite) but different calcite clast size. Apart from a) the calcite in all images is Carrara marble. All images are in plain polarized light. a) ENGX23 (6 µm chelometric). b) ENGX28 (18 µm). c) ENGX5 (31 µm). d) ENGX26 (57 µm). e) ENGX9 (130 µm). f) ENGX30 (361 µm). All samples have been uniaxially deformed to axial strains of <1% (loading direction is left/right parallel). The difference in colour between the images is due to different cameras being used. Note in e) sections of the halite have been polished away due to the hardness contrast between calcite and halite. ........................................330

Fig. 10.5. Photomicrographs of ENGX30 (141 µm clasts, 0.64 calcite: 0.36 halite). The calcite (dark phase) is Solnhofen limestone. The sample has been uniaxially deformed to an axial strain of approximately 0.8% (loading direction is left/right parallel). Note that the Solnhofen limestone clasts have a weak shape fabric, induced during cold pressing. .........................................................331

Fig. 10.6. Plot displaying the relationship between calcite clast size and calcite contiguity in constant calcite volume fraction (approximately 0.60 calcite: 0.40 halite) tests. Red dots represent the Carrara marble tests, the blue dot represents the Solnhofen limestone test. ........................................................................333

Fig. 10.7. Plot displaying the relationship between halite mean free path and calcite clast size in the constant volume fraction (approximately 0.60 calcite: 0.40 halite) tests. Red dots represent the Carrara marble tests, the blue dot represents the Solnhofen limestone test. ........................................................................334

Fig. 10.8. Plots displaying the general response of the samples to deformation in ENGX26 (0.62 calcite: 0.38 halite, 57 µm Carrara marble). Top left: Aggregate stress vs. elastic strain in each phase. Top right: Calcite axial elastic strain vs. halite axial elastic strain. Middle left: Calcite stress vs. aggregate stress. Middle right: Halite stress vs. aggregate stress. Bottom left: Equivalent stress vs. aggregate stress. Bottom right: Calcite axial stress vs. halite axial stress. The uncertainty in the stress and strain data is about the same size as the symbols. Unloading data (represented by the purple symbols) was collected from 65 MPa down to 25 MPa. ........................................................................336

Fig. 10.9. Example plots of aggregate stress vs. elastic strain (left) and h.k.l stress vs. phase equivalent stress (right) for calcite single peaks (previous page) and halite single peaks (this page) in ENGX26 (0.62 calcite: 0.38 halite, 57 µm Carrara marble). The bracketed numbers represent the single peak in question. The small black arrows indicate the point of halite yield. The purple lines indicate the unloading behaviour. The lines either side of the key symbols represent the uncertainties associated with the strain calculations. If no lines can be seen, the errors are of the same approximate size as the symbols. ..............339

Fig. 10.10. Plot of halite volumetric strain vs. calcite volumetric strain, both in the axial direction. The arrows indicate the onset of yielding in each experiment. The predicated pre-yield elastic strain partitioning
is shown for the cases of homogeneous stress (Reuss), homogenous strain (Voigt) and the Hashin-Shtrikman (HS) upper and lower boundaries

**Fig. 10.11.** Plot of halite vs. calcite axial stresses. Arrows represent the values of halite axial stress at which yielding begins. The homogeneous stress line is included; deviation from this line indicates partitioning of deformation into the calcite.

**Fig. 10.12.** Plots of phase equivalent stress vs. equivalent stress for single peak data. Top left) CC (00.6); top right) HL (200); bottom left) CC (01.2); bottom right) CC (10.4). Note the different y-axis scales on the HL (200) and CC (01.2) and the different scale on the x-axis on the HL (200). The 1:1 line represents the point at which no partitioning of the deformation on to the specific crystallographic plane takes place. The key applies to all plots.

**Fig. 10.13.** Plot displaying the relationship between a) halite mean free path and the aggregate stress at the point of halite yield and b) calcite contiguity and aggregate stress at the point of halite yield in the constant volume fraction (approximately 0.60 calcite: 0.40 halite) tests. Red dots represent the Carrara marble tests, the blue dot represents the Solnhofen limestone test and the green dot represents ENGX20 (6 µm chelometric grade calcite, 0.37 calcite: 0.62 halite).

**Fig. 10.14.** Plot displaying the relationship between a) halite mean free path and the slope of the post-yield axial stress and b) calcite contiguity and slope of the post yield axial stress in the constant volume fraction (approximately 0.60 calcite: 0.40 halite) tests. Red dots represent the Carrara marble tests, the blue dot represents the Solnhofen limestone test and the green dot represents ENGX20 (chelometric grade calcite, 0.37 calcite: 0.62 halite).

**Fig. 11.1.** Hall-Petch relationship between halite mean free path and aggregate stress at the point of halite yield. Plotted using ENGX20 in addition to the constant volume fraction (0.60 calcite: 0.40 halite) tests. Note that ENGX 5 has been excluded from the fit but is shown on the graph as a cross.
List of tables

**Tab. 2.1.** Table displaying the theoretical values of n associated with each growth controlling mechanism that can be applied to the normal grain growth equation (Eq. 2.8). γ is surface free energy, r is pore size. (Modified from Covey-Crump, 1997 after Brook, 1976). ..............................................45

**Tab. 2.2.** Table displaying the transport mechanisms and material sources for the mechanisms in. All mechanisms result in material deposition at grain boundary necks. (Adapted from Kang, 2005). ..............63

**Tab. 2.3.** Table displaying the range of activation enthalpies for hetero-diffusion in halite. The temperatures at which the activation enthalpies were determined. (From Bénière, 1999). .........................74

**Tab. 3.1.** Table displaying the impurity content of the halite starting material. .................................................75

**Tab. 3.2.** Calibrated Eurotherm and Variac settings resulting from the thermal profile calibrations. The Nimonic 1 calibration used prior to the start of this study is also shown (Dec-09). .............................................88

**Tab. 3.3.** Table displaying the calculated inverse normal distribution values for the two approximations discussed in the text. ..................................................................................108

**Tab. 4.1.** Table displaying the grain size and statistic results for the 330 °C data set. Note that a distribution was not obtained for HL24, because, although the thin-section was of high enough quality to allow visual grain size measurements to be made under the microscope, it was of insufficient quality to allow accurate tracing of grains from optical photomicrographs. .................................................................120

**Tab. 4.2.** Table displaying the grain size results for the 380 °C data set. .................................................................125

**Tab. 4.3.** Table displaying the grain size results for the 437 °C data set. Note that due to the large grain size of HL11 the number of grains that could be traced was statistically invalid, as such, no distribution was obtained. ........................................................................................................130

**Tab. 4.4.** Table displaying the grain size results for the 480 °C data set. Note that due to the large grain size, a statistically valid number of grains could not be traced in HL14, and thus, no grain size distribution was measured. ........................................................................................................135

**Tab. 4.5.** Table displaying the grain size results for the 500 °C data set. Note that grain size distributions could not be obtained for four samples; HP56, HP54, HP19 and HP55. The large grain size of HP19 did not allow a statistically sufficient number of grains to be traced. In the remaining three remaining samples, while the thin-sections were of high enough quality to allow visual grain size measurements to be made under the microscope, they were of insufficient quality to allow accurate tracing of grains from optical photomicrographs. .................................................................140

**Tab. 4.6.** Table displaying the grain size results for the 511 °C data set. Note that a distribution was not obtained for HL2 because, although the thin-section was of high enough quality to allow visual grain size measurements to be made under the microscope, it was of insufficient quality to allow accurate tracing of grains from optical photomicrographs. .................................................................147

**Tab. 4.7.** Table displaying the grain size results for the 600 °C data set. The large grain size of HP38 did not allow a statistically sufficient number of grains to be traced. ........................................................................................................152

**Tab. 4.8.** Table displaying the δ₀ and t₀ values determined for each data set. .........................................................158

**Tab. 4.9.** Table displaying the slope (m) and correlation coefficient (R²) for all data sets. Note that the R² value for the 437 °C data set is due to there being only two data points. .........................................................164

**Tab. 4.10.** Table summarising the correlation coefficient, R², results for each temperature set. .........................164

**Tab. 4.11.** Table summarising the range of α and β values, for samples best described by the Weibull distribution, obtained in the process of calculating the Weibull cumulative distributions. .............................165

**Tab. 5.1.** Table displaying the results for the variable confining pressure tests. .........................................................171

**Tab. 6.1.** Table displaying the samples subjected to grain size-porosity analysis. Measured grain size refers to the mean linear intercept grain size as determined from optical photomicrographs and reported in Chapter 4. Note that the tracings used for the porosity analysis come from much smaller subareas of the sample. ........................................................................................................175

**Tab. 6.2.** Table displaying the samples that were imaged for porosity investigation, but, due to time constraints, were not analysed. ........................................................................................................176
Tab. 7.1. Table summarizing the activation enthalpies, and the temperatures at which they were obtained, for Cl diffusion in NaCl discussed in §2.5.2. ........................................................................................................... 252

Tab. 8.1. Table of the independent components of the calcite and halite elastic stiffness tensors (c) and isotropically averaged effective elastic moduli, calculated from these tenors, used for the calculations in this study. K is the bulk modulus, G is the shear modulus, E is the Young’s modulus and ν is the Poisson’s ratio (all given in GPa). (From Covey-Crump et al., 2013).................................................................................................................................................. 280

Tab. 9.1. Table displaying the sieve size fraction used for each calcite grain size. .................................................................................................................. 291

Tab. 9.2. Table displaying all the peaks that could be identified within the whole pattern diffraction fit seen in Fig. 9.6. Note halite is given in terms of hkl and calcite is given in terms of hk.l. .............................................................. 297

Tab. 9.3. Table displaying the calcite and halite peaks that were selected for single peak analysis. Note that in the single peak fits and plots used throughout the remainder of this study the nomenclature for (10.8) becomes (01.8), (10.2) becomes (01.2) and (21.5) becomes (12.5). .......................................................... 302

Tab. 9.4. Table of directional Young’s modulus (E_{h.k.l}) and directional Poisson’s ratio (ν_{h.k.l}) for the single peaks analysed in this study. These are self-consistent values obtained using the formulation of Kröner (1958). Table compiled by Covey-Crump. ................................................................................................................................. 313

Tab. 10.1. Table summarizing the microstructural and mechanical results for the neutron diffraction tests carried out for this study. f_{powder} is the volume fraction of the calcite:halite powders measured during sample preparation. f_{whole pattern} is the volume fraction determined from the whole pattern fit. f_{true} is the volume fraction corrected using Eq. 9.6 and Eq. 9.7 to take into account porosity, hence they do not equal 1. Uncertainties associated with the volume fractions are estimated from those of the Rietveld refinements to be ±0.001. d_{cc start} is the calcite clast size fraction used in the sample preparation stage and L_{cc} is the mean calcite intercept length and is a measure of calcite clast size in thin-section. ........................................................................................................................................ 322

Tab. 10.2. Table summarizing the contiguity, mean free path and axial stress at the point of halite yield results. .............................................................................................................................................................. 343

Tab. 10.3. Table summarizing the contiguity, mean free path and axial halite stress at the point of halite yield data results. .............................................................................................................................................................................. 345
Polycrystalline geological materials are not normally single phase materials and commonly contain second phases which are known to influence the grain size and mechanical properties of bulk material. Despite the well documented significance of second phases, there are relatively few detailed systematic experimental studies of the effect of second phases on isostatic high temperature grain growth in geological materials. Grain growth is a process that is fundamental to our understanding of how rocks behave in the lower crust / upper mantle where grain size is considered to play an important role in the localization of deformation in addition to determining the strength of materials at these pressure and temperature conditions. Furthermore, the effect that the spatial distribution and grain size of the second phases have on the mechanical properties of rocks is generally acknowledged, but it is not well constrained. Spatial variation is particularly significant in geological systems where a strength contrast exists between phases. With these two things in mind, a two-part study is presented in which the influence of a pore second phase on the microstructural evolution of halite during grain growth (Part I), and the influence of a calcite second phase on the mechanical behaviour of two phase calcite + halite aggregates (Part II), is investigated.

In Part I, high temperature (330 °C - 600 °C), high confining pressure (200 MPa) isostatic grain growth experiments were carried out on 38-125 μm reagent grade halite (99.5% NaCl) powder over durations of 10 secs up to 108 days. After hot-pressing, the halite displays a foam texture. Some porosity remained along the grain boundaries, the size and distribution of which appears to impact significantly on the resulting grain size, growth mechanism and kinetics of halite grain growth. Halite grain growth was found to be well described by the normal grain growth equation: 

\[ d^{1/n} - d_0^{1/n} = k_0(t - t_0)\exp(-H/RT) \]

where \( t \) is the duration of the growth period, \( t_0 \) is the time at which normal growth begins, \( d \) is the grain size, \( d_0 \) is the grain size at \( t_0 \), \( k_0 \) is a constant, \( H \) is the activation enthalpy for the growth controlling process, \( R \) is the universal gas constant, \( T \) is temperature and \( n \) is a growth constant. At 330 °C - 511 °C, the data is best described by \( n = 0.25 \) indicating growth controlled by surface diffusion around pores that lie on the grain boundaries. An activation enthalpy of 122±34 kJ/mol was obtained using the grain size data from these data sets. At 600 °C the data is best described by \( n = 0.5 \), suggesting that a transition to interface controlled growth takes place between 511 °C and 600 °C. To investigate the impact of porosity, the Zener parameter (\( Z = \text{pore size/pore volume fraction} \)) was determined for individual grains in 10 samples. A general trend of increasing \( Z \) with increasing halite grain size is observed, indicating pore elimination keeps pace with pore accumulation in the growing grains. In some samples, the largest grains display a decrease in the Zener parameter corresponding with an increase in pore volume fraction. These grains are interpreted as having experienced a short-lived, abnormal growth phase shortly after \( t_0 \) during which pore accumulation outpaced pore elimination. A model of pore controlled grain growth is proposed with a view to explaining these observations.

In Part II, calcite + halite aggregates of constant volume fraction (0.60 calcite : 0.40 halite) and varying calcite clast size (6 μm 361 μm) were axially deformed to <1% bulk strain at room temperature in a neutron diffraction beamline. Elastic strain and stress in each phase was determined as a function of load from the neutron diffraction data. The strain (and stress) behaviour correlates well with the microstructural parameters: 1) halite mean free path and 2) calcite contiguity.

Both phases behaved elastically up to aggregate axial stresses of 20-37 MPa, above these stresses the halite yielded plastically while the calcite remained elastic. Once yielding began, the rate of enhanced load transfer from halite to calcite with increasing applied load decreased with halite mean free path and increased calcite with contiguity. A Hall-Petch relationship between halite mean free path and aggregate yield stress was observed.
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1. Introduction

Polycrystalline geological materials, such as rocks and ice, are not ideal pure, single phase materials. All contain chemical impurities within the crystal lattice of the component minerals, and virtually all contain second phase impurities, here defined as other minerals besides the dominant mineral phase, together with pore space and other inclusions. This study is not concerned with the chemical impurities but is instead focussed on second phase impurities.

Second phases are known to influence the grain size of polycrystalline materials (e.g., geological materials (Freund et al., 2001; Hiraga et al., 2010), ceramics (Burke, 1957; Budworth, 1970) and metals (Gladman, 1966; Hsueh and Evans, 1983)) over a range of temperatures. At high temperatures, the presence of second phase impurities affects grain boundary motion which, in turn, impacts the grain size and the rate-significance of grain size sensitive deformation processes operating in the material. At lower temperatures, the distribution of second phase impurities within the system is significant as they can act to restrict dislocation movement, therefore affecting the strength of materials. The effect that the spatial distribution and size of the second phases have on the mechanical properties of rocks, in addition to the localization of deformation, is acknowledged but not well constrained (Fan et al., 1992; Fan and Miodownik, 1993; Fan et al., 1993).

Despite the well documented significance of second phases in natural geological materials (Herwegh and Kunze, 2002; Austin et al., 2008; Linckens et al., 2011a; Linckens et al., 2011b), there are relatively few detailed systematic experimental studies of the effect of second phases upon both the isostatic grain growth and deformation of geological materials. Part of the reason for this, particularly in the case of grain growth studies, is the dynamic nature of second phases, as their physical properties, such as size, shape, distribution, and orientation, can change throughout experiments. In addition, it has been shown that microstructures are sensitive even to small amounts of second phases (<5%) (Mas and Crowley, 1996; Krabbendam et al., 2003), thus resulting in controlled experimental interrogation being challenging. Indeed, it has been demonstrated that the presence of small amounts of second phases can cause grain boundary migration to be
reduced by several orders of magnitude (Humphreys and Hatherly, 2004). Impurities, in this regard, can commonly be sub-micron in scale, thus making an accurate impurity content assessment of the material difficult. All of these factors combine to make accurate measurements of properties such as grain boundary migration in a nominally “pure” material challenging (Humphreys and Hatherly, 2004).

At the outset of this study, the intention was to conduct isostatic grain growth experiments on synthetic calcite + halite aggregates with the aim of investigating the influence of a calcite second phase on halite grain growth. This aimed to build on the previous work of Brodhag and Herwegh (2010) on mineral analogues. To complement these tests, a series of neutron diffraction deformation experiments were carried out using the ENGIN-X apparatus, Rutherford Appleton Laboratory, Didcot, UK.

Calcite and halite were chosen to be used in this study for multiple reasons. The primary reason being that they are experimentally tractable. To investigate rigorously the influence of a pore second phase on grain growth and the spatial variation on plastic yielding, samples with controlled microstructures are needed. Calcite and halite can be fabricated into such samples at experimentally accessible temperatures. They are also both geologically significant minerals.

Halite is a significant mineral in the Earth’s shallow crust where it occurs naturally as evaporite deposits which can develop in kilometre scale basins (Wenk, 1999). Subsidence of these evaporite basins, in combination with the low specific gravity of halite, can result in upwards migration of the salt resulting in the formation of salt domes (Wenk, 1999). These structures have been cited as potential sites for the storage of radioactive waste (Hunsche and Hampel, 1999). Halite also is significant as a hydrocarbon trap (e.g., Duval et al., 1992).

Halite is not only a significant rock forming mineral but also has significance as an analogue for geological minerals (e.g., silicates (Shimamoto and Logan, 2013) and periclase (MgO) (Merkel et al., 2002)) on account of the similarities in crystal structure. The properties that potentially make halite a good analogue include the fact that it behaves plastically at relatively low pressures and temperatures and can be grown to grain sizes similar to those found in nature over experimental timescales. In addition, it has previously been demonstrated that the microstructures developed during halite
deformation at low temperatures are similar to those developed in high pressure and
temperature silicate rocks (Bestmann et al., 2005; Piazolo et al., 2006). Periclase is
considered to be a component of the Earth’s lower mantle and probably contributes
significantly to lower mantle rheology (Wenk and Van Houtte, 2004), therefore, by
understanding better the grain growth and deformation behaviour of halite, we can gain
some understanding of the behaviour of geological materials in the lower mantle.

Calcite is a major constituent of crustal shear zones (Busch and van der Pluijm, 1995) and
as such, has been the subject of many investigations concerning its physical properties at
high temperature (Walker et al., 1990; Covey-Crump, 1994, 1998). Lastly, the physical
and mechanical properties of both are well established.

Calcite grain growth kinetics are well established (Covey-Crump, 1997). Although many
other aspects of the physical properties of halite have been studied, e.g., dynamic
recrystallization (ter Heege et al., 2004), grain boundary migration (Piazolo et al., 2006),
and sintering (Goodall et al., 2006), there is very limited data on high temperature and
pressure isostatic grain growth. To address this deficiency, a series of isostatic grain
growth experiments were carried out on synthetic monomineralic halite samples. As this
initial part of the study progressed it became apparent that grain growth in halite is not as
simple as first expected and that the kinetics were complicated by the presence of <5%
porosity. These complications offered an opportunity to investigate the influence of
porosity on the microstructural evolution of a geological material. Consequently, the
calcite + halite aggregate isostatic high temperature, high pressure tests were not
undertaken. Instead, the porosity is treated as a second phase and its influence on the
grain growth kinetics, and microstructural evolution of halite, has been investigated.

The main body of the study presented here is divided into two parts: (Part I) the influence
of a pore second phase on the microstructural evolution of halite during grain growth,
and (Part II) the influence of a calcite second phase on the mechanical behaviour of two
phase calcite + halite aggregates. The findings of these two parts are then summarized in
Part III.

In Part I of this study, the influence of a pore second phase on the microstructural
evolution of polycrystalline halite aggregates is investigated through the use of high
temperature, high pressure isostatic grain growth tests on synthetic monomineralic halite
Grain growth is an important geological process observed in many geological materials, e.g., calcite (Olgaard and Evans, 1988; Covey-Crump and Rutter, 1989; Covey-Crump, 1997), olivine (Karato, 1989; Ohuchi and Nakamura, 2007; Skemer and Karato, 2007) and quartz (Michibayashi and Imoto, 2012).

Grain growth involves an increase in the grain size of a material. Changes in grain size impact not only on the resulting texture of the material, but also on its physical properties, e.g., strength. The concept of grain growth is fundamental to our understanding of how geological materials behave at the pressure and temperature conditions present at lower crustal / upper mantle depths where grain size is considered to play an important role in the localization of deformation (Rutter and Brodie, 1988; de Bresser et al., 2001; Evans et al., 2001; Platt and Behr, 2011). At these depths, deformation is grain size sensitive; therefore, anything that influences grain size, such as the presence of a second phase, has the potential to influence the strength of the geological material. This, in turn, will influence the localization of deformation in the material. If a section of rock in the lower crust or upper mantle experiences grain growth in the presence of a second phase whilst the remainder does not, the resulting grain size will be smaller than the surrounding second phase free material. This area will then preferentially accommodate deformation. Given sufficient time and deformation partitioning, this area of smaller grain sized material may develop into a shear zone. Indeed, natural shear zones are often found to be composed of smaller grain sized material than the surrounding rock (Platt and Behr, 2011). By understanding how the presence of a second phase influences the grain sizes attained during grain growth, we can understand better the circumstances that lead to smaller grain sizes, and potential subsequent localization of deformation, in nature.

Grain growth is of significance in material science, particularly in relation to the mechanical properties of metals and ceramics (Humphreys and Hatherly, 2004). In materials that are designed for use at low temperatures, a small grain size is optimal in order to improve strength and toughness. Whereas, for high temperature materials, a large grain size is desirable in order to improve high temperature creep (Humphreys and Hatherly, 2004). Therefore, understanding how grain growth occurs is pivotal in allowing the grain size to be controlled in materials.
Two types of grain growth are generally considered to occur, normal grain growth, in which the grains in a system coarsen as one which results in an increased average grain size and a foam-like texture, and abnormal grain growth, in which a small number of grains grow at the expense of the smaller surrounding grains and attain a larger size than the majority of grains within the microstructure (Ohuchi and Nakamura, 2007). There are numerous studies describing high temperature grain growth in geological materials (e.g., Covey-Crump and Rutter, 1989; Covey-Crump, 1997; Evans et al., 2001; Hiraga et al., 2010; Michibayashi and Imoto, 2012). However, there are relatively few studies that have examined abnormal grain growth in geological materials (e.g., Karato, 1989; Ohuchi and Nakamura, 2007). In the field of material science, the opposite is the case as there have been multiple simulation studies abnormal grain growth (e.g., Srolovitz et al., 1985; Rollett et al., 1989). These studies have cited the crystallographic orientation of grains and grain boundaries, resulting in boundary anisotropy, as a cause of abnormal growth. Abnormal grain growth has also been studied experimentally in material science (e.g., Lee et al., 2000a; Lee et al., 2000b; Rios and Gottstein, 2001; MacLaren et al., 2003), many of which have attributed the cause of abnormal growth to the presence of a second phase in the system.

The presence of a porosity second phase in geological systems has previously been shown to restrict grain growth via the application of a dragging / pinning force on the migrating boundary (e.g., Nichols and Mackwell, 1991; Evans et al., 2001; Azuma et al., 2012). The Zener parameter \( Z = \frac{d_p}{f_p} \), where \( d_p \) and \( f_p \) are the diameter and volume fraction of the second phase respectively (Smith, 1948)) has previously been applied in studies on geological materials in order to describe the influence of second phases on grain size (e.g., Olgaard and Evans, 1986; Mas and Crowley, 1996; Herwegh and Berger, 2004; Brodhag et al., 2011). However, none of these studies have gone as far as to examine the Zener parameter on a grain by grain basis. By determining the Zener parameter for individual grains, and correlating the results with grain size, insights can be gained into how the pore size and volume fraction varies spatially with halite grain size within individual samples.

The work presented in Part I is motivated, not only by the need to understand better the isostatic grain growth behaviour of halite under elevated pressure and temperature conditions, but also by how the microstructural evolution is affected by the presence of
small amounts of a pore second phase. By carrying out experiments over a wide range of temperatures and timescales and making detailed microstructural measurements of grain size, together with grain scale measurements of the Zener parameter, both of these aims have been accomplished.

In Part II of this study, the influence of particle spacing on the plastic yielding, and subsequent deformation partitioning, of calcite + halite aggregates, with calcite being the second phase, is investigated at low homologous temperatures. It has been shown previously that by quantifying the spatial variation of the phases within a system using topological parameters, such as contiguity (fraction of the total interface area of a phase that is in contact with grains of the same phase) and mean free path (mean distance between two particles of the same phase), one can begin to quantify the impact of phase distribution on the strength of materials (e.g., Golovchan and Litoshenko, 2003; Luyckx and Love, 2003; Luyckx and Love, 2006; Armstrong, 2011; Stadler et al., 2011). In addition to experimental investigations, the impact of these topological parameters has also been theoretically modelled (e.g., Makhele-Lekala et al., 2001; Engqvist et al., 2002; Abu Al-Rub and Ettehad, 2011). Despite the work done on the influence of these parameters, there is still uncertainty as to which exerts the greater influence on the mechanical response of a material (Carpinteri et al., 2009).

Investigations have been carried out on a number of two phase geological systems, including olivine and pyroxene (e.g., Ji et al., 2001), olivine and magnesiowüstite (e.g., Bystricky et al., 2006), calcite and quartz (e.g., Rybacki et al., 2003) and calcite and halite (e.g., Marques et al., 2010) with the aim of examining the mechanical response of each phase. These studies have highlighted the variation in the mechanical response of polyphase geological materials to deformation. However, none of these studies have attempted to correlate the mechanical response of geological materials with spatial variations of the constituent phases through the use of topological parameters.

With this in mind, the work presented in Part II is motivated by the need to understand more fully the yield behaviour, and subsequent partitioning of deformation, in polymineralic geological materials. In particular, this study explores the role that the spatial distribution of a mineral second phase (calcite) has on plastic yielding and subsequent deformation partitioning within calcite + halite aggregates at low homologous temperatures. By varying the clast size of the calcite in a suite of samples that were
compositionally similar, the spacing of the calcite clasts within the samples was controlled.

For many years, high temperature high pressure experiments such as those carried out in Part I, have been used in the field of Earth science to investigate grain growth and the influence of second phases in geological materials (Evans et al., 2001 and references therein). In Part II, neutron diffraction is used to examine the in situ mechanical response of both the aggregate and the constituent phases to the application of axial load. This technique has been utilized extensively in material science (e.g., Daymond and Bonner, 2003; Oliver et al., 2003; Bouchard et al., 2005; Preuss et al., 2006), however, there are relatively few studies in the Earth science field that have used this technique (Covey-Crump and Schofield, 2009 and references therein). Conventional rock deformation tests only allow the bulk response of an aggregate to be measured, and inferences about the response of each phase to deformation can only be made by examining thin-sections. Neutron diffraction, on the other hand, allows the elastic response of all the component phases in the sample to be monitored during deformation. The resulting diffraction patterns (and individual diffraction peaks) are used to measure the mechanical response of grains (and lattice planes) in a particular orientation, to the deformation in terms of stress and strain. Examination of thin sections resulting from the experiments allows correlations to be made between the mechanical response of each phase with specific microstructural features, in this case, the spatial distribution of the phases.

The penetrating nature of neutrons makes neutron diffraction an excellent technique to study the within-phase behaviour of deforming, polyminalic rocks. The experiments can be performed on samples of similar dimensions to those used in conventional rock deformation testing and correlate well with previous deformation studies, escaping many of the problems associated with small sample testing (Covey-Crump et al., 2001). The energy range of the neutrons enables diffraction data to be collected to sufficiently high resolution so as to observe subtle changes in lattice stress / strain of all the component phases simultaneously. Furthermore, the data can be collected with sufficient time resolution so as to observe the dynamic changes that are occurring during the in situ experiment. In addition, the experimental methods and protocols for in situ neutron diffraction experiments on dynamically deforming rocks are well developed and refined (e.g., Schofield et al., 2003; Covey-Crump and Schofield, 2009; Covey-Crump et al., 2013)
with a dedicated beamline available at the UK neutron source, ISIS (Daymond and Edwards, 2004; Santisteban et al., 2006).
Part I:
The influence of a pore second phase on the microstructural evolution of halite during grain growth
2. Relevant background on grain growth and second phases

2.1. Normal grain growth

Normal grain growth is defined by Atkinson (1988) as the mechanism by which a system of grains or crystals reduces its internal free energy by reducing its overall grain boundary area through increasing the average grain size. The grain size increase occurs due to a relatively small number of large grains growing at the expense of a greater number of small grains.

2.1.1. The stages of grain growth

Initially, grain growth was considered to consist of three growth stages followed by the establishment of a final grain size (Andrade and Aboav, 1966) (Fig. 2.1). Each stage is defined by changes in the ratio of grain size diameter ($D$) and final maximum grain size diameter ($D_f$) (Andrade and Aboav, 1966).

![Diagram](image)

*Fig. 2.1. Schematic graph displaying the four stages of grain growth. $D_0$ is the starting grain size, $D$ is the grain size and $D_f$ is the final maximum grain size. (Adapted from Covey-Crump and Rutter, 1989).*
In Stage I, growth is rapid when $D/D_f < 0.40$, the smaller this value, the more rapid the growth. The initial fast growth is due to release of internal stored strain energy during recrystallization. Once $D/D_f = 0.40$, Stage II is initiated and continues until $D/D_f = 0.65$. Growth in stage II is exponential and follows the normal grain growth law in Eq. 2.8 (described in detail in §2.1.3.2) and is termed the normal grain growth stage. When $D/D_f > 0.65$ Stage III begins at which point growth begins to slow. Stage IV is the establishment of the final stable grain size ($D_f$).

2.1.2. Behaviour up to the onset of grain growth

Normal grain growth occurs after the system has eliminated a statistically sufficient number of pre-existing defects within the crystals, usually via recrystallization. Recrystallization can be either static or dynamic. Formally, static recrystallization takes place under isostatic conditions while dynamic recrystallization occurs during deformation and facilitates the introduction of strain to the rock (de Bresser et al., 2001). In the case of this study, only static recrystallization need be considered owing to the fact that the grain growth experiments are conducted under purely isostatic conditions.

In the initial stages of microstructural equilibration there is competition to reduce the overall internal free energy of the system between (a) recrystallization – the removal of defects by forming new crystals with low defect densities and/or the removal of pores, and (b) grain growth – the reduction of overall grain boundary area by increasing grain size. The forces favouring recrystallization dominate until some critical point when sufficient defects have been removed as to allow grain growth to take place (Drury and Urai, 1990).

2.1.3. Characteristics of normal grain growth

Systems that behave according to the normal grain growth equation display a very characteristic equigranular, polygonal “foam-like” equilibrium texture (Fig. 2.2). Grains that have undergone normal grain growth show straight or gently curving grain boundaries. The intersection angle between grains at triple junctions is commonly
approximately 120° indicating the microstructure is in equilibrium and that grain boundary energies are isotropic.

![Photomicrograph of calcite displaying characteristic equilibrium normal grain growth textures. (From Covey-Crump, 1997).](image)

**Fig. 2.2. Photomicrograph of calcite displaying characteristic equilibrium normal grain growth textures. (From Covey-Crump, 1997).**

### 2.1.3.1. **Driving forces and theoretical analysis**

In order for grain growth to occur, driving forces must be present and the boundaries themselves must have some mobility. The driving forces arise from the need of the system to reduce its overall internal free energy. The two main driving forces are strain gradients between crystals and internal free surface energy (Herwegh and Kunze, 2002).

Recrystallization to a smaller grain size, during which boundary migration is away from the centre of curvature, increases the surface area/volume ratio of the system, i.e., increases the overall grain boundary area. This causes the grains to grow; the visual manifestation of which is curvature of the grain boundaries (Fig. 2.3). The more curved the boundary, the more surface tension and hence stored elastic energy in the crystal (Karato, 2008). This results in aggregates of smaller grains that tend toward more rapid growth. As the grains grow, boundary migration is always towards the centre of curvature of the boundary, this results in the smallest grains shrinking and eventually disappearing while the larger grains grow (Fig. 2.3). As growth proceeds, the curvature of the boundary, surface tension and surface area/volume ratio of the grains will decrease. Internal strain gradients will also decrease thus the driving force will reduce as growth takes place.
Fig. 2.3. Schematic diagram of grain boundary migration driven by surface energy in a recrystallizing aggregate. The starting microstructure is seen in the upper image. Note the starting shape of grains “s” and “b”. In this aggregate, grain “s” is shrinking, and grain “b” is growing. Grain boundary migration is shown by the arrows. Initially, triple junctions migrate to form dihedral angles of 120° which results in grain boundaries becoming curved. Grain boundary migration is towards the radius of curvature. This results in the small grains shrinking and the larger grains growing. Visually, growing grains have grain boundaries that are concave outwards while shrinking grains have convex outwards boundaries. (From Platt and Behr, 2011).

The original form of the normal grain growth equation was derived by Burke and Turnbull (1952). They presumed that the main driving force behind grain growth or grain boundary migration was the curvature of the grain boundary. As stated previously, this implies that smaller grains with more highly curved boundaries will tend towards rapid growth while larger grains with less curved boundaries will grow at a lower rate. In addition, the boundary energy was assumed to be identical across all boundaries. Based on the boundary energy and grain boundary curvature, Burke and Turnbull proposed that

\[ P = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \]  

Eq. 2.1

Where \( P \) is the driving force, \( \gamma \) is boundary energy and \( R_1 \) and \( R_2 \) are the principal radii of curvature of a grain. If it is presumed that the grain in question is spherical, then \( R = R_1 = R_2 \) and thus
\[ P = \frac{2\gamma}{R} \quad \text{Eq. 2.2} \]

An approximation was then made based on the average radius of a grain (\( \bar{R} \)) being proportional to the radius of curvature (\( R \)). This, in combination with the assumption that grain boundary energy is isotropic, turns Eq. 2.2 into

\[ P = \frac{\omega \gamma}{\bar{R}} \quad \text{Eq. 2.3} \]

where \( \omega \) is a geometric constant.

Boundary velocity is also considered to be proportional to the change in particle radius with time and as such

\[ \frac{dR}{dt} = cP \quad \text{Eq. 2.4} \]

where \( c \) is a constant. Combining Eq. 2.3 with Eq. 2.4 results in

\[ \frac{d\bar{R}}{dt} = \frac{\omega \gamma}{\bar{R}} \quad \text{Eq. 2.5} \]

and thus

\[ \bar{R}^2 - \bar{R}_0^2 = 2\omega \gamma t \quad \text{Eq. 2.6} \]

which in turn can be written in the more general form

\[ \bar{R}^n - \bar{R}_0^n = ct \quad \text{Eq. 2.7} \]

where \( \bar{R}_0 \) is the starting grain size, \( \bar{R} \) is the grain size at time \( t \) and \( n \) is the theoretical value representing the growth controlling mechanism of the system. In Burke and Turnbull’s (1952) initial treatment \( n \) was determined to be equal to 2, however, more recent studies of grain growth have expanded the range of potential \( n \) values (see §2.1.3.2. and Tab. 2.1). The rate constant \( c \) is commonly taken to have an Arrhenius temperature dependence. This is the parabolic grain growth equation and has been shown to be valid for 2-D and 3-D microstructures (Atkinson, 1988).

Burke and Turnbull assumed that growth was instantaneous upon reaching experimental temperature. In samples fabricated from powders, however, normal grain growth only begins once porosity has been significantly reduced (typically to less than a few percent). Neglecting this “sample conditioning” phase (i.e., assuming growth is instantaneous upon reaching experimental temperature) reduces the apparent growth rate of the system.
which impacts on the values of $n$ and $c$. In this study, the time at which the starting grain size is reached is taken into account. In addition, some of the nomenclature is changed from the original Burke and Turnbull analysis (Eq. 2.7).

2.1.3.2. Observed kinetics

Normal grain growth behaves according to the following equation, known as the normal grain growth equation

$$d^{1/n} - d_0^{1/n} = kt = k_0(t - t_0)\exp(-H/RT) \quad \text{Eq. 2.8}$$

where $t$ is the duration of the growth period in seconds, $t_0$ is the time at which normal growth begins, $d$ is the grain size in μm, $d_0$ is the grain size at the start of normal grain growth, i.e., the grain size at $t_0$, $k_0$ is a constant, $H$ is the activation enthalpy for the growth controlling process, $R$ is the universal gas constant, $T$ is temperature, $n$ is a growth constant with values typically varying between 0.25 to 1.0 depending on the growth rate controlling mechanism (Atkinson, 1988). A listing of theoretical values of $n$ with the corresponding growth controlling mechanisms is displayed in Tab. 2.1. However, the systems considered in these theoretical examinations consist of pure, isotropic, single phase systems. In geological systems, this is unlikely to be true for the vast majority of natural rocks. Experimental studies of the normal grain growth equation have yielded $n$ values of 0.25 and 0.33 owing to the presence of second phases (Anderson et al., 1984). Original theoretical treatments of the normal grain growth equation yielded $n$ values of 0.5 (Burke and Turnbull, 1952). In this study, only values of $n$ of 0.25, 0.33 and 0.5 are relevant.
Table displaying the theoretical values of $n$ associated with each growth controlling mechanism that can be applied to the normal grain growth equation (Eq. 2.8). $\gamma$ is surface free energy, $r$ is pore size. (Modified from Covey-Crump, 1997 after Brook, 1976).

<table>
<thead>
<tr>
<th>Pore Control</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface diffusion around pore boundaries</td>
<td>0.25</td>
</tr>
<tr>
<td>Lattice diffusion through growing phase</td>
<td>0.33</td>
</tr>
<tr>
<td>Vapour transport across the pore (Vapour pressure is constant)</td>
<td>0.33</td>
</tr>
<tr>
<td>Vapour transport across the pore (Vapour pressure is equal to $2\gamma/r$)</td>
<td>0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Boundary Control</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure systems</td>
<td>0.5</td>
</tr>
<tr>
<td>Impure systems</td>
<td></td>
</tr>
<tr>
<td>Coalescence of second phases by lattice diffusion</td>
<td>0.33</td>
</tr>
<tr>
<td>Coalescence of second phases by grain boundary diffusion</td>
<td>0.25</td>
</tr>
<tr>
<td>Solution of second phase</td>
<td>1.0</td>
</tr>
<tr>
<td>Diffusion through continuous second phase</td>
<td>0.33</td>
</tr>
<tr>
<td>Impurity drag (low solubility)</td>
<td>0.33</td>
</tr>
<tr>
<td>Impurity drag (high solubility)</td>
<td>0.5</td>
</tr>
</tbody>
</table>

2.1.3.3. Grain size distributions

Studies that have utilised the Burke and Turnbull analysis conclude that in a system that behaves according to Eq. 2.8, the mean normalized grain size distribution will rapidly reach a quasi-stationary state in the lead up to the onset of grain growth (Alley et al., 1986).

Log normal grain size distributions are commonly used when examining normal grain growth within a system. This distribution type frequently provides a good first order approximation of experimental results although it is inaccurate in detail (Fayad et al., 1999). The Weibull distribution was first proposed by Weibull (1951) and has since been demonstrated to provide a better description of normal grain growth than the log normal distribution (Fayad et al., 1999). A special case of the Weibull distribution that is often used to describe grain size distributions produced by normal grain growth is the Rayleigh distribution (Louat, 1974).

Fayad et al. (1999) noted from a wide range of experimental and computer simulation grain growth studies that the Weibull distribution consistently provided a better fit to the data than other grain size distribution profiles. The Weibull distribution has significantly
lower errors when compared with the log normal distributions (3-4% compared to 14-16%). The Weibull distribution was used by Rios (2000) to re-examine previously published grain growth data (Rios, 1999), and he came to similar conclusions to those of Fayad et al. (Fig. 2.4). In addition, the Weibull distribution has a distinctly different shape when compared to another widely used grain size distribution function – that of Hillert (1965).

![Probability distribution plot comparing the Weibull distribution of Fayad et al. (1999) (dots) to the data of Rios (1999) (solid line). The dashed line is the classic quasi-stationary distribution of Hillert (1965). R is grain radius. (Adapted from Rios, 2000).](image)

2.1.4. **Factors leading to the cessation of growth**

The presence of second phases may interrupt the four stage scenario outlined in Fig. 2.1 and lead to premature cessation of growth in Stage III and Stage IV. During Stage III, growth begins to slow which is thought to reflect the increasing influence that the decrease in the number of sites at which atoms can leave / join a grain boundary has on the grain as its radius of curvature becomes very large. Second phases also influence cessation of growth as either second phase concentration at the grain boundaries increases and pinning takes place, or grains begin to impinge upon each other and the forces driving growth are reduced, i.e., grain boundary curvature is lower. The presence of second phases may have some influence on the onset of this stage as they could act to
reduce the effective energy within the system by posing an obstacle to grain boundary migration.

2.2. Abnormal grain growth

During grain growth, it is possible for a small number of grains within a system to grow to a significantly larger size compared to the remainder of the grains; this is known as abnormal grain growth or secondary recrystallization. Ohuchi and Nakamura (2007) define a grain that has experienced abnormal growth as being over five times the mean grain size. It should be noted that this figure is arbitrary and has no physical significance. These grains also display characteristic textural differences when compared to grains that have undergone normal grain growth (Fig. 2.5) resulting from the rapid increase in grain size. Abnormal grains possess highly curved, lobate grain boundaries in addition to lacking the 120° triple junctions characteristic of normal grain growth textures (Fig. 2.2).

Fig. 2.5. Abnormal grain growth in nickel annealed at 0.9 $T_m$ for 30 seconds then at 0.5 $T_m$ for 30 minutes. Note the clear microstructural differences between the smaller matrix grains and the large abnormal grains. (From Lee et al., 2000b)
In comparison to normal grain growth, abnormal grain growth is poorly understood. The majority of literature on the subject comes from the material science (e.g., Longworth and Thompson, 1991; Rios and Gottstein, 2001; MacLaren et al., 2003) and computer simulation fields (e.g., Srolovitz et al., 1985; Rollett et al., 1989; Frost et al., 1992) in addition to theoretical studies (e.g., Thompson et al., 1987; Rios, 1994; Rios, 1997). There are very few examples of abnormal grain growth studies on geological materials (Karato, 1989; Bestmann et al., 2005; Piazolo et al., 2006).

The mechanism that causes certain grains to begin growth before the remainder of the system has started is also poorly understood. There are various potential causes of abnormal grain growth, all of which centre around non-uniformities within the system. These include variations in second phase concentration (Lange and Hirlinger, 1984; Srolovitz et al., 1985; Liu and Patterson, 1993) (see §2.3 for a full discussion), starting grain size (Karato, 1989) and grain boundary wetting by a liquid phase (Lee and Freer, 1998). Grain boundary energy anisotropy is also considered to be a potential cause of abnormal growth (Kunaver and Kolar, 1993). Anisotropy can be caused by factors such as coalescence of the second phase, grain boundary faceting (Lee et al., 2000a; Lee et al., 2000c) and crystallographic orientation of grains and grain boundaries (Srolovitz et al., 1985; Rollett et al., 1989; Holm et al., 2003). The latter gives rise to grain boundary anisotropy by establishing differences in misorientation angle between grains. The larger the misorientation angle, the larger the mobility of the grain. If a grain has a sufficiently different misorientation angle, it will tend towards abnormal growth (Rollett et al., 1989).

2.3. Second phase influence on grain growth

During grain growth, second phases have the potential to exert a pinning/dragging force on the migrating boundary (Evans et al., 2001). These second phases come in the form of minerals (Olgaard, 1990; Mas and Crowley, 1996) and pores (Karato, 1989; Covey-Crump, 1997).

The extent to which boundary movement is prohibited is dependent upon the nature of the second phases and the driving force of the boundary (Fig. 2.6). If the second phases are immobile then, upon interaction with the second phases, the boundary will initially be pinned or the rate of boundary migration will be reduced. When a boundary encounters
a second phase, in order to keep moving, it has to either drag that phase with it or break-free of the phase. Hence, boundary mobility is influenced by impurity mobility. Moreover, there is an energy saving in having the impurity phase on the boundary as grain boundary area will be smaller. For breakaway of the boundary from a second phase to occur, an extra length of grain boundary has to be created and so the driving force for growth needs to be significant. When it is not significant, dragging or pinning occurs resulting in growth slowing or ceasing completely. As can be seen in Fig. 2.6, the interstitial grain boundary between the second phases will continue to migrate, assuming the driving force is sufficient.

![Diagram of the effect that second phases have on the migrating boundary of a matrix grain depending on the relative strength of driving and pinning forces. (Adapted from Krabbendam et al., 2003).](image)

If the second phases are mobile, the pinning/dragging forces can dynamically change over time. After initial interaction, the migrating boundary can sweep additional second phases along. As migration proceeds, the boundary will consume the surrounding grains and incorporate their second phases into the boundary. Increasing the volume fraction of second phases along grain boundaries results in an increase in the pinning/dragging forces acting upon the boundary. The result of this can either be slowing or cessation of growth depending on the volume fraction of second phases and the boundary driving forces.
If the driving force is sufficiently high, break-away will take place and second phases will become inclusions (Fig. 2.6). However, this is not the most energy efficient configuration for the system owing to the fact that during grain growth, the system is reducing the overall internal free energy of the system via a reduction in grain boundary area. In order for the grain to encompass the second phase, additional grain boundary has to be created which increases the effective grain boundary area of the system. Therefore, unless the grain boundary has a considerably high migration rate, the second phases will likely remain on the boundary.

Physical properties associated with the second phases themselves influence the type of interaction between the boundary and second phase. For instance, shape of the second phase is significant, particularly in the case of a mineral second phase. The orientation of the second phase with respect to the migrating boundary will also be significant. For instance, if a migrating boundary approaches an elongate mica crystal along its long axis the matrix grain will have to create far more boundary area to encompass the grain than if it were to approach from the short axis direction. The former case would result in more efficient pinning as the creation of grain boundary is energy inefficient.

Second phases can either be rigid or deformable. In both cases, a dragging force is applied as the boundary passes but a rigid second phase causes the dihedral angle between the two phases always to be 180° (Fig. 2.7) (Evans et al., 2001). This situation is dependent upon the second phase being completely spherical and rigid which is unlikely to be true in nature. Since a deformable second phase can change its shape, the dihedral angle may approach 120°, i.e., equilibrium, which is more likely to cause cessation of growth. Indeed, it is likely that the second phase will preferentially change its shape to attain the most favourable energy state.
Fig. 2.7. Schematic diagram of the differences between rigid (left) and deformable (right) second phases. The dihedral angle ($\psi$) is more likely to approach equilibrium in the deformable particle and thus will result in a more efficient pinning regime. The dragging force exerted is dependent upon the deformability and boundary energies of each phase. Breakaway occurs if the migration force exceeds the pinning force. (Adapted from Evans et al., 2001)

2.3.1. Mineral second phases

There have been several studies examining the influence of mineral second phases on recrystallization and grain growth. These have been either experimental (e.g., Olgaard, 1990; Yamazaki et al., 1996; Wang et al., 1999) or focused on natural samples examined with the aim of relating their microstructure to the geological setting in which they are found (Austin et al., 2008). Many of the studies on natural materials have been concerned with grain growth in mylonites in areas such as the Alps (Herwegh and Jenni, 2001; Herwegh and Kunze, 2002; Herwegh and Berger, 2003; Herwegh et al., 2005; Ebert et al., 2007a; Ebert et al., 2007b; Austin et al., 2008; Ebert et al., 2008; Herwegh et al., 2008), Greece (Krabbendam et al., 2003) and South Korea (Song and Ree, 2007).

Mineral analogues have also been utilized in order to allow continuous observation of the growing matrix phase. One of the most recent studies of this type was carried out by Brodhag and Herwegh (2010) where norcamphor ($\text{C}_{7}\text{H}_{10}\text{O}$, bicyclo[2.2.1]heptan-2-one), a quartz analogue, was grown under atmospheric pressure and temperatures of 50 °C.
Tests were carried out with glass spheres acting as analogues to mineral second phases. Sample material was pressed between two glass plates thus allowing constant monitoring of the grain size change.

It was found that three pinning regimes (single, multiple and clustered) were observed to be in operation during the tests (Fig. 2.8). The dominant regime was dependent upon the second phase volume fraction in conjunction with the location of the second phases on the grain boundary. Clustered particle pinning was the most efficient pinning regime – clustering tended to occur at grain boundary triple junctions. The least effective of the three types of pinning was single particle pinning where a single sphere of the second phase was located either at a triple junction or along the grain boundary. In such cases, although some pinning force is exerted onto the boundary by the second phase, the remainder of the grain is free to grow. The intermediate regime, multiple particle pinning, occurs when several particles of the second phase were located at either triple junctions or along grain boundaries. In this case a string of particles may be present along a single grain boundary, resulting in a large pinning force being exerted on the boundary. Of particular interest from these experiments was the finding that the dominant pinning regime can change during growth.

![Diagram of the ideal pinning regimes found in natural rocks. (Adapted from Brodhag et al., 2011)](image)

The main limitation of these mineral analogue tests is the use of glass spheres as second phases as, in nature, the second phases are not, in general, spherical or of constant size. The type of second phase can also vary from area to area within natural rocks and each species of mineral second phase will have its own physical properties which will impact on growth.

In order to address this shortcoming, the authors carried out a microstructural study of marbles from the Adamello contact aureole, Italy (Brodhag et al., 2011). The three
pinning regimes were found to be present in the natural samples; furthermore, each regime was dominant within a different temperature range. Clustered particle pinning was dominant at low temperatures, and single particle pinning was dominant at intermediate temperatures. Multiple particle pinning operates over a range of temperatures. At high temperatures, second phases were located along grain boundaries whilst at intermediate temperatures they were found at triple junctions. When comparing the influence of the second phase size and volume fraction, Brodhag et al. (2011) found the latter was the controlling factor in determining the dragging force exerted by the second phases.

An area of particular interest has been the role that second phases play in localizing deformation in the lower crust and upper mantle. The idea of strain localization caused by differences in grain size was first considered by Rutter and Brodie (1988) who proposed that dynamic recrystallization, and the accompanying reduction in grain size, results in a switch from grain size insensitive to grain size sensitive deformation. In principle, this is accompanied by a drop in the strength of the rock (Fig. 2.9). However, de Bresser et al. (1998; 2001) argued that rapid growth of the newly recrystallized grains returns the system to grain size insensitive conditions resulting in only a small overall strength drop. Furthermore, it was suggested that a boundary region exists between the two deformation fields. Upon a rock reaching this region, the forces of grain growth would balance the forces of recrystallization resulting in the system remaining in the boundary region. Nevertheless, the presence of second phases in the rock potentially provides a mechanism of keeping the recrystallized grains small if they inhibit/prevent grain growth.
Fig. 2.9. Deformation mechanism map showing stress vs. grain size for olivine. Strain rate (dashed lines) in s\(^{-1}\). The map also includes the stress/recrystallized grain size curve for olivine (heavy line). The solid arrows represent the evolution of a rock undergoing recrystallization while deforming at constant strain-rate. Accompanying the reduction in grain size is a drop in strength. In a monomineralic system, grain growth would then take place, and the rock would proceed along the dashed arrow, the overall result being an increase in rock strength. If the system contains second phases it is possible that the rock would remain in a weaker, smaller grain size state owing to the pinning force of the second phases. (Adapted from de Bresser et al., 2001).

It has been demonstrated that this is the case for the Wadi al Wasit shear zone, Oman, by Linckens et al. (2011b). They found that strain localization increased in conjunction with the degree of mylonitisation. In ultramylonites, it was found that second phases exerted a significant influence on the degree of strain localization. In addition, differences in rock strength were present between monomineralic and polymineralic regions of the mylonites owing to the grain size difference arising from the presence of second phases. A change in deformation mechanism from dislocation to diffusion creep is observed and is thought to be the cause of the strain localization.

The scenario described by de Bresser et al. (1998; 2001) has since been disputed. Citing recrystallization via grain boundary bulging as a mechanism of grain size reduction, Platt and Behr (2011) suggested that second phases play relatively little role in the localization of deformation. Their reasoning behind this is that zones of deformation at lower crustal and upper mantle levels likely evolve at constant stress. The result would be an increase in strain rate as opposed to a drop in stress. Increased strain leads to increased dislocation formation within grains which in turn leads to continuous recrystallization. The overall consequence is that grain growth will be continually prohibited by recrystallization creating new grains. Platt and Behr (2011) surmise that as long as tectonic conditions remain stable, weakening, and hence localization, will continue to take place.
2.3.2. Solute impurities

Some of the first studies to examine the interaction between a migrating boundary and solute impurity atoms were carried out by Lücke and Detert (1957), Lücke and Stuwe (1963, 1971) and Cahn (1962). These studies proposed that impurity atoms are preferentially accommodated along dislocations and grain boundaries because the lattice structure there is more open. Consequently, when those dislocations/grain boundaries move, it is energetically favourable for the solute impurities to move with them. Whether they do depends on the interaction between solute mobility and dislocation/grain boundary migration driving force. The controlling factors that determine the pinning/dragging effect that an impurity has on a migrating boundary are the boundary migration rate and the diffusivity of the impurity. For instance, consider a system in which the grain boundaries possess a high migration velocity and the solute impurities have a high diffusivity. In this case, the impurities will have the ability to diffuse with the migrating boundary. Visually this would appear as if the boundary is sweeping the impurities along with it as in Fig. 2.6. If the system contained impurities with a low diffusivity, then diffusion of the impurity would be unable to keep up with the migrating boundary resulting in boundary break-away and the impurity becoming incorporated into the grain (Fig. 2.6). Assuming impurities are continually encountered by the moving boundary, the migration rate will be controlled by the rate at which the impurities can be diffused across the boundary.

In a system with boundaries that migrate at lower velocities, impurities with a lower diffusion rate will exert a greater dragging force than an impurity with a higher diffusion rate. In these circumstances, the effective impurity concentration along a given boundary is also more likely to increase with time. Low migration velocities will reduce the diffusion rate needed for impurities to keep pace with the moving boundary. This results in fewer impurities diffusing past the boundary and into the grain and the majority diffusing along with the boundary, thus imposing a dragging force and further reducing migration velocity. As further impurities are encountered and accommodated within the migrating boundary, the drag force will continue to increase, potentially ultimately resulting in stagnation of growth.

Lücke and Detert (1957) were the first to attempt to analyse the effect of impurities on grain boundary motion quantitatively. The authors were prompted by the observation
that as little as 0.01% manganese or iron, when introduced into high purity aluminium, could reduce the boundary migration rate by as much as sixteen orders of magnitude. They considered a straight grain boundary migrating through impurity atoms which are in solid solution. The authors first determined the concentration of impurities along the boundary \((C_B)\) as

\[
C_B = C e^{V/k_BT}
\]

Eq. 2.9

where \(C\) is the mean concentration of impurity atoms, \(V\) is the interaction energy between boundary and impurity, \(k_B\) is Boltzmann’s constant and \(T\) is absolute temperature. Combining Eq. 2.9, the effect of the attraction forces of a single impurity atom acting between the boundary and impurities \((f)\), and the density of impurity atoms \((n_D = 4\sqrt{2}/a^2, a\) is a lattice parameter) per cm\(^2\) of the boundary, an equation describing the drag force produced by impurities acting on the boundary \((p)\) was developed:

\[
p = n_D f = \frac{4\sqrt{2}}{a^2} C_B f = \frac{4\sqrt{2}}{a^2} f C e^{V/k_BT}
\]

Eq. 2.10

The net migration velocity of a boundary \((v)\) was then considered under the circumstances where both boundary and impurity move at the same velocity:

\[
v = M \cdot f = \frac{D}{k_BT} f = \frac{D_0 e^{-Q_D/k_BT}}{k_BT} f
\]

Eq. 2.11

where \(M\) is the mobility of the impurity which has the Einstein relation \(M = D/kT\), \(D\) is the diffusion coefficient of the impurity atom, \(D_0\) is the maximum diffusion coefficient and \(Q_D\) is the activation energy. By combining Eqs. 2.9, 2.10 and 2.11 a complete expression for the migration of a grain boundary under the drag force of solute impurities can be derived:

\[
v = \frac{p}{k_BT} \frac{a^2}{4\sqrt{2}} \frac{D_0}{C} \exp\left(-\frac{(Q_D + V)}{k_BT}\right)
\]

Eq. 2.12

As highlighted by Mendelev et al. (2001), a serious limitation of Lücke and Detert’s analysis is that it is only valid for boundaries which are stationary. Cahn (1962) aimed to address this deficiency by taking into consideration the flux of impurity atoms across the boundary \((J)\) which leads to an impurity concentration profile (Fig. 2.10), and developed the following equation (after Mendelev et al., 2001)
\[ J = -\frac{D C}{k_B T} \frac{d\mu}{dx} - vC = D \frac{dC}{dx} - \frac{D C}{k_B T} \frac{dE}{dx} - vC \quad \text{Eq. 2.13} \]

where \( \mu \) is the chemical potential of the impurity, \( D \) is the diffusion coefficient in the direction normal to the boundary and \( E \) is the impurity-boundary interaction energy. If the boundary is stationary (i.e., \( v = 0 \)), then \( J = 0 \), this returns us to Lücke and Detert’s original equation (Eq. 2.9). The concentration profile is expected to reach a steady state, in which case \( J = -vC \), and Eq. 2.13 becomes (Mendelev et al., 2001)

\[ D \frac{dC}{dx} + \frac{D C}{k_B T} \frac{dE}{dx} + vC = vC \quad \text{Eq. 2.14} \]

Based upon a single impurity atom exerting a drag force of \(- (dE/dx)\), the overall drag force applied by the impurities \( (P_i) \) was determined by Cahn (1962) to be

\[ P_i = -n_D \int_{-\infty}^{+\infty} (C_B - C) \frac{dE}{dx} dx \quad \text{Eq. 2.15} \]

The variation in the terms in the above equations can be displayed graphically (Fig. 2.10) as a function of distance from the grain boundary.
The effect of solute impurities upon a boundary migrating at $v > 0$ was then considered. At low velocities, the impurity concentration profile deviates from the symmetrical curve determined for a boundary of $v = 0$ (Fig. 2.10c). As the boundary migrates, the impurity atoms cause a drag effect behind the migrating boundary hence the higher concentration of impurities behind the boundary in comparison to the area approaching the boundary (Fig. 2.10c). The pressure ($P_B$) driving boundary migration in this low velocity regime was found to be (Humphreys and Hatherly, 2004)

$$P_B = \frac{v}{M_0} + \alpha' vC$$

Eq. 2.16

where $M_0$ is the mobility of an impurity-free boundary and $\alpha'$ is a constant.

At higher velocities Eq. 2.15 becomes

$$P = \frac{v}{M_0} + \frac{\theta C v}{a \alpha' v^2}$$

Eq. 2.17

where $\alpha''$ is a constant. Given the increased velocities, $v/M_0$ is likely to become the term that dictates driving pressure for boundary migration; it is also apparent from Eq. 2.16 that higher velocities will diminish the drag effect of impurities. Eqs. 2.15 and 2.16 can be combined to give one expression that describes the overall driving force.

$$P = \frac{v}{M_0} + \frac{\alpha C v}{1 + \alpha' v^2}$$

Eq. 2.18

At steady state, the driving force is determined as

$$P(v, C_B) = P_0(v) + P_1(v, C_B)$$

Eq. 2.19

where $P_0(v)$ is the intrinsic driving force in an impurity free system. $P_0$ is given by

$$P_0(v) = \lambda v = \frac{v}{M_0}$$

Eq. 2.20

where $\lambda$ is the intrinsic drag coefficient.

A summary of the findings by Lücke and Detert (1957), Lücke and Stuwe (1963, 1971) and Cahn (1962) can be seen in Fig. 2.11. In a pure system ($C_B = 0$) there is no dragging force acting on the boundary. Once impurities are introduced the curve deviates to the right, initially by a small amount ($C_{B1}, C_{B2}$), because of the impurity/boundary interaction effects, larger driving forces are required to produce the equivalent change seen in the pure system. Despite this deviation, the curve is still continuous. At larger concentrations
of impurities ($C_{B3}$) the curve deviates significantly from the pure system and displays an S-shape. The section of the curve with the shallower slope represents a low velocity boundary (Eq. 2.15) “loaded” with impurities (Lücke and Stüwe, 1971). In this regime, the velocity of the boundary decreases with increasing impurity concentration. In the higher velocity section, the boundary is effectively impurity free because there is sufficient driving force for it to break free of any impurities encountered.

![Diagram](image)

**Fig. 2.11.** Schematic graph of the hypothesised form of the grain boundary velocity curves as a function of the driving force at different boundary impurity concentrations ($C_B$) where $C_B < C_{B1} < C_{B2} < C_{B3}$. Dashed lines represent the discontinuous transition from each regime. (Modified from Humphreys and Hatherly, 2004).

A major limitation of these initial studies is the assumption that the grain boundary remains straight during migration. More recent studies (e.g., Lee et al., 2000b; Lee et al., 2000c) have established that grain boundaries migrate via the formation of kinks, resulting in non-planar, faceted boundaries on the atomic scale. As noted by Mendelev et al. (2001), impurity diffusivity and interaction energy have not been quantified in experimental studies making accurate comparisons between these studies and this theoretical treatment extremely difficult.
2.3.3. Pores as second phases

It has long been known in the fields of both Earth and material science that the presence of pores within a material has the potential to restrict grain growth (Hsueh and Evans, 1983; Karato, 1989; Nichols and Mackwell, 1991; Azuma et al., 2012; Roessiger et al., 2012). Some of the first studies to examine the interaction between porosity and grain growth were carried out by Coble (1961a, b) and Nichols (1966). Studies by Coble focused on the formation and evolution of pores during the sintering of various types of powder. Key to this investigation was the role of pore-related diffusion during sintering.

Porosity behaves in a similar way to impurities in that pores impose a drag force on a moving boundary. At low boundary migration velocities, pores are mobile and move with the boundary as it migrates (Alley et al., 1986). Liu and Patterson (1993) proposed a model for pore controlled growth in which two distinct regimes were established to describe the influence that pores have on a migrating boundary. If a large enough area fraction of pores is present along a boundary then growth will be controlled by these pores; this corresponds to the loaded boundary stage in the impurity analysis. Conversely, if little to no porosity is present, the boundary will effectively be free from the influence of porosity and growth will depend on the intrinsic mobility of the boundary. A clear linear boundary, given by $A = [R_C/4q][(M_p/M_b) + 1]$, was experimentally determined between these two regimes by Liu and Patterson (1993)

\[
d \leq \frac{R_C}{4q} \left[ \frac{M_p}{M_b} + 1 \right] S_{vp}^{sp}
\]

\[
d \leq AS_{vp}^{sp}
\]

Eq. 2.21

where $d$ is the mean grain size, $q$ is a factor relating grain size to boundary curvature, $R_C$ is the degree of contact between the boundary and the second phase ($R_C = 1$ at unity), $M_p$ is pore mobility, $M_b$ is boundary mobility and $S_{vp}^{sp}$ is pore surface area per volume. On a plot of inverse grain size vs. $S_{vp}^{sp}$, microstructures growing under pore-controlled conditions were defined by Eq. 2.21. The microstructure will cease to be controlled by porosity if the right hand side of Eq.2.21 reduced to less than the left hand side. The position and slope of the boundary, defined by Eq. 2.21, was found to vary with changes in $M_p/M_b$ and $R_C$. Increasing either of the two factors was found to increase the
potential for pore-controlled growth. This model is, however, only valid for immobile pores (Groza, 1999).

One significant difference between pores and other types of second phases is their greater ability to behave dynamically. As pores are mobile, they can be moved along the boundaries upon which they lie via diffusion. If two pores come into contact with each other, they can coalesce. Although this will not alter the overall porosity volume, it will decrease the total porosity surface area.

Nichols (1969) divides this process of coalescence into two stages, firstly a rapid stage of contact and coalescence between multiple pores takes place which then proceeds into a prolonged stage of volume adjustment in which pressure equilibrium is re-established within the pores. The first stage involves a decrease in surface area and an increase in strain energy in the boundary surrounding the pores arising from the process of coalescence. The following stage of re-equilibration eliminates this strain energy in addition to increasing the surface area by an amount equal to the decrease during coalescence. Nichols points out that because of this, any change in free energy during both stages is due to gas expansion within the pores which in turn makes the process of coalescence thermodynamically favourable. The final pore size is given by \( r_f^2 = r_1^2 + r_2^2 \) where \( r_{1,2} \) are the radii of the two pores prior to coalescence.

Three important diffusion mechanisms are known to operate on the atomic scale in the presence of porosity; surface diffusion, volume diffusion and vapour diffusion (Nichols, 1969). Although more than one of these processes can occur at the same time, each mechanism is dominant at a given stage of pore coalescence. The initial stage of pore coalescence is dominated by surface diffusion while the post-coalescence stage of volume adjustment has volume diffusion as its dominant mechanism (Nichols, 1969). Vapour diffusion is considered to be the most significant process during post-coalescence movement of pores through the matrix (Nichols, 1969).

Sintering is the change in pore morphology and pore size together with limited grain growth that occurs when a powder compact is heated and converted into a solid specimen. As such, the principles involved in sintering are intimately related to those of grain growth and, together with the large amount of sintering literature (Kang, 2005 and references therein; German, 2010 and references therein), form a useful basis for this
study. Coble (1961a) identified three distinct stages of sintering. The first involves a change from negligible contact area between particles to approximately 20% of the cross-sectional particle area between particles being in contact. The areas of the particles that are in contact form “necks”, the formation of these necks has the additional result of causing compaction on the order of 10%. Due to the relatively small contact area between grains, grain growth is limited. As sintering proceeds and the amount of cross-sectional particle area in contact between particles increases, the restrictions on growth decrease. Coble defines the termination of the initial sintering stage to be at the first instance of growth.

The intermediate stage of sintering is characterised by the elimination of the original discrete particle texture and the formation of a pore and grain boundary system accompanied by a significant increase in the cross-sectional particle contact area. Limited grain growth is characteristic of this stage; in addition, triple junction dihedral angles are commonly 120°. Owing to the way in which the particles interact to form grain boundaries, it is common to find pores at these triple junctions. Pore interconnectivity during this phase is high with pores often occupying the entire side length of a particle. This stage terminates when the amount of cross-sectional particle contact area has increased to the point at which pore channels close and form isolated bodies. The porosity at this point is approximately 5-10% (Kang, 2005).

Upon entering the final stage of sintering, pores are frequently found at the intersections of three or four grains as this is the most energy efficient configuration for the system. Pores will continue to shrink throughout the remainder of this stage. Theoretically, the final stage of sintering is completed once all pores are eliminated. Eliminating pores has the consequence of reducing the force restricting grain boundary mobility, and thus the potential for grain growth increases as sintering goes to completion. Consequently, sintering effectively gives way to grain growth before full densification is achieved at a few percent porosity.

Multiple material transport mechanisms are in operation during the sintering, densification and growth processes (Fig. 2.12, Tab. 2.2). All six mechanisms involve transport of material to the grain boundaries. Once sintering has been completed and growth starts, pores become significant for the transport of material as they form the sites at which surface diffusion and evaporation/condensation takes place. Not displayed
in Fig. 2.12 is plastic deformation at the grain boundary and creep. These two mechanisms are important early in the sintering process when the individual grains are first pressurized because, at that stage, the contact areas are small, and the contact stresses correspondingly high (Kang, 2005).

![Fig. 2.12. Schematic diagram of the material transport mechanisms in operation during sintering and densification. The material sources are displayed in Tab. 2.2. (Adapted from Kang, 2005).]

<table>
<thead>
<tr>
<th>Material transport mechanism</th>
<th>Material source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice diffusion</td>
<td>Grain boundary</td>
</tr>
<tr>
<td>Grain boundary diffusion</td>
<td>Grain boundary</td>
</tr>
<tr>
<td>Viscous flow</td>
<td>Bulk grain</td>
</tr>
<tr>
<td>Surface diffusion</td>
<td>Grain surface</td>
</tr>
<tr>
<td>Lattice diffusion</td>
<td>Grain surface</td>
</tr>
<tr>
<td>Gas phase transport:-</td>
<td></td>
</tr>
<tr>
<td>Evaporation/condensation</td>
<td>Grain surface</td>
</tr>
<tr>
<td>Gas diffusion</td>
<td>Grain surface</td>
</tr>
</tbody>
</table>

Tab. 2.2. Table displaying the transport mechanisms and material sources for the mechanisms in. All mechanisms result in material deposition at grain boundary necks. (Adapted from Kang, 2005).

A large body of work concerning the effect of pores on grain growth has been conducted on ice (e.g., Alley et al., 1986; Azuma et al., 2012; Roessiger et al., 2012). Bubbles in ice have been shown to have a similar effect on boundary migration as second phases. Assuming the presence of a large number of uniformly distributed bubbles, Alley et al.
(1986) constructed velocity curves with similar morphology to those in Fig. 2.11. They determined that systems containing pores with high mobility would have a velocity curve similar to that of $C_{b1}$ whilst systems containing exclusively low velocity pores have curves resembling that of $C_{b2}$.

Alley et al. (1986) found that when a migrating boundary and a bubble interact, the bubble changes shape to become more lenticular as illustrated in the two intermediate stages shown in Fig. 2.7. The change in shape of the pore establishes a vapour pressure gradient between the pore-boundary front and the remainder of the pore behind the boundary because of the difference in the radius of curvature between these parts of the pore boundary. This gradient allows diffusion of atoms from the pore-boundary front to the area behind the boundary, and the net result is the migration of the pore with the boundary (Alley et al., 1986; Azuma et al., 2012).

In normal grain growth tests on synthetic polycrystalline ice, Azuma et al. (2012) demonstrated that the presence of porosity influences the growth exponent in the normal grain growth equation. As predicted by theoretical studies of normal grain growth, the growth exponent for samples containing no bubbles was 0.5 whereas samples in which grain growth was influenced by air bubbles had much lower values, 0.17-0.1. This reduction in the growth exponent value is accompanied by a decrease in the activation energy from 110-120 kJ/mol in bubble free samples to 40-70 kJ/mol in samples containing bubbles.

2.4. Quantifying second phase effects

2.4.1. Zener parameter

The principal influences exerted by second phase particles on grain growth are captured by the volume fraction ($f_p$) and size ($d_p$) of the particles, and are accommodated in the Zener parameter ($Z$), first introduced by Zener (in Smith, 1948);

$$Z = d_p/f_p$$

Eq. 2.22

For a full derivation of the equation, see Manohar et al. (1998). Small values of $Z$ imply a greater influence exerted by the second phase particles. The two components of the Zener parameter are closely related in terms of their impact on grain growth (Fig. 2.13).
At constant volume fraction, the Zener parameter decreases with decreasing particle size – the pinning effect is more significant if the second phase particles are less dispersed. At constant particle size, the Zener parameter decreases with increasing second phase particle volume fraction – the pinning effect is greater the higher the volume fraction of second phases.

Fig. 2.13. Schematic diagrams displaying the effect of varying the Zener parameter. Black ellipses are second phases and the clear grains are the matrix phase. In rocks with smaller Z values, the growing matrix will interact with the second phases at a smaller grain size than in rocks with larger Z values. This has the potential to keep the grain size smaller. (Adapted from Herwegh and Berger, 2004).

2.4.2. Zener plot

The Zener parameter allows the construction of so called Zener plots to help visualize graphically the significance of second phase effects (Fig. 2.14). The typical form taken by Zener plots can be seen in Fig. 2.14 where Z is plotted against matrix grain size. A clear change in the slope of the data can be seen between low Z values (large $f_p$ and small $d_p$) and high Z values (small $f_p$ and large $d_p$). At low Z values, the second phases impose a significant pinning force on the matrix phase resulting in the final grain size being small. At high Z, the second phases exert little pinning force on the matrix thus allowing it to grow unimpeded.

Effectively the Zener parameter can be thought of as a description of the overall mean free path length within a material. At larger Z values, the inter-particle distance is large, resulting in the second phases exerting little pinning pressure on the matrix grains. The opposite is the case for smaller Z values; here the second phases are relatively close to each other thus creating an overall larger pinning force.
Fig. 2.14. Example Zener plot of calcite stable matrix grain size vs. Zener parameter. Note the clear discrimination between pore controlled and boundary controlled fields. Note that even through the slope of the data points in the “Weakly affected by second phase” region are horizontal, this is rarely the case. Typically a reduction in the slope occurs. (From Herwegh and Berger, 2004)

2.4.3. Refinements of the Zener parameter

Zener and Smith’s initial analysis made approximations that are not necessarily valid in geological systems. For instance, second phase particles are treated as spherical but in geological systems this is generally not the case. The second phases were also approximated as being both rigid and immobile. Again, we know that this is not always the case in geological systems. As stated previously, pores are not rigid bodies and have been shown to have their morphology affected by any migrating boundaries that they come into contact with (Alley et al., 1986; Evans et al., 2001). Pores can also be swept up by grain boundaries during migration thus demonstrating that second phases can be mobile. Smith and Zener also restricted their analysis to the case in which the second phases do not undergo any chemical reactions during growth. In geological systems, chemical reactions can cause the formation of new minerals which may have significantly different pinning properties compared to the original second phase.

Later studies (Olgaard and Evans, 1986; Mas and Crowley, 1996) modified the original Zener equation to account for the location of second phases along grain boundaries. One of the assumptions made by Zener was that second phases are uniformly distributed throughout the system. In the majority of systems, this is not the case. In order to attempt to take these variations into account Eq. 2.22 was modified to

\[ d_{max} = N \left( \frac{d_p}{f_{p}^{m}} \right) \]  

Eq. 2.23
where \( d_{\text{max}} \) is the measured matrix grain size, \( N \) is an empirically derived constant and \( m \) is a factor dependent upon the geometric position of the second phases. If second phases are randomly dispersed throughout the matrix, then \( m = 1 \), if located along grain boundaries, \( m = 1/2 \) and if located at matrix grain intersection points, \( m = 1/3 \) (Olgaard and Evans, 1986).

Incorporating this \( m \) factor into the Zener equation is particularly significant when considering the pinning effect of porosity in geological materials over large timescales. Over long periods of time, the location and size of porosity potentially changes as grain boundaries move and either sweep the pores along with the boundary or incorporate them into the grains to form inclusions. Pores will continue to be eliminated during grain growth via grain boundary diffusion resulting in certain areas potentially becoming free of porosity. Unlike individual mineral crystals, multiple pores can easily coalesce into one large pore, effectively increasing the \( d \) value in the Zener parameter whilst keeping the \( f \) value constant which has the effect of reducing the effective pinning force. However, the \( m \) factor takes account of this issue. Pores are more likely to coalesce at triple junctions as these provide the most efficient pinning regime (Kang, 2005; Brodhag and Herwegh, 2010; Brodhag et al., 2011). Therefore, the \( m \) factor compensates for the effective decrease in the Zener parameter by increasing the effective volume fraction of pores when the \( m \) factor is taken into account.

It should be noted that the values of \( m \) stated here are based upon the entirety of the second phase volume fraction being located at the relevant location, i.e., along grain boundaries or at triple junctions. In natural systems, it is more likely that the second phases will be distributed along both grain boundaries and at triple junctions, hence the value of \( m \) in geological materials is likely to lie in-between 1, 0.5 and 0.3. Indeed, this is found to be the case in natural geological studies (Mas and Crowley, 1996), and in studies involving metal and ceramic materials (Olgaard and Evans, 1986 and references therein). Most published values lie between 0.3 and 0.5 thus indicating that second phases have a tendency not to be randomly distributed throughout a material but instead clustered along grain boundaries and at triple junctions (Olgaard and Evans, 1986).

Since the first description of the Zener parameter various studies have been undertaken that have resulted in other changes being made to the original equation (see Table 1 in Olgaard and Evans (1986) for a summary of the modified equations). However, until
recently, little effort has been made to incorporate the Zener parameter into the normal grain growth equation (Eq. 2.8) explicitly. Upon first examination this appears to be reasonable, in that one of the assumptions key to the normal grain growth equation is that the system is pure. However, given that natural systems are rarely pure, it is important that the influence of second phases be taken into account. In an attempt to address the presence of second phases, Brodhag and Herwegh (2010) modified the normal grain growth equation based on the observation that \( n \) and \( k \) values are dependent upon the \( Z \) value. In their experiments on norcamphor, they observed that \( n \) and \( k \) in Eq. 2.8 increases with increasing \( Z \) (Fig. 2.15). Empirically, these effects are well described by

\[
n = a_n \cdot Z^{b_n} \tag{Eq. 2.24}
\]

and

\[
k = a_k \cdot Z^{b_k} \tag{Eq. 2.25}
\]

where \( a_n \) and \( a_k \) are constants and \( b_n \) and \( b_k \) describe the slope of the data in the pore controlled region (Fig. 2.15). Eqs. 2.24 and 2.25 are then substituted into the normal grain growth equation to give

\[
ad^{a_n}Z^{b_n} - d_0^{a_n}Z^{b_n} = a_k \cdot Z^{b_k}(t - t_0) \tag{Eq. 2.26}
\]
Fig. 2.15. Experimental data obtained by Brodhag and Herwegh (2010) for static grain growth tests using norcamphor and glass spheres. The graphs display the linear relationship, and hence dependence, of a) \( n \) and b) \( k \) on \( Z \) when growth is influenced by second phases. There is no change in \( n \) and \( k \) at larger values of \( Z \), that is the original normal grain growth equation (Eq. 2.8) then applies (From Brodhag and Herwegh, 2010).

This new equation allows the prediction of grain growth kinetics that includes \( Z \) values. Brodhag and Herwegh (2010) applied the equation to their experimental data for norcamphor to produce an experimental duration integrated Zener type plot.
2.5. Previous work on halite boundary migration and diffusion kinetics

For information on the crystal structure of halite see §8.3.

2.5.1. Past work on halite grain boundary migration

There is a large range of previous work regarding halite grain boundary migration in the field of Earth science. Research has taken place on halite microstructural evolution during boundary migration within deformed then annealed (314 °C-450 °C) polycrystals of extremely dry (<5 ppm water) synthetic halite using electron backscatter diffraction analysis (Bestmann et al., 2005; Piazolo et al., 2006). These studies found that both slow (10^{-9}-10^{-10} \text{ m/s}) and fast (10^{-7}-10^{-6} \text{ m/s}) strain-induced grain boundary migration were in operation, with the migration velocity increasing and grain boundaries becoming smoother and straighter with increasing temperature. The increase in boundary migration velocity was primarily attributed to the temperature dependence of mobility and local variations in driving force. However, at lower temperatures, solute impurity drag significantly impacts the velocity, whereas at higher temperatures, this becomes less influential and the anisotropy of the boundary arising from differences in crystallographic orientation becomes significant.

Studies on statically recrystallized wet halite samples have also been carried out (e.g., Schenk and Urai, 2004; Schenk et al., 2006; Desbois et al., 2012). Schenk and Urai (2004) and Schenk et al. (2006) observed, in halite samples annealed at room temperature, that the process of initial normal grain growth gave way to a period of abnormal grain growth once normal grain growth had ceased. Abnormal grains were found to have a euhedral cubic crystal shape, not the textures commonly associated with abnormal growth (Fig. 2.5). The cause of abnormal growth, together with the euhedral grain shape, was attributed to a combination of grain boundary migration via the formation and movement of atomic ledges and the distribution of the brine phase along grain boundaries which acted to increase the grain boundary anisotropy and boundary mobility. In the presence of a fluid, the boundary will migrate via a process of dissolution, diffusion and precipitation (Urai et al., 1986).

There are numerous studies examining boundary migration during dynamic recrystallization and deformation mechanism of NaCl during axial compressive creep.
experiments (e.g., Urai et al., 1986; Spiers et al., 1990; Peach et al., 2001; ter Heege et al., 2004, 2005a, b). Spiers et al. (1990) highlighted the significance of solution-precipitation creep, facilitated by the presence of a fluid phase at the grain boundary, as a deformation mechanism in NaCl deformed at low temperatures (20 °C-90 °C) and pressures (0.5-2.2 MPa). The rate of pressure solution was found to be controlled by the rate of grain boundary diffusion. In similar experiments carried out at higher temperature (75 °C-240 °C) on dry (5 ppm water) and wet (9-46 ppm water) synthetic polycrystalline halite samples, ter Heege et al. (2004, 2005b) found that only subgrain-rotation, not boundary migration, took place in the dry samples. In agreement with Spiers et al., at these elevated temperatures, grain boundary migration in wet samples was assisted by the presence of a grain boundary fluid. A similar transition was found by Guillope and Poirier (1979) in compressional creep tests on NaCl dynamically recrystallized single crystals. At low temperatures, recrystallization occurs by subgrain rotation, these subgrain boundaries then migrate at higher temperatures. Uniaxial compression tests on dry synthetic NaCl samples at temperatures of 250 °C-780 °C by Franssen (1994) observed that boundary migration becomes increasingly more significant with increasing temperature with recrystallization by grain boundary migration becoming dominant at temperatures of 450 °C and above.

Much work has been carried out on halite in the material science community with halite behaviour during sintering being a particular focus (e.g., Swinkels and Ashby, 1981; Goodall et al., 2006). The latter authors found, from sintering halite powders of various particle sizes under atmospheric pressures, at temperatures of 500 °C and 700 °C, that, after initial plastic yielding at contact areas between grains, sintering either takes place by vapour condensation or by surface diffusion. Only the latter of these was shown to result in densification, the extent of which increases with decreasing halite particle size.

Despite some studies having described grain growth in wet halite (e.g., Schenk and Urai, 2004; Schenk et al., 2006; Desbois et al., 2012), there appears to have been no systematic attempt to establish the isostatic grain growth kinetics of halite at elevated temperatures and confining pressures. It is this gap in halite knowledge that this study aims to address.
2.5.2. Past work on halite diffusion kinetics

Halite is an ionic compound, the principal anion and cation of which are Cl\(^-\) and Na\(^+\). Cl\(^-\) is commonly considered to be the rate controlling ion as it is the slowest diffusing species (Senseny et al., 1992). It has been reported that grain boundaries can act to enhance the rate of Cl\(^-\) diffusion, but not Na\(^+\) diffusion (Heard, 1972). However, it has been shown that, although the rate of Cl\(^-\) diffusion increases in the presence of grain boundaries, it never exceeds Na\(^+\) (Franssen, 1994).

There is an extensive range of activation enthalpy values reported for NaCl, however, the range in these reported values is considerable (Frost and Ashby, 1982). These come from studies on sintering of halite powders, uniaxial compressive creep studies and laboratory measurements using electrical conductivity, electromagnetism and measurements of atomic motion of radioactive isotopes (Frost and Ashby, 1982; Bénière, 1999).

There is a distinct lack of kinetic diffusion data for halite for the pressure and temperature conditions used in this study. One study that has, however, been conducted at similar conditions to those used here was carried out by Heard (1972), in which polycrystalline halite samples were extended at confining pressures of 200 MPa and temperatures of 23 °-400 °C. These tests resulted in an activation enthalpy of 98.32 kJ/mol which correlates with Na\(^+\) diffusion in single NaCl crystals at temperatures below 550 °C (75.3-96.2 kJ/mol) (Aschner, 1954). Based on the kinetic data discussed below, it is apparent that this value is considerably lower than similar studies carried out at atmospheric pressures. This reduction in activation enthalpy was attributed to the presence of water in the halite acting to enhance grain boundary diffusion (Frost and Ashby, 1982).

From the sintering of 75 µm NaCl powder under atmospheric pressure at temperatures of 586 °-701 °C, Goodall et al. (2006) determined an activation enthalpy of 150 kJ/mol. This was correlated with Cl\(^-\) grain boundary diffusion activation enthalpy values (155 kJ/mol) previously determined in creep experiments by Burke (1968) conducted under atmospheric pressure at temperatures of 365 °-550 °C.

In the same tests described in §2.5.1., Franssen (1994) observed a switch in rate controlling mechanism and activation enthalpy with increasing experimental temperature. At temperatures of 250 °-450 °C, Franssen (1994) calculated an activation
enthalpy of 129±8 kJ/mol which was close to activation enthalpy values of core diffusion (103-155 kJ/mol). At temperatures of between 500 °C-780 °C, the activation enthalpy increases to 227±10 kJ/mol which was considered by Franssen (1994) to represent a switch in the rate controlling diffusion process to lattice diffusion of Cl⁻ (214-217 kJ/mol) (Frost and Ashby, 1982). Burke (1968) observed a similar increase in activation enthalpy to 201 kJ/mol at temperatures above 550 °C.

An activation enthalpy value of 217 kJ/mol has also been determined for surface diffusion of Cl⁻ at 700 °C-750 °C (Swinkels and Ashby, 1981). However, there appears to be little in the way of further information for surface diffusion in NaCl.

Diffusion kinetics have been demonstrated to vary with misorientation angle of migrating halite grain boundaries (Sun and Bauer, 1970). At misorientation angles of 30°, an activation energy of 144.7 kJ/mol was calculated, which indicates self-diffusion across grain boundaries. Conversely, at misorientation angles of 5°, the activation enthalpy increases to 212.3 kJ/mol, which corresponds to bulk self-diffusion of the Cl⁻ ion.

The determined self-diffusion activation enthalpy value for the Na⁺ cation range from 61.3 to 223 kJ/mol within the temperature range 300-1073 K. For the slower diffusing halite anion, Cl⁻, the range of activation enthalpy values for self-diffusion is similarly large (33-260 kJ/mol) over a temperature range of 500-1080 K (Bénière, 1999). Activation enthalpies for the hetero-diffusion of foreign cations, anions and neutral species are displayed in Tab. 2.3.
Tab. 2.3. Table displaying the range of activation enthalpies for hetero-diffusion in halite. The temperatures at which the activation enthalpies were determined. (From Bénière, 1999).

<table>
<thead>
<tr>
<th>Ion</th>
<th>( H ) (kJ/mol)</th>
<th>( T ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubidium (Rb(^+))</td>
<td>191-203</td>
<td>872-1060</td>
</tr>
<tr>
<td>Cesium (Cs(^+))</td>
<td>178-193</td>
<td>823-1023</td>
</tr>
<tr>
<td>Calcium (Ca(^{2+}))</td>
<td>82-155</td>
<td>633-1068</td>
</tr>
<tr>
<td>Strontium (Sr(^{2+}))</td>
<td>88-131</td>
<td>721-1068</td>
</tr>
<tr>
<td>Barium (Ba(^{2+}))</td>
<td>77-146</td>
<td>673-1023</td>
</tr>
<tr>
<td>Yttrium (Y(^{3+}))</td>
<td>102</td>
<td>833-1053</td>
</tr>
<tr>
<td>Manganese (Mn(^{2+}))</td>
<td>60-91.6</td>
<td>623-1048</td>
</tr>
<tr>
<td>Cobalt (Co(^{2+}))</td>
<td>102-128</td>
<td>733-1033</td>
</tr>
<tr>
<td>Nickel (Ni(^{2+}))</td>
<td>25-125</td>
<td>473-1023</td>
</tr>
<tr>
<td>Copper (Cu(^+))</td>
<td>139</td>
<td>623-923</td>
</tr>
<tr>
<td>Silver (Ag(^+))</td>
<td>67-193</td>
<td>473-999</td>
</tr>
<tr>
<td>Gold (Au)</td>
<td>218</td>
<td>643-723</td>
</tr>
<tr>
<td>Zinc (Zn(^{2+}))</td>
<td>49-102</td>
<td>813-1073</td>
</tr>
<tr>
<td>Cadmium (Cd(^{2+}))</td>
<td>25-89</td>
<td>548-928</td>
</tr>
<tr>
<td>Mercury (Hg(^{2+}))</td>
<td>55</td>
<td>722-822</td>
</tr>
<tr>
<td>Lead (Pb(^{2+}))</td>
<td>95</td>
<td>620-842</td>
</tr>
<tr>
<td>Uranium (U(^{4+}))</td>
<td>175</td>
<td>773-1016</td>
</tr>
<tr>
<td>Fluoride (F(^-))</td>
<td>173</td>
<td>900-1014</td>
</tr>
<tr>
<td>Bromide (Br(^-))</td>
<td>187-206</td>
<td>773-1038</td>
</tr>
<tr>
<td>Iodide (I(^-))</td>
<td>196-221</td>
<td>803-1034</td>
</tr>
<tr>
<td>Sulphate (SO(_4^{2-}))</td>
<td>108</td>
<td>813-1013</td>
</tr>
<tr>
<td>Hydrogen (H)</td>
<td>26.4</td>
<td>623-773</td>
</tr>
<tr>
<td>Helium (He)</td>
<td>21</td>
<td>573-773</td>
</tr>
</tbody>
</table>
3. Experimental strategy for the 200 MPa confining pressure tests

3.1. Starting material

Reagent grade halite powder (99.5 %+ NaCl) was obtained from Fisher Scientific. The impurity content as supplied by the manufacturer is listed in Tab. 3.1.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halite (NaCl)</td>
<td>&gt;99.5</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Total Phosphorus (P)</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Total Silicon (Si)</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Total Sulphur (S)</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

The powder was crushed and sieved by S.J. Covey-Crump and P.F. Schofield, for this study the 38-125 µm sieve fraction has been used.

3.2. Experimental apparatus

3.2.1. Nimonic 1

The Nimonic 1 triaxial deformation apparatus was employed during this study. There are three such machines in the Rock Deformation Laboratory at the University of Manchester all of which were designed and constructed in-house by Prof. E.H. Rutter and Mr. R.F. Holloway. Nimonic 1 (Fig. 3.1, Fig. 3.2, Fig. 3.3), the apparatus used in this study, was originally assembled in 1980, although it has since received several major refurbishments so that almost nothing of the original apparatus remains. The apparatus is capable of maintaining conditions of up to 700 °C and 300 MPa safely for long periods of time.
(longer than one month). The only limiting factor in the duration of an experiment is the stability of the copper jacket that houses the sample in the de-ionised water confining fluid. Over time, the copper is etched from the jacket and precipitated onto the cooler regions of the upper piston. Given sufficient time, the jacket becomes thin enough to rupture, causing the test to fail.
Fig. 3.1. Diagram of the Nimonic 1 triaxial deformation apparatus. The apparatus is top loading. It is capable of confining pressures of approximately 300 MPa and temperatures of approximately 700 °C (Covey-Crump, 1992). (Diagram adapted from Mariani, 2002).
Fig. 3.2. Photograph of the Nimonic 1 apparatus showing the components above the support frame (see Fig. 3.1). The image displays the machine as it would look inside its protective cage during an experiment.
The Nimonic name originates from the material used for the pressure vessel; this being a nickel-cobalt-chromium-molybdenum alloy (Nimonic 105 alloy). The basic alloy contains approximately \( \leq 68\% \) nickel, 14-16\% chromium, 18-22\% cobalt, 4.5-5.5\% molybdenum and 4.5-5.9\% aluminium in addition to minor amounts of carbon, silicon, copper, iron, manganese, titanium, lead, sulphur, boron and zirconium, each of which constitute \( \leq 1.5\% \).
3.2.1.1. **The central section**

The central section of the apparatus, which houses the sample, consists of a pressure vessel surrounded by two furnaces; one upper and one lower (Fig. 3.1, Fig. 3.2). Each of the furnaces is independently controlled by a variable transformer (Variac) that is in turn regulated by a Eurotherm controller. Surrounding the furnaces is a layer of ceramic fibre thermal insulation. A pressure transducer is inserted through the confining pressure inlet pipe; this monitors the pressure within the vessel.

3.2.1.2. **Top closure section and sealing units**

The top section of the machine consists of two tensile collars that are secured to each other via eight tensile bolts; between these sits a block that houses the top sealing assembly (Fig. 3.1, Fig. 3.3). The sample assembly and upper piston are inserted into the pressure vessel via a 28.36 mm diameter hole in the top of the tensile collar.

Surrounding the sealing block is a brass water cooling jacket. Outside this jacket are copper coils that carry water around the top closure and allow heat to be taken away from the sealing block and tensile collars. Below the tensile collar is another brass water cooling jacket. These measures are in place in order to keep the temperature around the top closure below 100 °C and to stabilize the temperature profile along the axial column of the apparatus. A thermocouple is inserted into the sealing block. In the event of the temperature going over 100 °C this thermocouple shuts down the furnaces. The water in the cooling system is continuously circulated around the laboratory via a pump system. To ensure that the water does not become too hot, two air conditioning units keep the laboratory at a constant temperature of 23 °C.

The upper piston and sample assembly are secured into the Nimonic 1 apparatus via a sealing nut which is screwed above the seal assembly; above this a second nut is inserted to retain the piston (Fig. 3.1). These two nuts, together with the sealing assembly, prevent either the upper piston or the confining fluid from leaving the top of the pressure vessel.
The seal assembly is comprises a stainless steel packing piece, a rubber O-ring (BS616), a nylon packing piece, a brass mitre ring split into an inner and outer section, and a stainless steel mitre block (Fig. 3.4). The base of the mitre block is tapered to a 45° angle (Fig. 3.5) and the split mitre rings also have the same angle (Fig. 3.6). The seal is provided by the O-ring. An initial partial seal is made by the O-ring when the piston sealing nut is tightened after placing the sample assembly in the apparatus. The seal is completed when the confining pressure is introduced, forcing the stainless steel packing piece against the O-ring resulting in the O-ring expanding. The mitre ring configuration provides some flexibility in the way that the O-ring is squeezed when the confining pressure is applied. Since the O-ring loses its rubber-like elastic qualities at high temperature, the top closure (and bottom closure) need to be kept cool, hence the use of the water cooling jackets. Repeated pressure cycles also results in the O-ring losing its elastic-like properties; therefore, the O-ring is checked before every test run and replaced when appropriate.

*Fig. 3.4. Photograph of the upper piston sealing unit (shown upside down).*
Fig. 3.5. Photograph displaying the tapered top edge of the stainless steel mitre block.

Fig. 3.6. Photograph of the split mitre ring section of the top sealing unit.
3.2.1.3. **Bottom closure section**

The bottom closure section consists of components similar to those that make up the top closure section. Directly at the top of the bottom closure section is a tensile collar configuration that is the same as that on the top closure. The bottom closure also contains the same water cooling configuration that is present on the top closure.

The confining pressure inlet pipe is located in the bottom closure section of the Nimonic 1 apparatus. The inlet into the pressure vessel itself is within the bottom closure above the lower sealing assembly.

At the base of the tensile collar lies the internal load cell (Fig. 3.7). Assembled in-house, this load cell has the same design of seal assembly as used in the top closure block (Fig. 3.7). The way in which the load cell works is described elsewhere (e.g., Covey-Crump, 1992) – this is not relevant here because no deformation experiments were performed on the Nimonic 1 apparatus. The load cell makes up the base of the lower piston; the remainder of which is made up of an extensional piece that sits on top of the load cell assembly. The upper end of the lower piston is part of the sample assembly.

The force gauge sits on a universal ball joint (Fig. 3.8) which acts to transfer the load to the sample. The use of the ball joint allows consistent alignment of the force gauge and the loading piston throughout the application of axial load. In order to prevent the force gauge from rotating during load application, an anti-rotation pin, located at the base of the force gauge (Fig. 3.7), is used to hold the force gauge in place.
Fig. 3.7. Photograph of the internal load cell unit used in the Nimonic 1 apparatus emphasizing the sealing arrangement. When in the machine, the lower piston extension piece sits flush with the threaded end of the force gauge.

Fig. 3.8. Photograph displaying the universal axial load joint.
4.2.1.4. **Maintenance during the project**

Few problems with the apparatus were encountered during the project. The most significant experimental problem was a period of continuous jacket ruptures. This was overcome by adjusting the sample assembly technique and the heating and pressurising procedure (discussed in §3.3).

In May and June 2013, a leak developed around the top of the bottom sealing block that resulted in a gradual drop in confining pressure at a rate of 10 MPa/hr. In an attempt to resolve the problem, the tensile bolts around the lower collar were tightened by hand as it was thought that they might have loosened due to repeated heat cycles. The leak persisted, and it was decided that a full disassembly was required in order to examine the individual components and fully ascertain the source of the problem.

Upon disassembly, it was found that the leak was caused by a slight separation of the seal at the join between the pressure vessel and the bottom closure block. The problem was resolved by re-machining the top surface of the lower closure block, doing so involved having the seal that caused the leak to be re-machined as it is part of the block.

The Nimonic 1 apparatus was then reassembled and a number of tests were run using a hollow alumina sample. Initially, the tests involved only confining pressure in order to ascertain whether the seal was properly repaired. Once it became apparent that this was the case, temperature was introduced to ensure that the seal remained intact whilst at elevated temperature and pressure conditions.

**3.2.2. Thermal profile calibration**

In order to ensure that experimental temperatures are accurate thermal profiles of the apparatus were undertaken twice over the course of this study. Nimonic 1 is designed to be at maximum temperature over a length of a few centimetres adjacent to the sample (hot spot) and to cool away from this hot spot to a fixed temperature below approximately 100 °C at the ends of the pressure vessel. Specimen temperature is measured using a thermocouple inserted down the upper piston to a point a few centimetres above the sample and just above the hot spot. Consequently, the thermal profile calibration is essential to (a) establish that the temperature is constant along the
length of the sample and (b) allow the temperature recorded by the thermocouple to be corrected to the actual sample temperature.

Considering the sensitivity of grain growth to temperature, it is essential that the calibrated temperature settings are correct. Variations of a few degrees Celsius can impact on the resulting grain size, and, therefore, the calculated kinetic values.

To allow the accurate detection of the temperature at the centre of the sample, a hollow alumina cylinder 21 mm in length was used. The cylinder has a 1 mm hole drilled parallel to its long axis thus allowing a stainless steel type-K thermocouple to be passed to the top of the lower piston. A 0.5 mm diameter thermocouple measuring 495 mm long is used for the profile.

To establish which, if any, of the power input / control temperature settings need to be adjusted the Nimonic 1 apparatus was set to the previously calibrated settings and a profile taken. The profile was obtained by retracting the thermocouple in 1 mm intervals for the first 30 mm then at 2 mm intervals up to 100 mm then finally at 10 mm intervals up to 200 mm. The temperature is measured in mV and is converted to °C in the logging program using the formula;

\[
Temp (°C) = 1.677193924 \times 10^{-3}T^3 - 0.1054483859T^2 + 25.78447301T - 2.605351278 + T_L
\]

Eq. 3.1

Where \( T \) is temperature in mV and \( T_L \) is the temperature of the laboratory reference junction (30 °C).

If the desired temperature was not attained at the centre of the sample, or the thermal hotspot was not located in the same position as the specimen, the Variac and Eurotherm settings were adjusted. The system was allowed to re-equilibrate for at least two hours then the profile was repeated. The final thermal profiles obtained under optimal settings are displayed in Fig. 3.9 and Fig. 3.10, the Variac and Eurotherm calibrations are shown in Tab. 3.2.
Fig. 3.9. Graph displaying the thermal profile of Nimonic 1 taken in January 2011. The grey rectangle and the black dot represent the sample and the position of the thermocouple respectively.

Fig. 3.10. Graph displaying the thermal profile of Nimonic 1 taken in January of 2012. The grey rectangle and the black dot represent the sample and the position of the thermocouple respectively.
Tab. 3.2. Calibrated Eurotherm and Variac settings resulting from the thermal profile calibrations. The Nimonic 1 calibration used prior to the start of this study is also shown (Dec-09).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Dec-09 Variac (%)</th>
<th>Eurotherm</th>
<th>Jan-11 Variac (%)</th>
<th>Eurotherm</th>
<th>Jan-12 Variac (%)</th>
<th>Eurotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>N/A</td>
<td>N/A</td>
<td>45</td>
<td>21.3</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>350</td>
<td>N/A</td>
<td>N/A</td>
<td>50</td>
<td>25</td>
<td>46</td>
<td>24.9</td>
</tr>
<tr>
<td>400</td>
<td>53</td>
<td>28.1</td>
<td>54</td>
<td>29</td>
<td>50</td>
<td>28.8</td>
</tr>
<tr>
<td>450</td>
<td>58</td>
<td>32.1</td>
<td>59</td>
<td>33.6</td>
<td>54</td>
<td>32.8</td>
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<tr>
<td>500</td>
<td>60</td>
<td>36.4</td>
<td>62</td>
<td>38</td>
<td>59</td>
<td>36.9</td>
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<tr>
<td>600</td>
<td>70</td>
<td>44.8</td>
<td>73</td>
<td>45.4</td>
<td>66</td>
<td>45</td>
</tr>
<tr>
<td>650</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>70</td>
<td>49.2</td>
</tr>
<tr>
<td>700</td>
<td>77</td>
<td>52.5</td>
<td>80</td>
<td>53.9</td>
<td>75</td>
<td>53.2</td>
</tr>
</tbody>
</table>

3.3. Experimental procedure

3.3.1. Sample fabrication and assembly

Samples are fabricated in jackets of commercial purity copper tubing cut to length. The initial wall thickness of the tubing is 0.25 mm. The jackets were first annealed in order to make them more malleable. This was done by heating until red hot and by then immediately quenching them in cold water. Copper oxide generated during heating is removed by placing the jacket in dilute nitric acid for a few seconds.

The jacket was placed in a split-die assembly (Fig. 3.11), a Nimonic alloy spacer was inserted at the bottom of the jacket to prevent the powder escaping during the test. Halite powder was added to the jacket in three or four stages; after each stage the powder was tamped down by hand in order to reduce porosity. Using a split-die has the benefit of preventing the walls of the jacket from barrelling out when the powder is compressed. Once the halite had been added, a second Nimonic alloy spacer was placed on top of the powder and the jacket was removed from the split-die and transferred to a lathe.
In order to mount the jacket on the pistons, both the upper and lower pistons were secured in each end of the lathe, the upper piston in the stationary section and the lower piston in the mobile section. To reduce the risk of the jacket snagging as it was mounted, each end of each piston was lubricated with copper grease. Before the sample was mounted, Nimonic alloy swaging rings were placed around the jacket. These rings serve to create a seal between the jackets and the piston preventing the confining fluid from penetrating the ends of the jacket and contaminating the sample during the experiment. The inside of the rings is tapered so that when pressed onto the piston to the point at which the copper just yields they form a tight seal between the swaging ring, jacket and piston. The halite filled jacket was mounted onto the pistons by first hand-pressing one end of the jacket onto the lower piston and then slowly bringing the two ends of the lathe together until the pistons touch the Nimonic spacers.

The swaging rings were pressed onto both pistons using a hand press. To reduce friction between the jacket and the swaging rings, the outer surface of the jacket where the seal...
is to be made was coated with a thin film of copper grease. The final sample assembly can be seen in Fig. 3.12.

![Diagram and Photograph]

*Fig. 3.12. Left: Schematic diagram of the sample assembly. Right: Photograph of the assembly. Scale applies to both images.*

Care was taken to ensure that all the individual components were clean before each experiment. Once the sample was assembled, a pressure pipe was screwed into the top of the upper piston, and the entire assembly was placed into the Nimonic 1 apparatus. Finally, a 1 mm diameter, stainless steel sheathed, type-K thermocouple was inserted down the pressure pipe and upper piston (the specimen thermocouple). The thermocouple was secured to the pressure pipe by an Aminco stainless steel block. This block has a hole machined in its side that was not sealed during the experiments. This, therefore, acted as a vent for the sample during the test.
3.3.2. Pressurising and heating procedure

Before any heating takes place, confining pressure must be added to the pressure vessel in order to compress the jacket around the sample powder. This is done by introducing the confining medium (de-ionised water) into the sample chamber via a hydraulic pump (SC pump; Hydraulic Engineering Corp. Serial No. 22646). Confining fluid is added in four stages; the confining pressure is taken to 30 MPa (approximately 4,500 psi), 75 MPa (approximately 10,800 psi) and 100 MPa (approximately 14,500 psi), after raising the pressure to each of these increments the sample was allowed to equilibrate for 10 minutes. Finally, the sample was taken to starting pressure of about 180 MPa (approximately 26,100 psi). In initial tests, this stepped pressurising technique was not utilised, and samples were taken straight to experimental pressures. This resulted in a high occurrence of jacket ruptures owing to rapid stretching for the jacket around the piston ends. Introducing the stepping procedure resulted in fewer jacket ruptures.

A stepped heating technique was also utilised. The halite powder was isostatically hot pressed by heating the sample at 85% furnace power from room temperature up to 100 °C below the desired experimental temperature. At this point, the furnaces were turned to the calibrated power level. Allowing the specimen to slowly reach experimental temperature in this way minimises the temperature overshoot. Heating of the pressure vessel causes the confining pressure to rise with temperature; the result of this is that when the desired experimental temperature is reached the confining pressure will be 200 MPa (approximately 30,000 psi).

3.3.3. Data logging and end test procedures

Data was logged throughout the experiment (including the pressurising and heating stages) using three TTI 1705 True RMS programmable multimeters connected to an Acorn PC. The data was recorded using the RockDef logging program developed in-house by E.H. Rutter. During the tests, temperature and confining pressure was logged. During the heating stage, logging rate was set to 60 seconds. After temperature had stabilized, the logging rate was adjusted to either 600, 1200 or 3600 seconds based on the required test duration.
Upon termination of the experiment, the furnaces were switched off, and the sample allowed to cool. Cooling from 600 °C to room temperature took approximately 2 ½ hours. Upon reaching room temperature, the confining pressure was allowed to drain from the pressure vessel over the course of 1 minute.

3.3.4. Thin-section preparation

Thin-sections were made by first cutting the samples in half along their long axis. Before mounting on glass slides, the cut samples were polished on a glass plate using 400 µm alumina polishing powder (Buehler UK Ltd.) to remove any significant surface topography/scratches generated while cutting. Because halite is water soluble, two different lubricating mediums were used. When cutting the samples in half, turpentine substitute was used because it is both low cost and has a similar viscosity to that of water (the fluid usually used to cool the saw blade). For the polishing phase, diethylene glycol, C₄H₁₀O₃ (BHD Ltd.) was used. Once any marks had been removed, a final polish was carried out using 5 µm alumina polishing powder in order to ensure that as few air bubbles as possible would be trapped in the mounting resin when the sample was glued to the slide.

The halite half-cylinders were mounted to frosted glass slides using Crystalbond Mounting Adhesive (SPI Supplies). The Crystalbond is supplied in the form of a solid bar and so must be melted first. This was done by using a razor blade to slice a small amount of adhesive off the bar and placing this onto a frosted glass slide on a hot plate. Once the adhesive had melted the sample was pressed onto the slide. To remove any air bubbles, the sample was moved around the slide for a few seconds and then reset in the centre. One advantage of using Crystalbond is that it cools quickly, allowing the polishing of the sample to be started within around 10 minutes of mounting. Crystalbond can also be dissolved with acetone. The primary benefit of this is that if any mistakes were made during the mounting, e.g., large air bubbles trapped under the sample, then the specimen could be removed from the slide and remounted without damage.

Initial polishing of the mounted sample was done by hand on a glass plate with 400 µm alumina powder. Once the specimen had been thinned to a thickness of approximately 0.5 mm, it was transferred to an Engis Kent Mark II rotating polisher (Fig. 3.13). The
sample was polished at a slow speed using 0.3 µm alumina powder until the thin-section was approximately 5-30 µm thick. Sections thinner than standard optical thin sections were required because of the fine grain size (for accurate visualization of the grain boundaries the section should not be thicker than one grain). As the thin-section approached its final thickness, it was periodically removed from the polisher and checked under a transmitted light microscope to establish that it was not becoming too thin and to take steps, if needed, to avoid any wedging of the sample.

![Engis Kent Mark II rotating polisher](image)

Fig. 3.13. Photograph of the Engis Kent Mark II rotating polisher. The machine polishes samples through rotation of the polishing plate and lateral movement of the arm that holds the thin-section. The thin-section holder itself is free to rotate thus improving polishing efficiency. 15 cm ruler for scale.

Any scratches from the surface of the halite were removed by gently wiping a lightly damp cloth over the sample and immediately drying. In addition to removing scratches, the water etches the grain boundaries resulting in the boundaries being accentuated when viewed under a microscope. This makes grain size measurements much more straightforward and accurate.
After thin-section fabrication, the sections, and the remaining sample half-cylinders, were stored in a desiccation box with silica gel. The gel was changed on a weekly basis. During microscope work, only the samples that were required were taken from the desiccation box as to minimise the exposure of the samples to the atmosphere.

3.4. Data acquisition

3.4.1. Grain size data

Grain size data was obtained through the use of an optical microscope (Jenapol) and thin-sections. Grain sizes were obtained using the linear intersect method (Underwood, 1970), which involves counting the number of grains along a line across the thin-section.

Transects are chosen by moving the section by an arbitrary amount in an arbitrary direction and by then counting the grains that intersect the cross-hairs under the field of view. This process was repeated forty times per sample in order to give a statistically valid number of grains (approximately 250 grains, however in the samples with the largest grain size the number of grains counted reduced to 150). Twenty transects were counted along the length of the sample and twenty transects along the width of the sample in order to eliminate any potential preferred shape orientation that may have developed. As discussed below, many of the samples contain areas of abnormal grain growth. When this was the case, grain counting was not carried out in these areas. Hence, the grain size measurements reported here all come from areas of sample that have textures resembling those produced by normal grain growth.

The width of the field of view is known, and so the number of grains along the intersection divided by the width of the field of view gives the grain size. The grain sizes given here were determined by dividing the total number of intersected grains by the total length of intersection line.

On a 2D section through a 3D microstructure the linear intercept grain size observed is smaller than the true grain size because the plane of section does not go through the centre of all the grains visible in the finished section. The mean linear intercept grain size is directly proportional to the three dimensional grain size (Thompson, 1972) but the constant of proportionality depends on grain shape, grain size distribution, and other
microstructural variables (Han and Kim, 1995). For spherical grains of the same size the constant of proportionality is 1.5 (Han and Kim, 1995). However, as it is clear that the halite used in this study is neither spherical nor equi-sized, no corrections of this kind were applied. Provided the grain size distributions are quasi-stationary, the only effect of not applying this correction is to change the magnitude of $k_0$ in the normal grain growth equation (Eq. 2.8); the values of $n$ and $H$ are unaffected (Covey-Crump, 1997).

### 3.4.2. Grain size distribution data

In order to obtain grain size distribution data, tracings were made from optical photomicrographs of the thin-section. To accomplish this, photomicrographs were taken of the thin-sections at x10 magnification and then manual tracings were made of the grain boundary network using either hard copies of the photomicrographs on a light box or electronic copies of the photomicrographs loaded within Adobe Illustrator CS3. In order to acquire accurate grain sizes and size distribution results, a minimum of 150 grains were traced per sample, however, in poor quality samples or those displaying abnormal grain growth or a lack of grains displaying normal grain growth textures, this number could not be obtained. Using x10 magnification for the photomicrographs was found to be the most time efficient way to image sufficient numbers of grains. During the tracing, any incomplete grains on the edge of the micrographs were ignored.

Tracings made using a light box were scanned into a computer and saved as jpeg files. Tracings made in Adobe Illustrator CS3 were also saved as jpeg files (Fig. 3.14). Images were then loaded into the Java based freeware image analysis program ImageJ (version 1.46, June 26, 2012, (Schneider et al., 2012)). A number of steps were required to tidy up the tracings before they could be analysed. Initially, the scan was converted to an 8-bit image then converted again into binary. During this conversion, the thinner lines on the tracing were sometimes lost causing gaps to appear in the microstructure. As ImageJ obtains grain areas from complete grains, these gaps must be closed. This was done by using the dilate function within ImageJ. This function examines every pixel in the image independently and detects if any of the adjoining pixels are those included in a grain boundary. If this turns out to be the case, the pixel in question is assigned as part of the grain boundary, and the process is repeated until all grain boundary gaps are filled. By the end of this stage, the grain boundaries can become overly thick, thereby reducing the
real grain area. To reduce this effect, the erode function in ImageJ was used. This function is essentially the opposite of the dilate function.
Fig. 3.14. Top: Photomicrograph of HP65 (500 °C, 00d 48h 00m). Middle: Grain boundary tracing of the above photomicrograph completed using Adobe Illustrator. Bottom: Image produced after processing the tracing in ImageJ. Width of all three images is 1450 µm.
A potential problem in using this process is that the grain interior of smaller grains can be completely occupied by grain boundaries during dilation. When the boundaries are eroded the grain interior will not return and so the grain is lost from the image. This issue was addressed by zooming into these grain boundaries as much as possible and selecting only the desired pixels to erode and dilate.

The area of each grain is calculated by first entering a scale representing the length of the original micrograph. ImageJ then calculates the area of the image and then the area of each individual grain. A text file is produced listing the area results for each grain. The grain area data was then exported into MS Excel and converted into grain size using the formula

\[ d = 2\sqrt{A_r/\pi} \]  

Eq. 3.2

that is, the grain size is calculated as the diameter \( d \) of a circle of area \( A_r \). Histograms of \( \log_{10}(d/\bar{d}) \) were plotted, where \( \bar{d} \) is the arithmetic mean value of \( d \). In these histograms, the data were sorted into 12 size bins, and a distribution curve plotted for each sample. Binning was carried out as it allows easier visual comparison between samples. This is particularly relevant in data sets that contain many samples, e.g., 600 °C. Using the STDEV, SKEW and KURT functions in MS Excel, the standard deviation, skewness and kurtosis of the size distributions were obtained.

The full suite of tracings used to determine the grain size distributions can be found in Appendix 14.3.

3.4.3. Electron microscope imaging

3.4.3.1. Electron microscope operating conditions

A LEO 1455 VP (Variable Pressure) SEM based at the Natural History Museum (London, UK) was used to obtain high resolution images of porosity along grain boundaries. This was carried out in two sessions in March 2013 and December 2013. During the use of the SEM, chamber pressure was approximately 20 Pa, the spot size was 500 µm and the working distance varied between 14-17 mm. In the March 2013 session, the beam current was 15 kV while in the December session it was 20 kV. All images were obtained using back-scattered electron signal.
The advantage of using this particular low vacuum SEM over a high vacuum SEM is that thin-sections do not need to be coated and hence can easily be re-used without the need to potentially contaminate the specimen by removing the coating.

3.4.3.2. Pore analysis procedures

A similar technique to that outlined in §3.4.2 was used to examine pore volume fraction and size around a given grain. SEM images were transferred into Adobe Illustrator CS3 where the grain boundaries were traced, and the grain area found using the procedure outlined in §3.4.2 (Fig. 3.15b). The same approach was taken with the grain boundary pores; each grain boundary was viewed in high magnification and examined for potential pores (Fig. 3.15c). This proved difficult at times owing to the small size of some of the pores. Many pores are sub-5 µm in size, and when the SEM image is zoomed into this level, the smallest pores appear pixelated and thus have poorly defined boundaries making accurate identification of the smallest pores difficult. The majority of the samples were imaged at a magnification of between x150 and x250. At these magnifications, the maximum pore diameter that can be resolved is approximately 0.36 µm. This corresponds to the area of 1x1 pixel.
Fig. 3.15. Top: Scanning electron microscope image of HL7 (511 °C, 00d 05h 00m). Middle: Grain boundary tracing image produced after being analysed by ImageJ. Bottom: Pore tracing image produced after being analysed by ImageJ. The width of all three images is 1555 µm.
The problem of image resolution was encountered again whilst using ImageJ during conversion of the image to binary. Pixels in ImageJ are of a fixed size and, as a result, when the smallest pores were converted to binary their diameters were about one pixel. As a consequence, pores <0.36 µm in diameter all have the same diameter in the data presented here. The only way of addressing this is to re-image the thin-sections at a higher magnification to obtain higher pore resolution at the tracing and binary conversion stage. However, this results in more individual images needing to be analysed due to the decreased number of grains within each image. Both time constraints and SEM availability meant that this could not be carried out. At least 200 pores were traced in each image, and more typically this number is about 500; this is considered statistically sufficient for the purposes of this study.

The resulting pore area data was transferred to MS Excel and converted to pore size using Eq. 3.2, the data was then binned and a histogram plotted as described in §3.4.2. Tracings were re-examined and pores correlated with the grains around which they lie. This allowed the average pore size and pore volume fraction of a given grain to be determined. The latter was calculated by dividing the total pore area by the grain area; this has been shown to be a valid approach when determining volume fraction in a two phase material containing no shape fabric (Underwood, 1970). Note that the pore area was not added to the grain area in the volume fraction calculation. This is considered to be valid as the pore volume fraction is commonly less than 0.05 reducing to less than 0.001 at the largest grain size, therefore, only a marginal difference will be made to the calculated pore volume fraction. When assessing pore volume fraction and pore size, the grains were considered in isolation, that is, if a pore lies along the boundary between two grains, the pore was considered to belong to both grains and was effectively counted twice. If a pore was situated at a triple junction, it was effectively counted three times, once for each grain.

The full suite of tracings used to determine the pore size distributions and Zener parameter can be found in Appendix 14.4.
3.5. Data analysis

3.5.1. Establishing grain growth start time and starting grain size

In order to fit the normal grain growth equation (Eq. 3.8), it is necessary to establish when recrystallization has gone to completion. This is taken as the time ($t_0$) at which normal grain growth is initiated, and the grain size ($d_0$) at this time is taken as the initial grain size at the onset of normal grain growth. Failure to establish $t_0$ and $d_0$ accurately has a large impact on the values of the parameters obtained when fitting the normal grain growth equation unless one restricts the data used to $t >> t_0$ and $d >> d_0$ (see Covey-Crump, 1997).

When determining $d_0$ and $t_0$, each data set was considered individually. Firstly, data were plotted according to the normal grain growth equation (Eq. 2.8) as $\log_{10}(d^{1/n} - d_0^{1/n})$ vs. $\log_{10}(t - t_0)$ (with $n = 0.25$, see below) using $d_0 = 45$ µm and $t_0 = 10$ sec. A $t_0$ value of 10 seconds was chosen as this was the shortest test duration of the entire data set. A $d_0$ value of 45 µm was chosen because this was the grain size from the shortest duration experiment at the lowest temperature (experiment HP30 (350 °C, 10 sec)). The resulting plot should be non-linear with a change in the slope of the data distinguishing the transient period pre-growth period from the onset of grain growth. This change in slope was rarely identified with any great certainty (Fig. 3.16) due to either growth having started prior to the shortest test duration or the presence of samples with clearly anomalous grain sizes causing scatter in the data, and thus masking the change in slope (see §3.5.4).

Because of the difficulty in assigning values based purely on the graphical data, a number of constraining criteria were put in place to assist in the determination of $d_0$ and $t_0$. Firstly, $d_0$ was always considered to be larger than the grain size of the shortest duration test at the lowest temperature (HP30 (350 °C, 10 sec), 45 µm). Secondly, values of $d_0$ should increase smoothly with increasing temperature. Thirdly, $t_0$ should smoothly decrease with increasing temperature. Lastly, the choice of $d_0$ and $t_0$ should lead to the data having a slope of approximately 1 when the normal grain growth equation is fitted with $n = 0.25$ on the grounds that $n$ cannot meaningfully be less than 0.25 (Tab. 2.1). By applying these criteria, $d_0$ and $t_0$ were determined for all data sets (Fig. 3.17).
Fig. 3.16. Graph displaying the 500 °C data set. The data set has been fitted to the normal grain growth equation using values of \( n \) (0.25), \( d_0 \) (45 µm) and \( t_0 \) (10 sec). Note that no obvious change in slope is visible.

Fig. 3.17. Graph displaying the grain growth data for the 500 °C data after fitting the normal grain growth equation using values of \( n \) (0.25), \( d_0 \) (100 µm) and \( t_0 \) (48200 sec).
3.5.2. Evaluation of the grain growth exponent

In order to determine the most appropriate value of \( n \) for halite, each data set was considered individually. In accordance with the normal grain growth equation (Eq. 2.8) the data were plotted as \( \log_{10}(d^{1/n} - d_0^{1/n}) \) vs. \( \log_{10}(t - t_0) \), using the values of \( d_0 \) and \( t_0 \) obtained by the methods described in §3.5.1, and \( n \) values of 0.25, 0.33 and 0.5, i.e., the values attributed to the different growth controlling mechanisms in operation during normal grain growth (Tab. 2.1). The ‘correct’ value of \( n \) is the value for which the slope of the data, when plotted in this way, is equal, or closest, to 1. This process was repeated for all sample suites, an example plot is shown in Fig. 3.18 (see Appendix 14.1 for the equivalent plots of Fig. 3.18 for all temperature sets).

![Graph showing grain size data](image)

**Fig. 3.18.** Plot of 500 °C tests fitted to the normal grain growth growth equation using values of \( d_0 \) (100 µm) and \( t_0 \) (48200 sec) and \( n \) values of 0.25, 0.33 and 0.5. The slope of the line of best fit (\( m \)) is included for each \( n \) value. The most appropriate value of \( n \) is that with a best fit line closest to 1. In this case, \( n = 0.25 \) represents the best fit. The dashed line has a slope of 1.
3.5.3. Evaluation of the rate term in the growth equation

Once $n$ is known, the rate term in the normal grain growth equation ($k$) may be straightforwardly obtained by taking the natural log of each side of the normal grain growth equation (Eq. 2.8) and rearranging:

$$\ln(d^{1/n} - d_0^{1/n}) - \ln(t - t_0) = \ln(k)$$  \hspace{1cm} \text{Eq. 3.3}

Alternatively, for data from different temperatures

$$\ln(d^{1/n} - d_0^{1/n}) - \ln(t - t_0) = \ln(k_0) - (H/RT)$$  \hspace{1cm} \text{Eq. 3.4}

Hence, a plot of $\ln(d^{1/n} - d_0^{1/n}) - \ln(t - t_0)$ vs. $1/T$ should produce a straight line with slope $= -(H/R)$ and intercept $= \ln(k_0)$.

3.5.4. Complications introduced by anomalous samples

Although the areas from which the grain size measurements were taken displayed a microstructure similar to that of normal grain growth it is evident from visual inspection of $\log_{10}(d^{1/n} - d_0^{1/n})$ vs. $\log_{10}(t - t_0)$ plots that there is considerable scatter in several of the datasets (e.g., Fig. 3.19). This scatter is far greater than that observed in similar experiments on calcite (Covey-Crump, 1997). In the example illustrated in Fig. 3.19, one data point in particular has an anomalously small grain size while three have anomalously large grain sizes. In fitting the normal grain growth equation, data points that are clearly anomalous are not included in the fit. These anomalies can generally be attributed to greater boundary pinning (anomalously small grain sizes) or the inclusion of areas of abnormal grain growth in the grain size measurements (anomalously large grain sizes), as discussed on a case by case basis below. The conclusion that this study arrives at, is that all of the grain size data is to a greater or lesser extent influenced by pore-grain boundary interactions, and that the variability of these interactions from sample to sample inevitably introduces scatter in the datasets. Consequently, the uncertainty on the fitted parameters (particularly $k_0$ and $H$) in the normal grain growth equation is quite high. Deciding upon what samples display anomalous sizes is done through visual assessment of graphs, such as Fig. 3.19, together with examination of the microstructures displayed in each sample.
3.5.5. Fitting grain size distributions

Two types of distribution are used in this study: the log normal distribution and the Weibull distribution.

3.5.5.1. Fitting the log normal distribution

The probability density function of the normal distribution \( f(x) \) is given by

\[
    f(x) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left( -\frac{(x-\mu_x)^2}{2\sigma^2} \right) \tag{Eq. 3.5}
\]

Where \( x \) is the particle diameter normalized by the mean, \( \mu_x \) is the mean, \( \sigma \) is standard deviation and \( \sigma^2 \) is the variance. Note that after this section (§3.5.5.), the normalized particle diameter \( x \) will be referred to as \( d/\bar{d} \) when and \( d_p/\bar{d}_p \) when referring to the

---

**Fig. 3.19.** Graph displaying the grain growth data for the 500 °C data set fitted to the normal grain growth equation using values of \( n (0.25) \), \( d_0 (100 \mu m) \) and \( t_0 (48200 \text{ sec}) \). The circled data points are interpreted as not reflecting normal grain growth. The line of best fit (solid), when the four circled points are excluded, is shown.
distributions for grain size and pore size respectively, where $d$ and $d_p$ are grain and pore size, and $\bar{d}$ and $\bar{d}_p$ are the mean grain and pore size.

The corresponding cumulative density function ($F(x)$) is given by

$$F(x) = \phi \left( \frac{x-\mu}{\sigma} \right) = \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{x-\mu}{\sigma \sqrt{2}} \right) \right]$$  \hspace{1cm} \text{Eq. 3.6}

where $\phi$ is the standard Gaussian distribution. Eq. 3.6 may be linearized as,

$$\phi^{-1}[F(x)] = -(\mu/\sigma) + (1/\sigma)x$$  \hspace{1cm} \text{Eq. 3.7}

$\phi^{-1}[F(x)]$ is commonly referred to as the inverse cumulative distribution function. Note in the above two equations, the mean is the value of $x$ at $F = 0.5$ and the standard deviation corresponds to the value of $x$ at $F = 0.8415$ minus the mean.

A widely used approximation of $\phi^{-1}[F(x)]$ is proposed by Schmeiser (1979):

$$\phi^{-1}[F(x)] = \frac{[F(x)^{0.135} - (1-F(x))^{0.135}]}{0.1975}$$  \hspace{1cm} \text{Eq. 3.8}

This expression is accurate at values of $0.0028 \leq F(x) \leq 0.9972$ (Schmeiser, 1979). At values of $F(x) \geq 0.9972$ the expression becomes

$$\phi^{-1}[F(x)] = \frac{0.24[F(x)^{0.14} - (1-F(x))^{0.09}]}{0.1596}$$  \hspace{1cm} \text{Eq. 3.9}

At values of $F(x) \leq 0.0028$, the expression becomes

$$\phi^{-1}[F(x)] = -\left\{\frac{0.24[F(x)^{0.14} - (1-F(x))^{0.09}]}{0.1596}\right\}$$  \hspace{1cm} \text{Eq. 3.10}

Owing to the number of grain and pores analysed in this study, it is rare for more than a few data points to lie outside of $0.0028 \leq F(x) \leq 0.9972$.

A more precise (to nine decimal places) but cumbersome approximation of the inverse cumulative distribution function is that of Acklam (2003):

$$\phi^{-1}[F(x)] = \frac{(a_1Q^3 + a_2Q^4 + a_3Q^5 + a_4Q^6 + a_5Q + a_6)Q^{1/2}}{b_1Q^2 + b_2Q^4 + b_3Q^5 + b_4Q^6 + b_5Q + 1}$$  \hspace{1cm} \text{Eq. 3.11}

where $Q = (F - 0.5)^2$ for $0.02425 \leq F \leq 0.97575$

$$\phi^{-1}[F(x)] = -\left\{\frac{c_1Q^6 + c_2Q^7 + c_3Q^8 + c_4Q^9 + c_5Q + c_6}{d_1Q^6 + d_2Q^7 + d_3Q^8 + d_4Q + 1}\right\}$$  \hspace{1cm} \text{Eq. 3.12}
where \( Q = \left[ -2 \ln(1 - F) \right]^{1/2} \) for \( F \geq 0.97575 \)

\[
\phi^{-1} [F(x)] = \frac{c_1 Q^5 + c_2 Q^4 + c_3 Q^3 + c_4 Q^2 + c_5 Q + c_6}{d_1 Q^4 + d_2 Q^3 + d_3 Q^2 + d_4 Q + 1} \quad \text{Eq. 3.13}
\]

where \( Q = \left[ -2 \ln(F) \right]^{1/2} \) for \( F \leq 0.02425 \)

in which

\[
\begin{align*}
  a_1 &= -39.6968302866538 \\
  a_2 &= 220.946098424521 \\
  a_3 &= -275.928510446969 \\
  a_4 &= -30.6647980661472 \\
  a_5 &= 2.50662827745924 \\
  b_1 &= -54.4760987982241 \\
  b_2 &= 161.585836858041 \\
  b_3 &= -155.698979859887 \\
  b_4 &= 66.8013118877197 \\
  b_5 &= -13.2806815528857 \\
  c_1 &= -0.00778489400243029 \\
  c_2 &= -0.322396458041136 \\
  c_3 &= -2.40075827716184 \\
  c_4 &= -2.54973253934373 \\
  c_5 &= 4.37466414146497 \\
  c_6 &= 2.9381639269878 \\
  d_1 &= 0.00778469570904146 \\
  d_2 &= 0.32246712907004 \\
  d_3 &= 2.445134137143 \\
  d_4 &= 3.75440866190742
\end{align*}
\]

From calculations of the inverse normal distribution function, it can be seen that there is relatively little difference between both the simple Schmeiser approximation and the more complex Acklam approximation (Tab. 3.3). Even at the largest \( F \) values of \( 0.99 \), the distribution functions are similar. Consequently, in this study, the less cumbersome Schmeiser approximation (Eq. 3.8) is used.

\textit{Tab. 3.3. Table displaying the calculated inverse normal distribution values for the two approximations discussed in the text.}

<table>
<thead>
<tr>
<th>( F )</th>
<th>Schmeiser ( \phi^{-1} [F(x)] )</th>
<th>Acklam ( \phi^{-1} [F(x)] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.6</td>
<td>0.2517321194</td>
<td>0.2533471031</td>
</tr>
<tr>
<td>0.7</td>
<td>0.5215420353</td>
<td>0.5244005134</td>
</tr>
<tr>
<td>0.8</td>
<td>0.8385594133</td>
<td>0.841612332</td>
</tr>
<tr>
<td>0.9</td>
<td>1.281278359</td>
<td>1.281551559</td>
</tr>
<tr>
<td>0.95</td>
<td>1.649306985</td>
<td>1.644853682</td>
</tr>
<tr>
<td>0.99</td>
<td>2.317171018</td>
<td>2.326347874</td>
</tr>
</tbody>
</table>

108
By plotting \( \ln(x) \) vs. \( \phi^{-1}[F] \), a linear cumulative distribution curve should be produced if the size distribution is best described as a log normal distribution.

### 3.5.5.2. Fitting the Weibull distribution

The Weibull distribution probability \( f(x) \) and cumulative distribution \( F(x) \) functions are given by:

\[
f(x) = \frac{\beta}{\alpha} x^{\beta-1} \exp\left[-\left(\frac{x}{\alpha}\right)^{\beta}\right] \quad \text{Eq. 3.14}
\]

\[
F(x) = 1 - \exp\left[-\left(\frac{x}{\alpha}\right)^{\beta}\right] \quad \text{Eq. 3.15}
\]

where \( \alpha \) and \( \beta \) are constants. Fayad et al. (1999) found from their simulations of normal grain growth that \( \beta = 2.5 \) and

\[
\alpha = \frac{1}{\Gamma\left[1 + (1/\beta)\right]} \quad \text{Eq. 3.16}
\]

where \( \Gamma \) is the gamma function.

Eq. 3.15 may be linearized as

\[
\ln(x) = \ln \alpha + \left(\frac{1}{\beta}\right) \ln\left[-\ln(1 - F)\right] \quad \text{Eq. 3.17}
\]

The Weibull distribution is fitted by plotting \( \ln(x) \) vs. \( \ln[-\ln(1 - F)] \), this results in a linear cumulative distribution curve if the size distribution is best described as a Weibull distribution.

### 3.5.6. Analysis of porosity using Zener plots

The porosity in 10 samples was analysed to recover pore size and pore volume around each halite grain. Within each sample, at least three areas were analysed. The area data for each pore and grain were transferred to MS Excel and the pore size and grain size calculated using Eq. 3.2 (see §3.4.2 and §3.4.3.2). Examples of the porosity seen in these samples can be seen in Fig. 3.20. The pores around a given grain were then identified, and the mean pore size and pore volume fraction were determined for each grain. The latter was calculated by
dividing the total pore area around a given grain by the area of that grain. From these values a grain specific value of the Zener parameter \( Z \) was obtained using \( Z = d_p/f_p \) and a Zener plot \( (d_{halite} \text{ vs. } Z) \) for each sample (e.g., Fig. 3.21). In addition, the data was binned based on halite grain size, and a Zener plot, together with plots of both pore size vs. halite grain size and pore volume fraction vs. halite grain size, were generated for different sub-areas of each sample so that the variation within samples could be explored.
Fig. 3.20. High magnification SEM images of the pores traces in this section of the study. Top) HL9 (437 °C, 68d 16h 36m). Bottom) HL5 (511 °C, 00d 15h 56m). Note that the majority of pores lie along grain boundaries with occasional pores occurring as inclusions within grains.
Fig. 3.21. Graph displaying the grain size and $Z$ value of every grain analysed in HL24 (330 °C, 01d 23h 08m). The blue lines are drawn from the origin through the 5% and 95% $Z$ grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free. Note that for the sake of preserving detail, a grain with a $Z$ value of 23078 (grain size = 91 µm) is omitted from this plot. Note that this graph is repeated in §6.1.1. (Fig. 6.4) for the convenience of the reader.

3.6. Confidence in the grain and pore size measurements, pore volume fraction determination, and kinetic value determination

The main source of potential errors associated with grain growth studies of this type are those associated with size measurements as the measured grain size impacts on the determined kinetic values. The linear intercept method has been rigorously tested and has been shown to provide representative 3D grain size measurements, providing the sample does not contain fabric and that a sufficient number of grains are measured (Underwood, 1970). As stated in §3.4.1 and in §3.4.2, at least 250 grains were counted in all samples except those that displayed anomalously large grain sizes where this number was reduced to 150. This number is considered to be statistically valid for this study (Fig. 3.22). By randomly selecting grains at cumulative intervals of 10 and calculating the average size, the mean size stabilises after approximately 100 grains. This indicates that the cumulative mean grain size measurement becomes approximately constant (varies by <3 µm thereafter) before the total number of grains are measured. This gives confidence
in the grain sizes being representative. The same process can be applied to pore size, but at intervals of 100 pores. Similarly to grain size, the average pore size stabilizes after approximately 700 pores are measured, with average pore size varying by <0.02 µm thereafter (Fig. 3.23). Therefore, pore size stabilises before the total number of pores is counted. Since the variation in pore size after stabilization is near to the limit for pore size resolution, confidence in the pore size measurement is secured.

Fig. 3.22. Cumulative grain size plot for HL21 (330 °C, 107d 23h 36m). Each point represents the cumulative mean grain size at intervals of 10 grains.
Fig. 3.23. Cumulative pore size plot for HL24 (330 °C, 01d 23h 08m). Each point represents the cumulative mean pore size at intervals of 100 pores.

The confidence in pore volume fraction more difficult to quantify as it is calculated on a grain by grain basis. A measure of confidence can be gained if each of the mean values of the components used to calculate pore volume fraction (pore area and grain area) stabilise before the total number of pores and grains are counted, in a similar fashion to grain and pore size. From examination of Fig. 3.24 and Fig. 3.25 this appears to be the case, therefore, confidence in the determined pore volume fraction is secured. In HL 24, cumulative average grain area remains approximately constant while, as in Fig. 3.23, average pore area stabilizes after approximately 700 pores are counted.
Fig. 3.24. Cumulative grain area plot for HL24 (330 °C, 01d 23h 08m). Each point represents the cumulative mean grain size at intervals of 50 grains.

Fig. 3.25. Cumulative pore area plot for HL24 (330 °C, 01d 23h 08m). Each point represents the cumulative mean grain size at intervals of 100 grains.
The error associated with the determination of $n$ is minimal as the method described in §3.5.2 has been previously tested and shown to give representative values of $n$ (Covey-Crump, 1997). It will be shown that, aside from the 437 °C data set, the data can always be well described ($m > 0.8809$) by one of the three theoretical values of $n$ (0.25, 0.33 and 0.5). This secures confidence in the determined value of $n$.

The main source of errors with regards to data processing relates to the determination of $d_0$ and $t_0$ and the calculation of the activation enthalpy. Given the difficulty in determining $d_0$ and $t_0$, and the need to introduce fours pre-set criteria in order to obtain values, it is clear that there is some potential error. With the apparent sensitivity of halite to the presence of small amounts of porosity, this uncertainty is unavoidable without further experiments aimed at firmly establishing $d_0$ and $t_0$. It will be shown that, based on the criteria, the values of $d_0$ and $t_0$ show approximately linear relationships with temperature, therefore, displaying self-consistency. Errors in $d_0$ and $t_0$ impact on the grain size change during growth, this, in turn, will influence the determined activation enthalpy and the error associated with the value. An error on the activation enthalpy has been determined and is shown together with the calculated activation enthalpy in §4.4.2.
4. Experimental results I: 200 MPa confining pressure tests

4.1. Starting material characterization

When undertaking an experimental study it is common place to characterise the starting material through various analytical techniques. The halite microstructure present after application of the confining pressure can be seen in Fig. 4.1 while the microstructure for the shortest duration, lowest temperature test can be seen in Fig. 4.2. An obvious transformation in texture and grain size takes place during the heating stage.

![Photomicrograph displaying the microstructure present after the application of 200 MPa confining pressure.](image)

*Fig. 4.1. Photomicrograph displaying the microstructure present after the application of 200 MPa confining pressure.*
The chemical composition of the starting halite powder is given in Tab. 3.1.

Water has a significant impact on the mechanical behaviour of halite and has been shown to influence grain boundary mobility (ter Heege et al., 2004), and so it is important to establish the water content of the starting material. Thermogravimetric analysis of the halite powder showed that, at temperatures of up to 100 °C, a mass loss of just 1.21% took place. At higher temperatures, there was no further change in mass. This is interpreted as indicating that any surface-absorbed water is driven off by 100 °C. Given that the experiments in this study are conducted at temperatures of at least three times this value, and the samples were vented through the upper piston, water is considered to be absent from the experimental samples. Between experiments, the halite powder was stored in sealed glass jars and kept in a desiccation box to prevent contact with moisture in the air. Silica gel was also kept in the desiccation box and changed on a weekly basis.
4.2. Summary of experiments carried out

Over the course of this study, a total of 65 grain growth experiments were carried out by J. Tant (see Appendix 14.2 for a full experiment list). The vast majority of these experiments were performed at temperatures of 500 °C and 600 °C and were of durations ranging from 10 seconds to 35 days after reaching temperature. An additional 33 experiments that had been carried out by S.J. Covey-Crump between April 2001 and September 2003 were also made available for microstructural analysis. These tests were conducted at temperatures of 330 °C, 380 °C, 437 °C, 480 °C and 511 °C for durations of between 5 minutes and 108 days. Both suites of tests were carried out at an isostatic confining pressure of 200 MPa.

A number of the experiments carried out by J. Tant failed due to jacket rupture or sample disintegration upon jacket removal. Owing to the softness of halite, some samples were also polished away during thin-sectioning thus preventing grain size data being obtained. As a result, grain sizes were obtained from 62 samples.

13 additional experiments were also carried out with a view to investigating the viability of controlling the starting porosity of halite samples systematically; grain sizes were obtained from 6 of these tests. This was carried out by varying the experimental confining pressure from 200 MPa to 100 MPa and 70 MPa. The rationale behind this being that at lower confining pressures less porosity would be eliminated, resulting in a higher starting pore volume fraction. If this is correct, and confining pressure can provide a method of controlling porosity, then a test carried out at 70 MPa would have a smaller grain size than a test of equal duration carried out at 100 MPa owing to increased pore volume fraction. A description of the findings from these lower confining pressure tests is deferred until Chapter 5.

4.3. Survey of the datasets obtained at 200 MPa confining pressure

4.3.1. 330 °C

A total of seven tests were carried out at 330 °C (Tab. 4.1, Fig. 4.3). Characteristic granoblastic, equigranular, polygonal normal grain growth textures closely resembling those of a foam texture are present throughout the data set (Fig. 4.4). Porosity is present
in all samples although the apparent pore volume fraction decreases with increased experimental duration (compare the boundary porosity of Fig. 4.4a and Fig. 4.4b).

Tab. 4.1. Table displaying the grain size and statistic results for the 330 °C data set. Note that a distribution was not obtained for HL24, because, although the thin-section was of high enough quality to allow visual grain size measurements to be made under the microscope, it was of insufficient quality to allow accurate tracing of grains from optical photomicrographs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Duration</th>
<th>Grain size (µm)</th>
<th>Skewness</th>
<th>Kurtosis</th>
<th>Log normal Standard Deviation</th>
<th>Weibull α</th>
<th>Weibull β</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL24</td>
<td>01d 23h 08m</td>
<td>64</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>HL23</td>
<td>06d 04h 21m</td>
<td>93</td>
<td>-0.78</td>
<td>0.45</td>
<td>0.29</td>
<td>1.12</td>
<td>1.80</td>
</tr>
<tr>
<td>HL25</td>
<td>11d 00h 00m</td>
<td>79</td>
<td>-0.88</td>
<td>1.84</td>
<td>0.29</td>
<td>1.13</td>
<td>1.88</td>
</tr>
<tr>
<td>HL20</td>
<td>21d 18h 10m</td>
<td>79</td>
<td>-0.66</td>
<td>0.71</td>
<td>0.26</td>
<td>1.13</td>
<td>2.10</td>
</tr>
<tr>
<td>HL22</td>
<td>37d 18h 07m</td>
<td>71</td>
<td>-0.88</td>
<td>1.49</td>
<td>0.24</td>
<td>1.13</td>
<td>2.22</td>
</tr>
<tr>
<td>HL19</td>
<td>73d 18h 37m</td>
<td>78</td>
<td>-1.07</td>
<td>1.50</td>
<td>0.29</td>
<td>1.13</td>
<td>1.92</td>
</tr>
<tr>
<td>HL21</td>
<td>107d 23h 36m</td>
<td>83</td>
<td>-0.84</td>
<td>2.00</td>
<td>0.24</td>
<td>1.13</td>
<td>2.28</td>
</tr>
</tbody>
</table>

![330 °C halite grain size data](image)

Fig. 4.3. Graph showing the grain size variation of the 330°C halite grain growth tests.
The change in grain size is slight (Fig. 4.3) making the assessment of $d_0$ and $t_0$ challenging. A potential change in slope can be seen around the third to last experiment. Based on the $d_0$ and $t_0$ at which the change in slope occurs, values for $t_0 = 3000000$ seconds (approximately 34.7 days) and $d_0 = 70 \, \mu m$ have been determined. The three longest duration tests seem to be on a satisfactory trend, and so $d_0$ and $t_0$ were assigned on the basis of these tests (just before third last test). This is consistent with the values of $d_0$ and $t_0$ that arise if the trend in these values with temperature as obtained at higher temperatures are extrapolated to 330 °C (see §4.4). However, there is scope to make $t_0$ and perhaps $d_0$ a little larger so that the $t_0$ is defined just prior to the second longest test (comparing the microstructures, Fig. 4.4, there is little difference between HL22 and HL19 but normal grain growth certainly seems to be underway by HL21). Using $t_0 = 3000000$ s, the three tests for which $t > t_0$ are well described by the normal grain growth equation with $n = 0.25$ (Fig. 4.5).
Fig. 4.5. Graph displaying the 330 °C halite grain growth tests that are interpreted to represent normal grain growth. The line of best fit (solid, with its slope, m, and the correlation coefficient, $R^2$, indicated) and a line with a slope of 1 (dashed) are shown.

The grain size distributions for all of the 330 °C tests, both before and after $t_0$, are approximately log normal (Fig. 4.6). The standard deviation varies little with experiment duration while the kurtosis increases with duration (Fig. 4.7), that is, the distributions become slightly more ‘peaky’. Comparison of the cumulative frequency distributions shows that grain size distribution is better described as a Weibull distribution than as a log normal one (compare the linearity of the data on Fig. 4.8 and Fig. 4.9), particularly at small grain sizes, but the difference between the two is marginal in the longest duration test.

$$d^{1/n} - d_0^{1/n} = k_0 (t-t_0) \exp \left( \frac{E}{RT} \right)$$

$n = 0.25$
$t_0 = 3,000,000 \text{ sec}$
$d_0 = 70 \mu\text{m}$

$m = 1$

$m = 0.8809$

$R^2 = 0.9999$
Fig. 4.6. Graph displaying the grain size distributions for the 330 °C grain growth tests.

Fig. 4.7. Graph displaying the statistical analysis of the log normal grain size distributions at 330 °C.
Fig. 4.8. Graph showing, for the 330 °C grain growth tests, the cumulative frequency (F) of grains larger than \( \bar{d} \) plotted so that it should give a straight line if well described as a Weibull distribution.

Fig. 4.9. Graph showing, for the 330 °C grain growth tests, the cumulative frequency (F) of grains larger than \( \bar{d} \) plotted so that it should give a straight line if well described as a log normal distribution.
4.3.2. 380 °C

Five experiments were carried out at 380 °C (Tab. 4.2, Fig. 4.10). Granoblastic, equigranular, polygonal normal grain growth textures closely resembling those of a foam texture are present throughout the data set (Fig. 4.11). Porosity is present along grain boundaries in all samples. There is an apparent increase in porosity at the longest experimental duration (Fig. 4.11d).

**Tab. 4.2. Table displaying the grain size results for the 380 °C data set.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Duration</th>
<th>Grain size (µm)</th>
<th>Skewness</th>
<th>Kurtosis</th>
<th>Standard Deviation</th>
<th>Log normal</th>
<th>Weibull</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL30</td>
<td>03d 17h 19m</td>
<td>97</td>
<td>-0.79</td>
<td>0.79</td>
<td>0.25</td>
<td>1.13</td>
<td>2.16</td>
</tr>
<tr>
<td>HL31</td>
<td>06d 18h 22m</td>
<td>92</td>
<td>-1.37</td>
<td>3.13</td>
<td>0.27</td>
<td>1.13</td>
<td>2.06</td>
</tr>
<tr>
<td>HL26</td>
<td>11d 21h 26m</td>
<td>90</td>
<td>-1.91</td>
<td>6.42</td>
<td>0.32</td>
<td>1.13</td>
<td>1.92</td>
</tr>
<tr>
<td>HL18</td>
<td>19d 23h 59m</td>
<td>103</td>
<td>-1.22</td>
<td>2.71</td>
<td>0.26</td>
<td>1.13</td>
<td>2.26</td>
</tr>
<tr>
<td>HL17</td>
<td>35d 17h 22m</td>
<td>111</td>
<td>-1.09</td>
<td>1.54</td>
<td>0.28</td>
<td>1.13</td>
<td>2.03</td>
</tr>
</tbody>
</table>

**380 °C halite grain size data**

\[
d^{1/n} - d_0^{1/n} = k_0 (t - t_0) \exp\left(\frac{-H}{RT}\right)
\]

\[
n = 0.25
\]

\[
t_0 = 10 \text{ sec}
\]

\[
d_0 = 45 \mu m
\]

**Fig. 4.10.** Graph showing the grain size variation of the 380 °C halite grain growth tests.
Fig. 4.11. Photomicrographs of the 380 °C halite grain growth experiments displaying the microstructural evolution of the data set. a) HL30, 03d 17h 19m. b) HL31, 06d 18h 22m. c) HL18, 19d 23h 59m. d) HL17, 35d 17h 22m.

Although the change in grain size over the range of experimental durations is small, the increase in grain size is clear (Fig. 4.10) making determination of $d_0$ and $t_0$ straightforward (Fig. 4.10). Based on the position of the change in slope on Fig. 4.10, values for $t_0 = 700000$ seconds (approximately 8 days) and $d_0 = 85$ µm have been determined. These values place the first two experiments in the pre-growth “conditioning” phase. The three longest duration experiments are well described by the normal grain growth equation with $n = 0.25$ (Fig. 4.12).
The grain size distributions for all of the 380°C tests, both before and after $t_0$, are approximately log normal (Fig. 4.13). The standard deviation shows little variation with experiment duration while the kurtosis and skewness are more variable (Fig. 4.14). HL26 has a considerably higher kurtosis value and a more negative skewness value than the remaining samples resulting in a more ‘peaky’, negatively skewed distribution (Fig. 4.13). Prior to HL26 the distributions display increasing kurtosis and more negative skew with increasing test duration whilst after HL26 the distributions have reduced kurtosis and less-negative skewness. Comparison of the cumulative frequency distributions shows that grain size distribution is better described as a Weibull distribution than as a log normal one (compare the linearity of the data on Fig. 4.15 and Fig. 4.16).
Fig. 4.13. Graph displaying the grain size distributions for the 380 °C grain growth tests.

Fig. 4.14. Graph displaying the statistical analysis of the log normal grain size distributions at 380 °C.
Fig. 4.15. Graph showing, for the 380 °C grain growth tests, the cumulative frequency (F) of grains larger than \( \bar{d}/d \) plotted so that it should give a straight line if well described as a Weibull distribution.

Fig. 4.16. Graph showing, for the 380 °C grain growth tests, the cumulative frequency (F) of grains larger than \( \bar{d}/d \) plotted so that it should give a straight line if well described as a log normal distribution.
4.3.3. 437 °C

Five tests were carried out at 437 °C (Fig. 4.17, Tab. 4.3). All tests produced microstructures that have equigranular, granoblastic, polygonal foam textures (Fig. 4.18). Porosity is also present in all experiments; the pore volume fraction appears to decrease as experimental duration increases (compare Fig. 4.18a and d).

Tab. 4.3. Table displaying the grain size results for the 437 °C data set. Note that due to the large grain size of HL11 the number of grains that could be traced was statistically invalid, as such, no distribution was obtained.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Duration</th>
<th>Grain size (µm)</th>
<th>Skewness</th>
<th>Kurtosis</th>
<th>Standard Deviation</th>
<th>α</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL16</td>
<td>03d 20h 44m</td>
<td>121</td>
<td>-1.01</td>
<td>1.80</td>
<td>0.13</td>
<td>1.13</td>
<td>2.13</td>
</tr>
<tr>
<td>HL27</td>
<td>06d 03h 58m</td>
<td>104</td>
<td>-1.41</td>
<td>2.16</td>
<td>0.14</td>
<td>1.13</td>
<td>1.99</td>
</tr>
<tr>
<td>HL11</td>
<td>19d 22h 49m</td>
<td>343</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>HL10</td>
<td>39d 01h 33m</td>
<td>115</td>
<td>-1.00</td>
<td>1.98</td>
<td>0.12</td>
<td>1.13</td>
<td>2.20</td>
</tr>
<tr>
<td>HL9</td>
<td>68d 16h 36m</td>
<td>94</td>
<td>-1.10</td>
<td>1.87</td>
<td>0.14</td>
<td>1.13</td>
<td>2.00</td>
</tr>
</tbody>
</table>

---

**437 °C halite grain size data**

\[
d^{1/n} - d_0^{1/n} = k_0 (t - t_0) \exp\left(\frac{-H}{RT}\right)
\]

- \( n = 0.25 \)
- \( t_0 = 10 \text{ sec} \)
- \( d_0 = 45 \mu m \)

\[
\log_{10}(d^{1/n} - d_0^{1/n})
\]

\[
\log_{10}(t - t_0)
\]

**Fig. 4.17.** Graph showing the grain size variation of the 437 °C halite grain growth tests.
There are no discernible grain size trends in the 437 °C grain size data. In an attempt to make some sense of the data, \( t_0 \) was arbitrarily chosen to be prior to the shortest duration test at \( t_0 = 100000 \) seconds (approximately 1¼ days) and \( d_0 = 90 \) µm, consistent with the trends of these \( t_0 \) and \( d_0 \) values obtained at other temperatures. It then follows that two samples (HL16 and HL11) have anomalously large grain sizes, and one (HL9) an anomalously small grain size. Two tests (HL27 and HL10) were then left with which to describe growth kinetics. However, these cannot be described by the grain growth equation unless \( n < 0.25 \) (Fig. 4.19). The grain size of HL27 actually agrees well with the grain size given by the normal grain growth equation fitted over the full temperature range of the data presented in this study, and so presumably HL10 also has an anomalously small grain size. There are no prominent microstructural features that indicate why good grain growth data were not obtained at this temperature.
The grain size distributions of all but one (HL10) of the 437 °C tests are approximately log normal (Fig. 4.20). HL10 has a bi-modal distribution which lends weight to the suggestion that HL10 is also anomalous. Standard deviation shows little variation with increasing test duration while kurtosis and skewness display marginal change, even in the bimodal distribution of HL10 (Fig. 4.21). Comparison of the cumulative frequency distributions shows that grain size distribution is better described as a Weibull distribution than as a log normal one (compare the linearity of the data on Fig. 4.22 and Fig. 4.23), particularly at the extremes of grain size.
Fig. 4.20. Graph displaying the grain size distributions for the 437 °C grain growth tests.

Fig. 4.21. Graph displaying the statistical analysis of the log normal grain size distributions at 437 °C.
Fig. 4.22. Graph showing, for the 437 °C grain growth tests, the cumulative frequency (F) of grains larger than \( d/\bar{d} \) plotted so that it should give a straight line if well described as a Weibull distribution.

Fig. 4.23. Graph showing, for the 437 °C grain growth tests, the cumulative frequency (F) of grains larger than \( d/\bar{d} \) plotted so that it should give a straight line if well described as a log normal distribution.
4.3.4. 480 °C

Five experiments were conducted at 480 °C (Tab. 4.4, Fig. 4.24). Equigranular, granoblastic, polygonal, normal grain growth textures resembling those of a foam texture are present in all of the tests (Fig. 4.25). Grain boundary porosity is visible in all experiments; the pore volume fraction seems to decrease significantly with increased experimental duration (compare Fig. 4.25a and d).

Tab. 4.4. Table displaying the grain size results for the 480 °C data set. Note that due to the large grain size, a statistically valid number of grains could not be traced in HL14, and thus, no grain size distribution was measured.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Duration</th>
<th>Grain size (µm)</th>
<th>Skewness</th>
<th>Kurtosis</th>
<th>Standard Deviation</th>
<th>α</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL33</td>
<td>03d 18h 47m</td>
<td>110</td>
<td>-1.61</td>
<td>3.70</td>
<td>0.28</td>
<td>1.13</td>
<td>2.12</td>
</tr>
<tr>
<td>HL29</td>
<td>07d 23h 08m</td>
<td>114</td>
<td>-1.10</td>
<td>1.36</td>
<td>0.32</td>
<td>1.12</td>
<td>1.71</td>
</tr>
<tr>
<td>HL14</td>
<td>11d 18h 43m</td>
<td>342</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>HL12</td>
<td>20d 02h 19m</td>
<td>164</td>
<td>-1.07</td>
<td>2.04</td>
<td>0.24</td>
<td>1.13</td>
<td>2.43</td>
</tr>
<tr>
<td>HL13</td>
<td>44d 01h 56m</td>
<td>166</td>
<td>-1.14</td>
<td>1.59</td>
<td>0.29</td>
<td>1.13</td>
<td>1.90</td>
</tr>
</tbody>
</table>

Fig. 4.24. Graph showing the grain size variation of the 480 °C halite grain growth tests.
The data set displays a grain size increase of 50 µm over the range of experimental durations. There is no definitive change in slope in Fig. 4.24 that would indicate the onset of grain growth, and so \( t_0 \) is assumed to be prior to the shortest test. Since the grain size data (Fig. 4.24) and microstructures (compare grain sizes in Fig. 4.25a and c) show a good increasing grain size trend, and since \( n = 0.25 \) is securely established at the other temperatures, \( t_0 \) and \( d_0 \) were chosen by finding values that were consistent with a slope of about 1 on a \( \log_{10}(d^{1/n} - d_0^{1/n}) \) vs. \( \log_{10}(t - t_0) \) plot subject to the condition that both values fall between those obtained at 437 ° and 500 °C. Using this process \( d_0 \) and \( t_0 \) were determined to be 90 µm and 80000 seconds (approximately 22 hours). Note that this places the onset of growth prior to the shortest experimental duration (HL33). Thus, all samples experienced grain growth. Although HL14 has an anomalously large grain size, data for the remaining four experiments are well described by the normal grain growth equation with \( n = 0.25 \) (Fig. 4.26).
Fig. 4.26. Graph displaying the 480 °C halite grain growth tests that are interpreted to represent normal grain growth. The line of best fit (solid, with its slope, m, and the correlation coefficient, $R^2$, indicated).

The grain size distributions for all 480 °C tests are approximately log normal (Fig. 4.27). Standard deviation shows minimal variation (Fig. 4.28). The shortest duration test (HL33) has a more ‘peaked’ distribution compared to the other tests, as shown by the high kurtosis value, while the remaining samples have similar kurtosis values. Comparison of the cumulative frequency distributions shows that the grain size distributions at 480 °C are better described by a Weibull distribution than by a log normal one (compare the linearity of data in Fig. 4.29 and Fig. 4.30).
Fig. 4.27. Graph displaying the grain size distributions for the 480 °C grain growth tests.

Fig. 4.28. Graph displaying the statistical analysis of the log normal grain size distributions at 480 °C.
Fig. 4.29. Graph showing, for the 480 °C grain growth tests, the cumulative frequency (F) of grains larger than d/\bar{d} plotted so that it should give a straight line if well described as a Weibull distribution.

Fig. 4.30. Graph showing, for the 480 °C grain growth tests, the cumulative frequency (F) of grains larger than d/\bar{d} plotted so that it should give a straight line if well described as a log normal distribution.
4.3.5. 500 °C

A total of sixteen tests were carried out at 500 °C (Tab. 4.5, Fig. 4.31). In the short (Fig. 4.32a and b) and intermediate (Fig. 4.32c, d and e) duration tests microstructures show equigranular, granoblastic, polygonal, foam textures associated with normal grain growth. In two of the longer duration tests, HP19 and HP20, only patches of grains displaying polygonal normal grain growth textures exist (Fig. 4.32f). The remainder of these samples consist of grains which have undergone abnormal grain growth to grain sizes >1 mm. This results in an inequigranular polygonal texture, the larger grains around the margins of Fig. 4.32f have interlobate boundaries indicative of abnormal grain growth. The cluster of smaller grains in the centre of Fig. 4.32f more closely resemble those seen in the shorter duration experiments, that is, they display foam-like textures associated with normal grain growth. Grain boundary porosity is present throughout the data set; the pore volume fraction seems to decrease with increasing test duration.

Tab. 4.5. Table displaying the grain size results for the 500 °C data set. Note that grain size distributions could not be obtained for four samples; HP56, HP54, HP19 and HP55. The large grain size of HP19 did not allow a statistically sufficient number of grains to be traced. In the remaining three remaining samples, while the thin-sections were of high enough quality to allow visual grain size measurements to be made under the microscope, they were of insufficient quality to allow accurate tracing of grains from optical photomicrographs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Duration</th>
<th>Grain Size (µm)</th>
<th>Skewness</th>
<th>Kurtosis</th>
<th>Standard Deviation</th>
<th>α</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP24</td>
<td>00d 00h 48m</td>
<td>68</td>
<td>-1.31</td>
<td>3.46</td>
<td>0.24</td>
<td>1.13</td>
<td>2.54</td>
</tr>
<tr>
<td>HP5</td>
<td>00d 00h 53m</td>
<td>74</td>
<td>-1.49</td>
<td>3.60</td>
<td>0.29</td>
<td>1.13</td>
<td>2.05</td>
</tr>
<tr>
<td>HP28</td>
<td>00d 01h 22m</td>
<td>77</td>
<td>-0.85</td>
<td>1.06</td>
<td>0.27</td>
<td>1.13</td>
<td>2.05</td>
</tr>
<tr>
<td>HP56</td>
<td>00d 02h 00m</td>
<td>87</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>HP29</td>
<td>00d 03h 00m</td>
<td>93</td>
<td>-1.01</td>
<td>2.66</td>
<td>0.24</td>
<td>1.13</td>
<td>2.30</td>
</tr>
<tr>
<td>HP26</td>
<td>00h 04h 04m</td>
<td>73</td>
<td>-1.30</td>
<td>3.24</td>
<td>0.27</td>
<td>1.13</td>
<td>2.19</td>
</tr>
<tr>
<td>HP54</td>
<td>00d 16h 00m</td>
<td>109</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>HP8</td>
<td>00d 20h 00m</td>
<td>90</td>
<td>-1.11</td>
<td>2.34</td>
<td>0.26</td>
<td>1.13</td>
<td>2.32</td>
</tr>
<tr>
<td>HP23</td>
<td>01d 01h 24m</td>
<td>113</td>
<td>-1.95</td>
<td>6.64</td>
<td>0.25</td>
<td>1.13</td>
<td>2.54</td>
</tr>
<tr>
<td>HP14</td>
<td>01d 21h 30m</td>
<td>116</td>
<td>-3.38</td>
<td>18.89</td>
<td>0.33</td>
<td>1.13</td>
<td>2.24</td>
</tr>
<tr>
<td>HP65</td>
<td>02d 00h 00m</td>
<td>120</td>
<td>-2.53</td>
<td>11.01</td>
<td>0.31</td>
<td>1.13</td>
<td>2.19</td>
</tr>
<tr>
<td>HP19</td>
<td>03d 00h 00m</td>
<td>396</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>HP18</td>
<td>05d 00h 38m</td>
<td>156</td>
<td>-2.32</td>
<td>11.68</td>
<td>0.32</td>
<td>1.13</td>
<td>2.15</td>
</tr>
<tr>
<td>HP20</td>
<td>12d 23h 00m</td>
<td>247</td>
<td>-0.36</td>
<td>0.57</td>
<td>0.29</td>
<td>1.13</td>
<td>1.93</td>
</tr>
<tr>
<td>HP55</td>
<td>17d 18h 47m</td>
<td>86</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>HP21</td>
<td>35d 00h 00m</td>
<td>102</td>
<td>-1.35</td>
<td>4.95</td>
<td>0.25</td>
<td>1.13</td>
<td>2.39</td>
</tr>
</tbody>
</table>
Fig. 4.31. Graph showing the grain size variation of the 500 °C halite grain growth tests.
The change in grain size over the range of experimental durations is considerable; however, there is no unambiguous change in the slope of the grain size data (Fig. 4.31). Since the grain size (Fig. 4.31) and microstructural data show a good increasing grain size trend, and since \( n = 0.25 \) is securely established at the other temperatures, \( t_0 \) and \( d_0 \) were chosen by finding values that were consistent with a slope of about 1 on a \( \log_{10}(d^{1/n} - d_0^{1/n}) \) vs. \( \log_{10}(t - t_0) \) plot subject to the condition that both values fall...
between those obtained at 480 °C and 511 °C, \( d_0 = 100 \mu m \) and \( t_0 = 48200 \) seconds (approximately 13½ hours) were determined. From these values, four samples were considered to represent normal grain growth and are best described by the normal grain growth equation with \( n = 0.25 \) (Fig. 4.33). There are clear anomalous samples with both large and small grain sizes.

![500 °C grain size data](image)

**Fig. 4.33.** Graph displaying the 500 °C halite grain growth tests that are interpreted to represent normal grain growth. The line of best fit (solid, with its slope, \( m \), and the correlation coefficient, \( R^2 \), indicated).

Upon first examination, the log normal grain size distributions (Fig. 4.34) appear to provide a good description of 500 °C data set, both before and after \( t_0 \). It is apparent from the kurtosis and skewness values that this is not the case (Fig. 4.35). Kurtosis increases at intermediate test durations resulting in four highly ‘peaky’ distributions (HP23, HP14, HP65 and HP18), the longest duration test also has a high kurtosis. Increases in kurtosis are accompanied by an increase in negative skew (that is, a relatively greater number of large grains than would be expected from a normal distribution). All samples, except HP28 and HP20, have negative skew values less than -1.01. Standard
deviation varies marginally between samples (Fig. 4.35 and Tab. 4.5). Cumulative frequency distributions show that, for all samples, the Weibull provides a better description of growth when compared to the log normal distribution (compare the linearity of the distributions in Fig. 4.36 and Fig. 4.37). These plots also highlight the variation between samples at the smallest extremes of grain size. Grain size distributions for samples that display anomalous grain sizes (HP20 and HP21) show little difference with regards to the remainder of the samples.

**Fig. 4.34.** Graph displaying the grain size distributions for the 500 °C grain growth tests.
Fig. 4.35. Graph displaying the statistical analysis of the log normal grain size distributions at 500 °C.

Fig. 4.36. Graph showing, for the 500 °C grain growth tests, the cumulative frequency (F) of grains larger than \( \frac{d}{\bar{d}} \) plotted so that it should give a straight line if well described as a Weibull distribution.
Fig. 4.37. Graph showing, for the 500 °C grain growth tests, the cumulative frequency (F) of grains larger than \( d / \bar{d} \) plotted so that it should give a straight line if well described as a log normal distribution.

4.3.6. 511 °C

Eight experiments were carried out at 511 °C (Tab. 4.6, Fig. 4.38). Microstructures in this data set are consistently homogeneous (Fig. 4.39) and display the equigranular, granoblastic, polygonal normal grain growth textures resembling those of a foam texture. Porosity is present in all samples, however, the apparent volume fraction of porosity decreases with experimental duration (compare the boundary porosity in Fig. 4.39a to that of Fig. 4.39d).
Tab. 4.6. Table displaying the grain size results for the 511 °C data set. Note that a distribution was not obtained for HL2 because, although the thin-section was of high enough quality to allow visual grain size measurements to be made under the microscope, it was of insufficient quality to allow accurate tracing of grains from optical photomicrographs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Duration</th>
<th>Grain Size (µm)</th>
<th>Skewness</th>
<th>Kurtosis</th>
<th>Standard Deviation</th>
<th>α</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL3</td>
<td>00d 00h 10m</td>
<td>93</td>
<td>-1.13</td>
<td>1.08</td>
<td>0.29</td>
<td>1.13</td>
<td>1.86</td>
</tr>
<tr>
<td>HL4</td>
<td>00d 00h 23m</td>
<td>102</td>
<td>-1.42</td>
<td>2.94</td>
<td>0.30</td>
<td>1.13</td>
<td>1.99</td>
</tr>
<tr>
<td>HL7</td>
<td>00d 05h 17m</td>
<td>102</td>
<td>-0.18</td>
<td>0.29</td>
<td>0.20</td>
<td>1.12</td>
<td>2.68</td>
</tr>
<tr>
<td>HL5</td>
<td>00d 15h 56m</td>
<td>136</td>
<td>-1.81</td>
<td>5.70</td>
<td>0.27</td>
<td>1.13</td>
<td>2.47</td>
</tr>
<tr>
<td>HL6</td>
<td>03d 21h 43m</td>
<td>129</td>
<td>-0.88</td>
<td>0.68</td>
<td>0.26</td>
<td>1.13</td>
<td>2.06</td>
</tr>
<tr>
<td>HL28</td>
<td>06d 06h 32m</td>
<td>160</td>
<td>-1.52</td>
<td>4.28</td>
<td>0.27</td>
<td>1.13</td>
<td>2.13</td>
</tr>
<tr>
<td>HL15</td>
<td>11d 20h 54m</td>
<td>135</td>
<td>-1.52</td>
<td>4.28</td>
<td>0.25</td>
<td>1.13</td>
<td>2.51</td>
</tr>
<tr>
<td>HL2</td>
<td>20d 00h 14m</td>
<td>193</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

$511 \, ^{\circ}C$ halite grain size data

\[ d^{1/n} - d_0^{1/n} = k_0 (t-t_0) \exp(-H/RT) \]

$n = 0.25$
$t_0 = 10 \text{ sec}$
$d_0 = 45 \, \mu m$

Fig. 4.38. Graph showing the grain size variation of the $511 \, ^{\circ}C$ halite grain growth tests.
The onset of grain growth is defined by a change in slope on Fig. 4.38 at about the duration of the third shortest duration test (HL7). Based on the position of the change, $d_0 = 110 \mu m$ and $t_0 = 30000$ seconds (approximately 8½ hours) were used. The three shortest duration tests were in the pre-growth stage and five were in the growth stage. HL5 has an anomalously large grain size although its microstructure is similar to that of the remaining samples. The four remaining specimens in the growth phase are best described by the normal grain growth equation where $n = 0.25$ (Fig. 4.40).
The grain size distributions for all of the 511 °C tests, both before and after $t_0$, are approximately log normal (Fig. 4.41). The standard deviation varies marginally with experiment duration while the kurtosis and skewness are more variable (Fig. 4.42). HL5, the sample with the anomalously large grain size, has the most ‘peaky’ and negatively skewed distribution. Comparison of the cumulative frequency distributions shows that grain size distribution is better described as a Weibull distribution than as a log normal one (compare the linearity of the data on Fig. 4.43 and Fig. 4.44).
**Fig. 4.41.** Graph displaying the grain size distributions for the 511°C grain growth tests.

**Fig. 4.42.** Graph displaying the statistical analysis of the log normal grain size distributions at 511 °C.
Fig. 4.43. Graph showing, for the 511 °C grain growth tests, the cumulative frequency (F) of grains larger than \( \bar{a} / \bar{d} \) plotted so that it should give a straight line if well described as a Weibull distribution.

Fig. 4.44. Graph showing, for the 511 °C grain growth tests, the cumulative frequency (F) of grains larger than \( \bar{a} / \bar{d} \) plotted so that it should give a straight line if well described as a log normal distribution.
4.3.7. 600 °C

Fourteen experiments were carried out at 600 °C (Tab. 4.7, Fig. 4.45). In terms of texture, the 600 °C data set displays equigranular, granoblastic, polygonal normal grain growth textures similar to a foam texture (Fig. 4.46). Grain size, however, is more variable than in previous data sets. In short duration tests, polygonal normal grain growth textures are present, and grain boundary porosity is common (Fig. 4.46a). Once growth has begun, anomalously large grains begin to appear within individual samples (e.g., Fig. 4.46c). The larger grains usually have more gently curving boundaries than the smaller grains that have generally straight boundaries. Boundary porosity can be seen throughout the data set, the apparent volume fraction of which decreases with increasing experimental duration (compare Fig. 4.46a and e).

Tab. 4.7. Table displaying the grain size results for the 600 °C data set. The large grain size of HP38 did not allow a statistically sufficient number of grains to be traced.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Duration</th>
<th>Grain Size (µm)</th>
<th>Skewness</th>
<th>Kurtosis</th>
<th>Log normal</th>
<th>Weibull</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Standard Deviation</td>
<td>α</td>
</tr>
<tr>
<td>HP37</td>
<td>&lt;5 mins</td>
<td>98</td>
<td>-0.68</td>
<td>0.70</td>
<td>0.22</td>
<td>1.13</td>
</tr>
<tr>
<td>HP41</td>
<td>00d 00h 10m</td>
<td>103</td>
<td>-0.73</td>
<td>1.66</td>
<td>0.27</td>
<td>1.13</td>
</tr>
<tr>
<td>HP42</td>
<td>00d 01h 00m</td>
<td>134</td>
<td>-1.09</td>
<td>4.43</td>
<td>0.26</td>
<td>1.13</td>
</tr>
<tr>
<td>HP45</td>
<td>00d 03h 16m</td>
<td>135</td>
<td>-0.24</td>
<td>0.07</td>
<td>0.26</td>
<td>1.13</td>
</tr>
<tr>
<td>HP47</td>
<td>00d 18h 00m</td>
<td>83</td>
<td>-0.78</td>
<td>1.15</td>
<td>0.23</td>
<td>1.13</td>
</tr>
<tr>
<td>HP36</td>
<td>00d 19h 42m</td>
<td>134</td>
<td>-0.70</td>
<td>0.98</td>
<td>0.22</td>
<td>1.13</td>
</tr>
<tr>
<td>HP38</td>
<td>01d 00h 00m</td>
<td>225</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>HP33</td>
<td>01d 01h 18m</td>
<td>190</td>
<td>-1.37</td>
<td>4.37</td>
<td>0.33</td>
<td>1.12</td>
</tr>
<tr>
<td>HP6</td>
<td>01d 21h 30m</td>
<td>79</td>
<td>-1.34</td>
<td>1.73</td>
<td>0.32</td>
<td>1.12</td>
</tr>
<tr>
<td>HP40</td>
<td>01d 23h 35m</td>
<td>173</td>
<td>-1.87</td>
<td>8.15</td>
<td>0.27</td>
<td>1.13</td>
</tr>
<tr>
<td>HP50</td>
<td>02d 20h 19m</td>
<td>194</td>
<td>-0.29</td>
<td>0.10</td>
<td>0.24</td>
<td>1.13</td>
</tr>
<tr>
<td>HP32</td>
<td>04d 17h 26m</td>
<td>190</td>
<td>-0.98</td>
<td>2.05</td>
<td>0.23</td>
<td>1.13</td>
</tr>
<tr>
<td>HP35</td>
<td>05d 22h 57m</td>
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<td>-0.61</td>
<td>0.47</td>
<td>0.28</td>
<td>1.13</td>
</tr>
<tr>
<td>HP48</td>
<td>01d 00h 00m</td>
<td>146</td>
<td>-0.83</td>
<td>2.67</td>
<td>0.24</td>
<td>1.13</td>
</tr>
</tbody>
</table>
Fig. 4.45. Graph showing the grain size variation of the 600 °C halite grain growth tests.

\[ \frac{d^{1/n} - d_0^{1/n}}{d_0^{1/n}} = k_0 (t-t_0) \exp\left(\frac{H}{RT}\right) \]

\[ n = 0.5 \]

\[ t_0 = 10 \text{ sec} \]

\[ d_0 = 45 \mu\text{m} \]

600 °C halite grain size data

\( \log_{10}(d_{1/n} - d_0^{1/n}) \)

\( \log_{10}(t-t_0) \)
Fig. 4.46. Photomicrographs of the 600 °C halite grain growth experiments displaying the microstructural evolution of the data set. a) HP37, <5 mins. b) HP42, 00d 01h 00m. c) HP33, 01d 01h 18m. d) HP40, 01d 23h 35m. e) HP32, 04d 17h 26m. f) HP35, 05d 22h 57m.

The onset of grain growth is clearly defined at this temperature at \( \log_{10}(t - t_0) = 3 \) and \( \log_{10}(d^{1/n} - d_0^{1/n}) = 4 \) (Fig. 4.45) making assessment of \( d_0 \) and \( t_0 \) more straightforward than in some data sets. Based on the position of the change in slope and the \( d_0 \) and \( t_0 \) values of the adjacent data sets, \( d_0 = 120 \mu m \) and \( t_0 = 4000 \) seconds (approximately 20 minutes) were determined. Hence, all but three of the tests were in the growth phase.

Of the eleven tests in the growth phase, three sample (HP6, HP47 and HP48) were considered to have anomalously small grain sizes, and three samples have anomalously
large grain sizes (HP33, HP38 and HP45). Apparent pore volume fraction in these tests is marginally higher than in those considered to have normal grain sizes. The remaining five tests are well described by the normal grain growth equation with $n = 0.5$ (Fig. 4.47), as opposed to 0.25, the value obtained for samples from tests at the other temperatures.

The grain size distributions for all tests, except HP50, are approximately log normal (Fig. 4.48) and HP50 has a bi-modal grain size distribution. Standard deviation varies minimally throughout the data set; however, kurtosis and skewness are more variable (Fig. 4.49). HP42, HP33 and HP40 all display large values of kurtosis and a large degree of negative skew. However, in terms of microstructure these samples are visually similar to the remainder of the data set. Comparison of the cumulative frequency distributions shows that, in general, grain size distribution at 600 °C is better described as a Weibull distribution than as a log normal one (compare the linearity of the data in Fig. 4.50 and Fig. 4.51). Four samples (HP35, HP45, HP48 and HP50) are best described by the log

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**Fig. 4.47.** Graph displaying the 600 °C halite grain growth tests that are interpreted to represent normal grain growth. The line of best fit (solid, with its slope, $m$, and the correlation coefficient, $R^2$, indicated).
normal distribution although the difference in correlation co-efficients between Weibull and log normal distributions for these samples is not statistically significant (<0.0182).

Fig. 4.48. Graph displaying the log normal grain size distributions for the 600 °C grain growth tests.

Fig. 4.49. Graph displaying the statistical analysis of the log normal grain size distributions at 600 °C.
Fig. 4.50. Graph showing, for the 600 °C grain growth tests, the cumulative frequency (F) of grains larger than $d/\bar{d}$ plotted so that it should give a straight line if well described as a Weibull distribution.

Fig. 4.51. Graph showing, for the 600 °C grain growth tests, the cumulative frequency (F) of grains larger than $d/\bar{d}$ plotted so that it should give a straight line if well described as a log normal distribution.
4.4. Synthesis of the 200 MPa confining pressure results

4.4.1. Normal grain growth start time and start grain size

The variation of both $d_0$ and $t_0$ (Tab. 4.8) with temperature is empirically well-described by an Arrhenius-type relationship (Fig. 4.52 and Fig. 4.53). In both cases, the correlation coefficient is >0.9 indicating that the values used for $d_0$ and $t_0$ in this study are self-consistent. As expected, with increasing experimental temperature, $d_0$ increases while $t_0$ decreases (Tab. 4.8). The validity of these results is shown by the high correlation coefficient between both $t_0$ and $d_0$ with 1000/T (Fig. 4.52 and Fig. 4.53).

Based on the $t_0$ values an activation enthalpy of 109 kJ/mol was calculated (Fig. 4.52). See §4.4.2. for a discussion on the determined kinetic values.

Tab. 4.8. Table displaying the $d_0$ and $t_0$ values determined for each data set.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$d_0$ (µm)</th>
<th>$t_0$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>330</td>
<td>70</td>
<td>3,000,000</td>
</tr>
<tr>
<td>381</td>
<td>85</td>
<td>700,000</td>
</tr>
<tr>
<td>437</td>
<td>90</td>
<td>100,000</td>
</tr>
<tr>
<td>480</td>
<td>90</td>
<td>80,000</td>
</tr>
<tr>
<td>500</td>
<td>100</td>
<td>48,200</td>
</tr>
<tr>
<td>511</td>
<td>110</td>
<td>30,000</td>
</tr>
<tr>
<td>600</td>
<td>120</td>
<td>4,000</td>
</tr>
</tbody>
</table>
Fig. 4.52. Graph displaying the relationship between the determined $t_0$ values and $1000/T$. The correlation coefficient, $R^2$, of the line of best fit is shown.

Fig. 4.53. Graph displaying the relationship between the determined $d_0$ values and $1000/T$. The correlation coefficient, $R^2$, of the line of best fit is shown.
4.4.2. Normal grain growth kinetics

An activation enthalpy $H$ was determined by plotting $[\ln(d^{1/n} - d_0^{1/n}) - \ln (t - t_0)]$ vs. $1/T$. This produces a straight line with slope $= -(H/R)$ and intercept $= \ln(k_0)$ (Fig. 4.54). These values were obtained using only samples considered to represent normal grain growth, i.e., those in Fig. 4.55. The 600 °C samples were not used due to being better described by $n = 0.5$. $[\ln(d^{1/n} - d_0^{1/n}) - \ln (t - t_0)]$ was determined separately for each temperature set, therefore weighting each temperature set equally. Because different numbers of tests were carried out at different temperatures, this method will produce slightly different kinetic values than those found by fitting each sample individually. Based on Eqs. 3.3 and 3.4, both methods are valid, as near identical values are returned in each case.

At temperatures between 330 °C and 511 °C, a growth exponent of $n = 0.25$ best describes the grain growth data (see Appendix 14.1). Based on the growth controlling mechanisms listed in Tab. 2.1, it can be inferred that grain growth in halite is controlled by one of two potential processes: either coalescence of second phases via grain boundary diffusion or surface diffusion around pore boundaries. Since no second phases were introduced into the starting material, the samples can be considered as pure, and so $n = 0.25$ implies that the grain growth was controlled by the rate of surface diffusion around pore boundaries. At 600 °C, the grain size data is best described by a growth exponent of $n = 0.5$ which corresponds to a switch in the growth controlling mechanism to interface controlled growth.

Using the method outlined above, an activation enthalpy ($H$) of 122±34 kJ/mol and a rate constant ($k_0$) value of 9.6326x10$^{10}$ μm$^{1/n}$ s$^{-1}$ were calculated using the line of best fit shown in Fig. 4.54. When obtaining $H$ and $k_0$, the longest duration 437 °C test was initially excluded from the $[\ln(d^{1/n} - d_0^{1/n}) - \ln(t - t_0)]$ calculation as, although it is considered to represent normal grain growth, the noisy nature of the 437 °C data set and the shallow slope of the data means that there is a degree of uncertainty as to whether this is the case. This resulted in marginal change in $H$ (<0.4 kJ/mol) and $k_0$ (1.72x10$^{10}$ μm$^{1/n}$ s$^{-1}$). As a result, the longest duration 437 °C test was included in the final calculation. The error on the activation enthalpy is calculated by passing a line through the extremes of the error bars: 1) maximum 511 °C error bar and the minimum 330 °C
error bar and 2) maximum 330 °C error bar and the maximum 330 °C error bar. The activation enthalpy of each of these lines is calculated using Eq 3.4.

Based on the growth controlling mechanism of surface diffusion around pore boundaries, it would be expected that this activation enthalpy, and that calculated from the determined $t_0$ values (109 kJ/mol), should correspond to surface diffusion in halite. This is not the case, as the activation enthalpy for Cl$^-$ surface diffusion is 217 kJ/mol (Swinkels and Ashby, 1981). The calculated values from this study are closer to that of grain boundary diffusion of the Cl$^-$ ion in halite, reported as 155 kJ/mol by Burke (1968) and as 150 kJ/mol by Goodall et al. (2006).
Fig. 4.54. Graph used to calculate the activation enthalpy and growth constant values for normal grain growth in halite. The 330 °C to 511 °C data sets are used as these data sets are best described by $n = 0.25$. The line is a line of best fit for the data. Owing to the Arrhenius relationship for the normal grain growth equation, the displayed line equation is used to calculate the activation enthalpy and growth constant. The correlation coefficient, $R^2$, is also shown. One standard deviation error bars are also shown.

The idealised position of each data set can be calculated using these kinetic values; these positions are displayed as lines on Fig. 4.55 together with all normal grain growth samples. From visual inspection, it is clear that the grain size data does not fit perfectly onto the idealised position of each temperature. Despite grain size measurements being taken from areas that display normal grain growth textures the data still contains some scatter, the source of which needs to be addressed.
Fig. 4.55. Graph displaying all halite grain size data interpreted as representing normal grain growth using an $n$ value of 0.25. The dashed lines represent the idealised positions of each data set based on the calculated kinetic values shown on the plot using the 330 °C to 511 °C data sets. The 600 °C data are shown plotted using $n=0.25$ for ease of comparison but are best described by $n = 0.5$.

4.5. Summary of the 200 MPa confining pressure results

In summarizing the above results, it is apparent that when the data sets are considered on an individual basis, they provide a reasonable general fit (Tab. 4.9). When the data from all data sets are amalgamated the fit to the idealized position is generally poor, and a degree of scatter is present. Microstructures consistently display approximately normal grain growth textures at all temperatures with pores almost exclusively being found along grain boundaries. Less than 5% of the total porosity is found as inclusions within grains, the distribution of which appears to be random. These pore inclusions are approximately of the same size as those found along grain boundaries. The consistent value of $n = 0.25$ indicates diffusion around pore boundaries as controlling growth in halite. The presence of pores in all samples at all temperatures suggests this is reasonable. However, the scatter in the normal grain growth data as shown by the correlation coefficient values of
<0.9 together with the samples that have clearly experienced abnormal grain growth suggests that halite has a tendency towards abnormal grain growth.

Tab. 4.9. Table displaying the slope (m) and correlation coefficient ($R^2$) for all data sets. Note that the $R^2$ value for the 437 °C data set is due to there being only two data points.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>m</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>330</td>
<td>0.8809</td>
<td>0.9999</td>
</tr>
<tr>
<td>380</td>
<td>1.0274</td>
<td>0.9629</td>
</tr>
<tr>
<td>437</td>
<td>0.3729</td>
<td>1.0000</td>
</tr>
<tr>
<td>480</td>
<td>0.9190</td>
<td>0.8772</td>
</tr>
<tr>
<td>500</td>
<td>0.9204</td>
<td>0.8162</td>
</tr>
<tr>
<td>511</td>
<td>0.9483</td>
<td>0.4851</td>
</tr>
<tr>
<td>600</td>
<td>0.9999</td>
<td>0.8819</td>
</tr>
</tbody>
</table>

From visual examination of the distribution curves, it is clear that halite grain size data can be considered to be approximately quasi-stationary. The data is best described as a Weibull distribution rather than a log normal distribution at all temperatures (Tab. 4.10). There is also no systematic variation in the slopes of the Weibull distributions with regards to experimental temperature or duration. Of the samples for which distributions were obtained, a total of four samples were better described as normal distributions, however, the difference in linearity between the Weibull and log normal distributions are not statistically significant (<0.0182).

Tab. 4.10. Table summarising the correlation coefficient, $R^2$, results for each temperature set.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Weibull $R^2$</th>
<th>Cumulative log normal $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>330</td>
<td>0.9890 - 0.9972</td>
<td>0.9607 - 0.9894</td>
</tr>
<tr>
<td>380</td>
<td>0.9838 - 0.9966</td>
<td>0.9391 - 0.9694</td>
</tr>
<tr>
<td>437</td>
<td>0.9712 - 0.9955</td>
<td>0.9073 - 0.9857</td>
</tr>
<tr>
<td>480</td>
<td>0.9839 - 0.9959</td>
<td>0.9398 - 0.9706</td>
</tr>
<tr>
<td>500</td>
<td>0.9844 - 0.9984</td>
<td>0.9394 - 0.9889</td>
</tr>
<tr>
<td>511</td>
<td>0.9791 - 0.9950</td>
<td>0.9417 - 0.9939</td>
</tr>
<tr>
<td>600</td>
<td>0.9682 - 0.9974</td>
<td>0.9025 - 0.9920</td>
</tr>
</tbody>
</table>

In the simulations of normal grain growth by Fayad et.al, (1999) predicted values of $\beta = 2.5$ and $\alpha = 1.127$ for the Weibull distribution. Grain size distributions in this study
(Tab. 4.11) show good agreement with the predicted $\alpha$ values. The range in $\beta$ values is larger than the range in $\alpha$ with only the upper values corresponding to those predicted by Fayad et al. (1999). The largest $\beta$ values display an approximate increase with experimental temperature.

**Tab. 4.11.** Table summarising the range of $\alpha$ and $\beta$ values, for samples best described by the Weibull distribution, obtained in the process of calculating the Weibull cumulative distributions.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\alpha$ values</th>
<th>$\beta$ values</th>
</tr>
</thead>
<tbody>
<tr>
<td>330</td>
<td>1.1246 - 1.1291</td>
<td>1.8031 - 2.2763</td>
</tr>
<tr>
<td>380</td>
<td>1.1273 - 1.1292</td>
<td>1.9231 - 2.2624</td>
</tr>
<tr>
<td>437</td>
<td>1.1283 - 1.1291</td>
<td>1.9924 - 2.1983</td>
</tr>
<tr>
<td>480</td>
<td>1.1200 - 1.1291</td>
<td>1.7071 - 2.4290</td>
</tr>
<tr>
<td>500</td>
<td>1.1267 - 1.1292</td>
<td>1.9290 - 2.5355</td>
</tr>
<tr>
<td>511</td>
<td>1.1248 - 1.1291</td>
<td>1.8622 - 2.5100</td>
</tr>
<tr>
<td>600</td>
<td>1.1222 - 1.1292</td>
<td>1.7343 - 2.5145</td>
</tr>
</tbody>
</table>
5. Experimental results II: Anomalous samples and the influence of porosity

5.1. Observations of abnormal grain growth

As outlined in §3.5.4, once the data are plotted with the determined $d_0$ and $t_0$ values, they are examined for any samples that lie a significant distance away from the majority of the data set. These samples are interpreted as representing abnormal grain growth. Abnormal grain growth is most commonly described in terms of grains that have grown larger than would be expected, however in the case of this study, samples which have attained a grain size smaller than would be expected are also considered to have undergone abnormal grain growth.

In tests such as HP14 (Fig. 5.1), clear abnormal grain growth can be seen to have taken place. This is the most extreme case of traditional abnormal grain growth seen in these tests. When grain size measurements, from areas such as those displayed in Fig. 5.2, are obtained, the results place HP14 on the 500 °C normal grain growth graph (Fig. 5.5). This suggests that both normal and abnormal grain growth processes are occurring simultaneously. The data sets that are interpreted to contain samples that have experienced abnormal grain growth are displayed in Fig. 5.3.
Fig. 5.1. Photomicrograph of HP14 (500 °C, 01d 21h 30m). Note the high occurrence of large grains with lobate boundaries characteristic of abnormal grain growth. Patches of smaller grains displaying a texture typical of that seen in normal grain growth are also present.

Fig. 5.2. Photomicrograph of a patch of grains displaying normal grain growth texture (relatively straight grain boundaries, 120° triple junctions) in HP14 500 °C (01d 21h 30m) (Fig. 5.1). Note the presence of porosity along many of the grain boundaries. The highly spotted areas of the image are an artefact of the thin-section being too thick and as a result porosity can be seen along the entire boundary as it curves into the slide.
Fig. 5.3. Graph displaying halite grain size data interpreted as representing normal grain growth (dots) and those interpreted as representing abnormal grain growth (crosses) using an $n$ value of 0.25. The dashed lines represent the idealised positions of each data set based on the calculated kinetic values shown on the plot using the 330 °C to 511 °C data sets. The 600 °C data are shown plotted using $n=0.25$ for ease of comparison but are best described by $n = 0.5$.

HP21 (500 °C, 35d 00h 00m) has a grain size much smaller than would be expected based on the remainder of the data set (Fig. 5.3). Given this, it would be expected that the entire sample would be made up of grains exhibiting normal grain growth textures, but this is not the case. Fig. 5.4 shows that abnormal grain growth occurred at the ends of the sample while grains displaying a normal grain growth texture are present in the central areas (Fig. 5.5). These abnormal grains would not factor into the grain size measurements owing to the fact that potential edge effects result in these areas being avoided when taking grain size measurements. In addition to the evident abnormal grain growth at the margins of the sample, there are larger grains within the central area of the specimen (Fig. 5.4). This sample exemplifies the variability in grain size within the grain growth test on halite.
Fig. 5.4. Photomicrograph of HP21 (500 °C, 35d 00h 00m). A large range of grain sizes is present. The central area of the sample contains grains that display textures that suggest the occurrence of normal grain growth.

Fig. 5.5. Higher magnification photomicrograph of HP21 (500 °C, 35d 00h 00m) displaying grains exhibiting a characteristic normal grain growth texture. Note the high occurrence of porosity within the sample despite the long test duration.
5.2. Experiments at different confining pressures

As the kinetic data suggests, grain growth in halite is controlled by the presence of porosity along the grain boundaries. Despite the same fabrication process being used to create the samples themselves, it appears that the amount of porosity in the samples is difficult to control. In an effort to control the starting porosity, a series of experiments were conducted at different confining pressures. The rationale behind this was that at lower confining pressures, less porosity would be eliminated during the introduction of the confining pressure resulting in increased pore volume fractions. Therefore, less porosity being eliminated results in more remaining porosity to impose drag on the migrating boundary. In turn, this would result in smaller grain sizes. If porosity can be accurately controlled through this method, the overall result should be smaller grain sizes in tests carried out at lower confining pressures.

For reasons not fully understood, reducing the confining pressure below 200 MPa resulted in an increased failure rate for these tests. A total of thirteen tests were carried out, only six of those below 200 MPa could be sectioned (Tab. 5.1).

<table>
<thead>
<tr>
<th>Duration (hrs)</th>
<th>Sample</th>
<th>Confining pressure (MPa)</th>
<th>Grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>HP63</td>
<td>70</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td>HP62</td>
<td>100</td>
<td>119</td>
</tr>
<tr>
<td></td>
<td>HP65</td>
<td>200</td>
<td>120</td>
</tr>
<tr>
<td>72</td>
<td>HP74</td>
<td>70</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>HP71</td>
<td>100</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>HP19</td>
<td>200</td>
<td>396</td>
</tr>
<tr>
<td>120</td>
<td>HP73</td>
<td>70</td>
<td>156</td>
</tr>
<tr>
<td></td>
<td>HP67</td>
<td>100</td>
<td>179</td>
</tr>
<tr>
<td></td>
<td>HP18</td>
<td>200</td>
<td>156</td>
</tr>
</tbody>
</table>

If the thinking behind these tests proved to be correct it is expected that grains sizes should increase with increased test duration but lower confining pressures should result in smaller grain sizes owing to increased porosity content. From examination of Fig. 5.6 it is apparent that neither of these predications hold true over the data set. Initially, after 24 hours all grain sizes are similar. After a further 24 hours, the expected grain sizes pattern is observed, however, anomalous growth took place in the 200 MPa sample.
After a total duration of 5 days, the 70 MPa and 200 MPa samples have near identical grain sizes while the 100 MPa sample has the largest grain size.

Variations in porosity with varying confining pressures can be seen in the microstructures (Fig. 5.7). Normal grain growth textures are prevalent throughout the entirety of the data set. Large (20 µm) pores are present at confining pressures of 70 MPa (Fig. 5.7a). Strings of pores are also seen along grain boundaries and pores of 20 µm or more can be seen at triple junctions. There are, what appear to be, small (<10 µm) pore inclusions within these some grains. However, it is possible that these are artefacts of the sectioning process due to the weakness of halite.

*Fig. 5.6. Plot displaying the grain size results for the variable confining pressure experiments. Temperature is at a constant 500 °C.*
As the confining pressure increases to 100 MPa, the pore size decreases to <10 μm (Fig. 5.7b). There is negligible change between the 70 MPa and 100 MPa grain sizes. Strings of pores remain along grain boundaries and large (>20 μm) pores are present at triple junctions.

Clear abnormal grain growth took place at all three confining pressures and experimental durations (Fig. 5.8). HP73 and HP71 are dominated by abnormal grain growth whilst HP65 contained isolated areas of abnormal grain growth. In all three samples displayed here, single grains of 1 mm or larger were found. These grains exhibit the characteristic abnormal grain growth textures.

Fig. 5.7. Photomicrographs of the 500 °C, 48 hour variable confining pressure tests. a) HP63, 70 MPa. b) HP62, 100 MPa. c) HP65, 200 MPa. Note the constant presence of porosity in all samples.
Fig. 5.8. Photomicrographs of abnormal grain growth in the variable confining pressure tests.  
a) HP73, 70 MPa, 120 hours.  
b) HP71, 100 MPa, 72 hours.  
c) HP65, 200 MPa, 48 hours.
6. Experimental results III: Zener parameter analysis of porosity effects

A total of eighteen samples were imaged using a variable pressure SEM based at the Natural History Museum, London, UK. Owing to time constraints, the porosity-grain size relationship could be fully processed for ten of these (Tab. 6.1), samples that were imaged but not analysed are shown in Tab. 6.2. The samples analysed were chosen in order to cover the range of experimental temperatures, timescales and microstructures. The full suite of tracings for each sample can be found in Appendix 14.4.

Tab. 6.1. Table displaying the samples subjected to grain size-porosity analysis. Measured grain size refers to the mean linear intercept grain size as determined from optical photomicrographs and reported in Chapter 4. Note that the tracings used for the porosity analysis come from much smaller subareas of the sample.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Sample</th>
<th>Duration</th>
<th>Halite grain size from tracings used for porosity analysis (µm)</th>
<th>Measured halite grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>330</td>
<td>HL24</td>
<td>01d 23h 08m</td>
<td>71</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>HL21</td>
<td>107d 23h 36m</td>
<td>77</td>
<td>83</td>
</tr>
<tr>
<td>380</td>
<td>HL17</td>
<td>35d 17h 22m</td>
<td>95</td>
<td>111</td>
</tr>
<tr>
<td>437</td>
<td>HL9</td>
<td>68d 16h 36m</td>
<td>100</td>
<td>94</td>
</tr>
<tr>
<td>480</td>
<td>HL29</td>
<td>07d 23h 08m</td>
<td>98</td>
<td>114</td>
</tr>
<tr>
<td>500</td>
<td>HP14</td>
<td>01d 21h 30m</td>
<td>112</td>
<td>116</td>
</tr>
<tr>
<td></td>
<td>HP21</td>
<td>35d 00h 00m</td>
<td>87</td>
<td>102</td>
</tr>
<tr>
<td>511</td>
<td>HL7</td>
<td>00d 05h 17m</td>
<td>96</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>HL5</td>
<td>00d 15h 56m</td>
<td>144</td>
<td>136</td>
</tr>
<tr>
<td>600</td>
<td>HP37</td>
<td>&lt;5 min</td>
<td>133</td>
<td>98</td>
</tr>
</tbody>
</table>
Tab. 6.2. Table displaying the samples that were imaged for porosity investigation, but, due to time constraints, were not analysed.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Sample</th>
<th>Duration</th>
<th>Temp (°C)</th>
<th>Sample</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>330</td>
<td>HL22</td>
<td>37d 18h 07m</td>
<td>380</td>
<td>HL26</td>
<td>11d 21h 26m</td>
</tr>
<tr>
<td>500</td>
<td>HP26</td>
<td>00d 04h 04m</td>
<td>600</td>
<td>HP33</td>
<td>01d 01h 18m</td>
</tr>
<tr>
<td></td>
<td>HP19</td>
<td>03d 00h 00m</td>
<td></td>
<td>HP32</td>
<td>04d 17h 26m</td>
</tr>
<tr>
<td></td>
<td>HP20</td>
<td>12d 23h 00m</td>
<td></td>
<td>HP35</td>
<td>05d 22h 57m</td>
</tr>
</tbody>
</table>

Grain sizes determined from the SEM images are generally close to those determined from the linear intercept method supporting the view that the SEM images come from representative areas of the samples.

6.1. 330 °C

Two samples from the 330 °C experiments were examined, HL24 from the recrystallization / sintering period well before \( t_0 \), and HL21 from within the normal grain growth period.

6.1.1. HL24

Porosity is present in all three areas analysed in HL24 (Fig. 6.1). Pores are distributed along grain boundaries with little porosity in the interior of grains. Pores are commonly found at triple junctions, and, although clustering of pores around triple junctions is a rare occurrence, triple junction pores often tend to be of a larger size (approximately 2-3 µm) than those that lie along the boundaries. Pores are rarely found as inclusions in grain interiors. Porosity ranges in size from 0.36 µm (maximum resolution) to 6.05 µm; the average size is 1.52 µm. The normalized pore size distribution is better described as a log normal distribution than as a Weibull distribution (Fig. 6.2).
Fig. 6.1.  a) Photomicrograph of Area 14 in HL24 (330 °C, 01d 23h 08m).  b) Tracings of the grain boundaries.  c) Tracings of the pores. The scale bar in a) applies to all three images.
Fig. 6.2. Pore size distributions for three areas in HL24 (330 °C, 01d 23h 08m)  a) Log normal pore size distribution curves in which pore size ($d_p$) has been normalized by mean pore size ($\bar{d}_p$), b) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a log normal distribution.
Individual grains in HL24 display a range in Zener parameter \((Z = d_p/f_p)\) values of 2-23078, that are log normally distributed (Fig. 6.3). The average \(Z\) value is 653.

The variation in \(Z\) value with halite grain size is shown in Fig. 6.4. Sorting this data to show average Zener parameter for halite grains of a given size (Fig. 6.5) shows that, up to about 70 µm, the Zener parameter increases with increasing grain size in all three areas examined. At larger grain sizes, a very different grain size / Zener parameter trend occurs in one area (Area 12) than in the other two. Breaking the Zener parameter up into its component pore size and pore volume terms shows that the increase in Zener parameter at small grain sizes corresponds to a sharp decrease in pore volume without significant change in pore size. At grain sizes larger than 70 µm the decrease in pore volume fraction with grain size is much smaller and almost non-existent in Area 12; as at smaller grain sizes, the pore volume changes little with increasing grain size although there is a small increase in pore size in Area 12. The small increase in pore size coupled with the approximately unchanging pore volume fraction for the largest grains of Area 12 means that in that area, the Zener parameter decreases at the largest grain sizes.
Fig. 6.3. *Z* distribution for HL24 (330 °C, 01d 23h 08m).

Fig. 6.4. Graph displaying the grain size and *Z* value of every grain analysed in HL24 (330 °C, 01d 23h 08m). The blue lines are drawn from the origin through the 5% and 95% *Z* grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free. Note that for the sake of preserving detail, an individual grain with a *Z* value of 23079 (grain size = 91 µm) has been omitted from this plot. Note that this graph is the same as Fig. 3.21 (§3.5.6.) and is repeated here for the convenience of the reader.
Fig. 6.5. Graphs displaying the relationship between halite grain size and a) Z, b) pore size and c) pore volume fraction in three areas of HL24 (330 °C, 01d 23h 08m).
6.1.2. HL21

Porosity is present throughout this sample (Fig. 6.6). Pore size ranges between 0.36 µm (maximum resolution) and 4.8 µm; the average pore size is 1.3 µm. Pores are distributed along boundaries, however, pores are occasionally found within the grains as inclusions. An increased density of pores along the grain boundaries immediately adjacent to triple junctions is a common feature. The normalized pore size distribution is better described as a log normal distribution than as a Weibull distribution (Fig. 6.7).
Fig. 6.6.  a) Photomicrograph of Area 10 in HL21 (330 °C, 107d 23h 36m).  b) Tracings of the grain boundaries.  c) Tracings of the pores. The scale bar in a) applies to all three images.
Fig. 6.7. Pore size distributions for three areas in HL21 (330 °C, 107d 23h 36m)  

a) Log normal pore size distribution curves in which pore size ($d_p$) has been normalized by mean pore size ($\bar{d}_p$), b) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a log normal distribution.
Individual grains in HL21 display a range in Zener parameter \(Z = d_p/f_p\) values of 6-5425, that are approximately log normally distributed (Fig. 6.8). The average Z value is 806.

The variation in Z values with halite grain size is shown in Fig. 6.9. Sorting this data to show average Zener parameter for halite grains of given a size (Fig. 6.10) shows that up to grain sizes of approximately 100 \(\mu\)m the Z value increases with increasing grain size. At larger grain sizes, Area 10 experiences a reduction in the Zener parameter. Breaking the Zener parameter down into its components reveals that, up to halite sizes of approximately 75 \(\mu\)m, pore volume fraction sharply decreases with no significant change in pore size. At larger halite grain sizes, pore volume fraction continues to decrease, but more gradually. Area 10 displays a small increase in pore volume fraction at the largest grain sizes with minimal change in pore size. This increase in pore volume fraction leads to the observed decrease in Zener parameter in Area 10.
Fig. 6.8. Z distribution for HL21 (330 °C, 107d 23h 36m).

Fig. 6.9. Graph displaying the grain size and Z value of every grain analysed in HL21 (330 °C, 107d 23h 36m). The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free.
Fig. 6.10. Graphs displaying the relationship between halite grain size and a) Z, b) pore size and c) pore volume fraction in three areas of HL21 (330 °C, 107d 23h 36m).
6.1.3. 330 °C comparison

Comparing the Zener parameter vs. halite grain size data from the sintering phase (HL24) and the grain growth phase (HL21) shows remarkably little difference (Fig. 6.11). As is to be expected given the longer anneal times, pore size and pore volume fraction in HL21 are both slightly smaller than in HL24, and the Zener parameter is slightly larger in HL21, suggesting that, in principle, boundary migration in HL21 is less pore influenced than in HL24. Of particular interest for the discussion in Chapter 7 is that the largest grains in HL24 have slightly larger pores around them while the largest grains in HL21 have slightly smaller pores. In addition, pore size in the pre-$t_0$ sample (HL24) displays increasing pore size with increasing halite size.
Fig. 6.11. Graphs displaying the relationship between grain size and a) average Z, b) average pore size and c) average porosity volume fraction in the 330 °C data set. Data obtained by collating and averaging data from the three areas examined in each sample.
6.2. 380 °C

6.2.1. HL17

Porosity is present in all three areas examined in HL17 (Fig. 6.12). Pores occupy large lengths of grain boundary; however, there are also large lengths of grain boundary that are free of pores (Fig. 6.12). Rare examples of pore clustering at triple junctions are seen, but the high pore density along boundaries makes this challenging to judge. Some pores located at triple junctions tend to be larger than those along the length of the grain boundary. Pores are seen in the grain interiors. Across the sample, the average pore size is 1.61 µm while individual pores range from 0.37 µm (maximum resolution) to 6.92 µm. The normalized pore distribution is better described as a log normal distribution than as a Weibull distribution (Fig. 6.13).
Fig. 6.12. a) Photomicrograph of Area 8 in HL17 (380 °C, 35d 17h 22m). b) Tracings of the grain boundaries. c) Tracings of the pores. The scale bar in a) applies to all three images.
Fig. 6.13. Pore size distributions for three areas in HL17 (380 °C, 35d 17h 22m)  a) Log normal pore size distribution curves in which pore size ($d_p$) has been normalized by mean pore size ($\bar{d}_p$), b) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a log normal distribution.
Individual grains in HL17 display a range of Zener parameter \((Z = d_p/f_p)\) values between 4 and 3238, that are log normally distributed (Fig. 6.14). The average \(Z\) value is 419.

The variation in \(Z\) value with halite grain size is shown in Fig. 6.15. Note that the data hugs the left blue line, that is, \(Z\) is mostly small in this sample. Sorting the data to show the average Zener parameter for halite grains of a given size (Fig. 6.16) shows that the Zener parameter increases with increasing halite grain size in both Area 4 and Area 14. Area 8 displays this same trend up to grain sizes of approximately 140 \(\mu m\) after which point \(Z\) shows little variation. Examining the individual components of \(Z\) reveals that pore size remains fairly constant. Pore volume fraction sharply decreases in all three areas up to halite grain sizes of approximately 100 \(\mu m\) after which volume fraction decreases more gradually in Area 4 and Area 14. In Area 8, porosity volume fraction increases slightly at the largest halite grain sizes, which, in combination with the slight pore size increase at the corresponding grain sizes in this area, results in the observed constant Zener parameter (Fig. 6.16a).
Fig. 6.14. Z distribution for HL17 (380 °C, 35d 17h 22m).

The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free.

Fig. 6.15. Graph displaying the grain size and Z of every grain analysed in HL17 (380 °C, 35d 17h 22m). The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free.
Fig. 6.16. Graphs displaying the relationship between halite grain size and a) Z, b) pore size and c) pore volume fraction in three areas of HL17 (380 °C, 35d 17h 22m).
6.3. 437 °C

6.3.1. HL9

This sample has anomalously small grain size. Porosity is present in all three areas examined in HL9 (Fig. 6.17). Pores sit along grain boundaries with rare single pores seen in the grain interiors. Pores are commonly observed at triple junctions. There is evidence of pore clustering on the grain boundaries immediately adjacent to triple junctions but this is a rare occurrence. Pore sizes vary from 0.68 µm (maximum resolution) to 6.6 µm; the average pore size is 2.34 µm. Pore size distributions are better described as a log normal distribution than as a Weibull distribution; however, Area 24 has a clear bi-modal size distribution (Fig. 6.18).
Fig. 6.17. a) Photomicrograph of Area 23 in HL9 (437 °C, 68d 16h 36m). b) Tracings of the grain boundaries. c) Tracings of the pores. The scale bar in a) applies to all three images.
Fig. 6.18. Pore size distributions for three areas in HL9 (437 °C, 68d 16h 36m) a) Log normal pore size distribution curves in which pore size \(d_p\) has been normalized by mean pore size \(\bar{d}_p\), b) cumulative frequency \(F\) of pores larger than \(d_p / \bar{d}_p\) plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency \(F\) of pores larger than \(d_p / \bar{d}_p\) plotted so that it should give a straight line if well described as a log normal distribution.
Individual grains in HL9 display a range in Zener parameter \( Z = \frac{d_p}{f_p} \) values of 4-8917, these are approximately log normally distributed (Fig. 6.19). The average value is 1013.

The variation in \( Z \) value with halite grain size is shown in Fig. 6.20. There is considerable variability in this sample above grain sizes of approximately 50 μm. Sorting this data to show average Zener parameter for halite grains of a given size reveals that all three areas display increasing Zener parameter with increasing halite grain size (Fig. 6.21). Examination of the constituents of the Zener parameter reveal a sharp reduction in pore volume fraction up to grain sizes of approximately 80-100 μm after which little reduction takes place. Pore size shows little variation within areas although there is a slight increase in pore size in Area 22. Area 24 has a smaller pore size than the other areas; however, this is balanced by having a consistently smaller pore volume fraction. Overall, this results in all three areas having similar Zener parameters for a given grain size.
Fig. 6.19. Z distribution for HL9 (437 °C, 68d 16h 36m).

Fig. 6.20. Graph displaying the grain size and Z value of every grain analysed in HL9 (437 °C, 68d 16h 36m). The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free.
Fig. 6.21. Graphs displaying the relationship between halite grain size and a) $Z$, b) pore size and c) pore volume fraction in three areas of HL9 (437 °C, 68d 16h 36m).
6.4. 480 °C

6.4.1. HL29

Four areas within HL29 were analysed, all of which contained porosity (Fig. 6.22, Fig. 6.23). Area 18 (Fig. 6.22) contains an anomalously large grain whilst the remainder of the areas contain grains more representative of normal grain growth. Pores are mainly found along grain boundaries and at triple junctions although the frequency of pores along grain boundaries is higher than at lower temperatures. The large grain in Fig. 6.22 contains a larger number of pores than the surrounding smaller grains (note that these are not shown on Fig. 6.22c). Certain boundaries have a much higher concentration of pores than others. Triple junction clustering is commonly observed. Pores range in size from 0.47 μm to 7.17 μm; the average pore size is 1.72 μm. The normalized pore size distribution is better described as a log normal distribution than as a Weibull distribution (Fig. 6.24).
Fig. 6.22.  a) Photomicrograph of Area 18 in HL29 (480 °C, 07d 23h 08m).  b) Tracings of the grain boundaries.  c) Tracings of the pores. The scale bar in a) applies to all three images.
Fig. 6.23.  a) Photomicrograph of Area 19 in HL29 (480 °C, 07d 23h 08m).  b) Tracings of the grain boundaries.  c) Tracings of the pores. The scale bar in a) applies to all three images.
Fig. 6.24. Pore size distributions for four areas in HL29 (480 °C, 07d 23h 08m) a) Log normal pore size distribution curves in which pore size ($d_p$) has been normalized by mean pore size ($\bar{d}_p$), b) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a log normal distribution.
Individual grains in HL29 display a range in Zener parameter \((Z = d_p/f_p)\) values of 3-7604, that are log normally distributed (Fig. 6.25). The average \(Z\) value is 484.

The variation in \(Z\) value with halite grain size is shown in Fig. 6.26. \(Z\) hugs the left hand line, indicating that the Zener parameter is smaller in this sample. Sorting this data to show average Zener parameter for halite grains of a given size (Fig. 6.27) indicates that the Zener parameter increases with increasing halite size for all areas except Area 13 where \(Z\) decreases at the largest halite grain sizes. The large grain in Fig. 6.22 can clearly be distinguished on account of the large grain size and high \(Z\) value. This is reflected in the average pore volume fraction and pore size around this grain. Pore size varies by small amounts in all areas. Pore volume fraction shows a sharp reduction up to halite grain sizes of approximately 80-100 µm after which, pore reduction becomes more gradual. Area 13 shows evidence of slight pore volume fraction increase at the largest grain sizes. This, in combination with the marginal pore size increase at the largest grain sizes results in the observed decrease in \(Z\).
Fig. 6.25. Log normal Z distribution for HL29 (480 °C, 07d 23h 08m).

Fig. 6.26. Graph displaying the grain size and Z of every grain analysed in HL29 (480 °C, 07d 23h 08m). The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free.
Fig. 6.27. Graphs displaying the relationship between halite grain size and a) $Z$, b) pore size and c) pore volume fraction in three areas of HL29 (480 °C, 07d 23h 08m).
6.5. 500 °C

Two samples from the 500 °C data set were examined; HP14, from the grain growth phase, and HP21, also from the grain growth phase but displaying an anomalously small grain size. Both of these samples contain evidence of abnormal grain growth.

6.5.1. HP14

Three areas were examined in HP14, all of which contained visible porosity (Fig. 6.28). Pores are mainly found along grain boundaries, the density of which varies from boundary to boundary. Triple junction pores tend to be of a marginally larger size than those that sit on the grain boundaries; there is also some degree of pore clustering around triple junctions. Pores are found within grain interiors as inclusions, the frequency of inclusions appears to increase with increasing grain size. Pores range in size from 0.43 µm (maximum resolution) to 25.53 µm; the average pores size is 2.68 µm. HP14 contains large grains that display abnormal grain growth textures. However, there are patches of grains between these large grains that display normal grain growth textures (Fig. 6.28a). Two grains in the top left of Fig. 6.28b could potentially be abnormal grains owing to their larger size and lobate boundaries. Pore size distributions are better described as being log normal than as a Weibull distribution (Fig. 6.29). Area 24 has a bi-modal distribution of pore size. Both Weibull and log normal distributions highlight the variation in the standard deviation of the pore size distributions in the three different areas of the sample.
Fig. 6.28.  a) Photomicrograph of Area 17 in HP14 (500 °C, 01d 21h 30m).  b) Tracings of the grain boundaries.  c) Tracings of the pores. The scale bar in a) applies to all three images. Note the white space represents a single large abnormal grain.
Fig. 6.29. Pore size distributions for three areas in HP14 (500 °C, 01d 21h 30m) a) Log normal pore size distribution curves in which pore size ($d_p$) has been normalized by mean pore size ($\bar{d}_p$), b) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a log normal distribution.
Individual grains in HP14 display a range in Zener parameter \( (Z = d_p / f_p) \) values of 16-2672, that are log normally distributed (Fig. 6.30). The average Z value is 484.

The variation in Z value with halite grain size is shown in Fig. 6.31. There is a distinct lack of grains with very large Z values although there are some grains with extremely small Z values. Sorting this data to show average Zener parameter for halite grains of a given size indicates that Z increases with increasing halite grain size in Area 24 and Area 16 (Fig. 6.32). Area 17 displays the same trend up until halite grain sizes of 400 µm where a reduction in the Zener parameter takes place. Breaking the Zener parameter down into its two constituents reveals clear differences in pore size between the three areas, but that the pore size does not change with grain size in any given area. This was also true in HL9 (437 °C, 68d 16h 36m) but with smaller differences in pore size. Pore volume fraction initially decreases sharply up to halite sizes of approximately 100-150 µm, after which, the reduction in pore volume fraction is less pronounced. Area 17 consistently has a higher pore volume fraction in comparison to the remaining two areas. In addition, at the largest halite grain sizes, the pore volume fraction sharply increases. This anomalously high pore volume fraction explains the reduced Zener parameter at the largest halite sizes in Area 17.
Fig. 6.30. Log normal Z distribution for HP14 (500 °C, 01d 21h 30m).

Fig. 6.31. Graph displaying the grain size and Z of every grain analysed in HP14 (500 °C, 01d 21h 30m). The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free.
Fig. 6.32. Graphs displaying the relationship between halite grain size and a) Z, b) pore size and c) pore volume fraction in three areas of HP14 (500 °C, 01d 21h 30m).
6.5.2. **HP21**

This sample has an anomalously small grain size. All areas examined contain visible porosity (Fig. 6.33). Pores are found mainly along grain boundaries with occasional pores observed as inclusions in grain interiors. Triple junction clustering is observed but it is not a pervasive feature. Pores range from 0.8 µm (maximum resolution) to 8.67 µm in size; the average pore size is 3.35 µm. Despite the anomalously small grain size of this sample, some large grains exhibiting abnormal grain growth type textures are present (Fig. 6.33). The normalized pore size distribution is better described as a log normal distribution than as a Weibull distribution (Fig. 6.34).
Fig. 6.33.  
a) Photomicrograph of Area 10 in HP21 (500 °C, 35d 00h 00m).  
b) Tracings of the grain boundaries.  
c) Tracings of the pores.  
The scale bar in a) applies to all three images.  
Note the white space represents an area in which tracing of the grain boundary challenging, hence no boundaries were traced.
Fig. 6.34. Pore size distributions for three areas in HP21 (500 °C, 35d 00h 00m) a) Log normal pore size distribution curves in which pore size ($d_p$) has been normalized by mean pore size ($\overline{d}_p$), b) cumulative frequency ($F$) of pores larger than $d_p/\overline{d}_p$ plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency ($F$) of pores larger than $d_p/\overline{d}_p$ plotted so that it should give a straight line if well described as a log normal distribution.
Individual grains in HP21 display a range in Zener parameter \( (Z = d_p/f_p) \) values of 7-3172, that are log normally distributed (Fig. 6.35). The average Z value is 299.

The variation in Z value with halite grain size is shown in Fig. 6.36. As in HP14, there is a distinct lack of grains with large Z values and there are also numerous grains with very small Z values. The main difference between the two samples is that grains in HP21 do not reach the size that grains in HP14 reach. Sorting this data to show average Zener parameter for halite grains of a given size (Fig. 6.37) reveals that all three areas display increasing Zener parameter with increasing halite grain size. Examining each of the constituents of the Zener parameter demonstrates that the volume fraction of pores abruptly diminishes up to grain sizes of approximately 80-100 µm. Above this grain size, the amount of pore volume fraction reduction with increasing grain size decreases. Pore size within the sample is variable from area to area; however, the pore size within each respective area varies minimally. This is not the case for the largest halite grain sizes in Area 14 where a dramatic reduction in pore size is observed.
Fig. 6.35. Log normal Z distribution for HP21 (500 °C, 35d 00h 00m).

Fig. 6.36. Graph displaying the grain size and Z of every grain analysed in HP21 (500 °C, 35d 00h 00m). The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free.
Fig. 6.37. Graphs displaying the relationship between halite grain size and a) Z, b) pore size and c) pore volume fraction in three areas of HP21 (500 °C, 35d 00h 00m).
6.5.3. 500 °C comparison

Comparing the growth phase Zener parameter vs. halite grain size data from a sample considered to represent normal grain growth (HP14) and a sample with an anomalously small grain size (HP21) highlights the differences between the two (Fig. 6.38). Somewhat counter intuitively, the longer duration test generally has a larger pore size that, aside from a decrease in size at intermediate halite grain sizes, increases with increasing halite grain size. Similarly, the shorter duration test displays increasing pore size with increasing halite grain size. HP21 also displays a substantially larger pore volume fraction at the smallest halite grain sizes. Of interest for the discussion in Chapter 7 is that the largest grain sizes in HP14 display an increase in pore volume fraction which consequently leads to a reduction in the Zener parameter.
Fig. 6.38. Graphs displaying the relationship between grain size and a) average $Z$, b) average pore size and c) average porosity volume fraction in the 500 °C data set. Data obtained by collating and averaging data from the three areas examined in each sample.
6.6. 511 °C

Two samples from the 511 °C data set were examined; HL7, from the pre-grain growth conditioning phase, and HL5, from the grain growth phase but which displays an anomalously large grain size.

6.6.1. HL7

Porosity was observed in all three areas examined in HL7 (Fig. 6.39). Pores range from 0.36 µm to 10.75 µm; the average pore size is 1.63 µm. Pores are mainly located along grain boundaries with rare pore inclusions within grain interiors. Pores located at triple junctions tend to be larger than the pores that form strings along grain boundaries. The normalized pore size distribution is better described as a log normal distribution than as a Weibull distribution (Fig. 6.40).
Fig. 6.39. a) Photomicrograph of Area 7 in HL7 (511 °C, 00d 05h 17m). b) Tracings of the grain boundaries, c) Tracings of the pores. The scale bar in a) applies to all three images.
Fig. 6.40. Pore size distributions for three areas in HL7 (511 °C, 00d 05h 17m) a) Log normal pore size distribution curves in which pore size ($d_p$) has been normalized by mean pore size ($\bar{d}_p$), b) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a log normal distribution.
Individual grains in HL7 display a range in Zener parameter \((Z = \frac{d_p}{f_p})\) values of 10-4930, that are log normally distributed (Fig. 6.41). The average \(Z\) value is 588.

The variation in Zener parameter with halite grain size can be seen in Fig. 6.42. The largest grains in this sample have \(Z\) values spread in between the two blue lines including four grains that plot in close proximity to the lines. Sorting this data to show average Zener parameter for halite grains of a given size (Fig. 6.43) shows that all three areas experience increasing \(Z\) with increasing halite grain size. However, Area 4 displays a decrease in \(Z\) at the largest halite grain sizes. Examination of the constituents of the Zener parameter indicates that pore size throughout the sample is approximately homogeneous; although all three areas display a slight increase in pore size at the largest halite grain sizes. All three areas display a sharp decrease in pore volume fraction until approximately 100 \(\mu\)m when the reduction in pore volume fraction becomes more gradual. At larger halite grain sizes, Area 7 displays continued volume fraction reduction, the volume fraction in Area 6 stabilizes while the pore volume fraction in Area 4 increases slightly. It is this increase that accounts for the reduced Zener parameter value at the largest halite grain sizes.
Fig. 6.41. Log normal $Z$ distribution for HL7 (511 °C, 00d 05h 17m).

Fig. 6.42. Graph displaying the grain size and $Z$ of every grain analysed in HL7 (511 °C, 00d 05h 17m). The blue lines are drawn from the origin through the 5% and 95% $Z$ grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free.
Fig. 6.43. Graphs displaying the relationship between halite grain size and a) Z, b) pore size and c) pore volume fraction in three areas of HL7 (511 °C, 00d 05h 17m).
6.6.2. HL5

Porosity was found in all three areas analysed in HL5 (Fig. 6.44). Pores range in size from 0.43 µm to 17.15 µm; the average pore size is 3.14 µm. Pores are found almost exclusively along grain boundaries with pores rarely occurring as inclusions in halite grains. Pores are commonly found at triple junctions. A high density of pores is also often seen around such triple junctions. The normalized pore size distribution is better described as a log normal distribution than as a Weibull distribution (Fig. 6.45). Area 12 has a much tighter distribution in comparison to the other areas which translates to a shallower distribution slope.
Fig. 6.44.  a) Photomicrograph of Area 12 in HL5 (511 °C, 00d 15h 56m).  b) Tracings of the grain boundaries.  c) Tracings of the pores. The scale bar in a) applies to all three images.
Fig. 6.45. Pore size distributions for three areas in HLS (511 °C, 00d 15h 56m)  a) Log normal pore size distribution curves in which pore size ($d_p$) has been normalized by mean pore size ($\bar{d}_p$), b) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency ($F$) of pores larger than $d_p/\bar{d}_p$ plotted so that it should give a straight line if well described as a log normal distribution.
Individual grains in HL5 display a range in Zener parameter \((Z = d_p/f_p)\) values of 30-11597, that are log normally distributed (Fig. 6.46). The average Z value is 1126.

The variation in Z value with halite grain size is shown in Fig. 6.47. A large number of grains have high Z values and very few grains sit close to the left hand line. Sorting this data to show average Zener parameter for halite grains of a given size (Fig. 6.48) indicates that all three areas display increasing Z values with increasing halite grain size. The largest grain sizes in Area 15 have a vastly increased Z value. Examination of the constituents of the Zener parameter reveals that these grains have larger pores along their boundaries in comparison to the remaining grains in Area 15. Aside from these larger grains, pore size within individual areas varies marginally, although pore size does vary from area to area. All areas show sharp reductions in pore volume fraction up to halite grain sizes of 100 µm after which point, porosity volume fraction decreases more gradually. Area 12 has a consistently higher pore volume fraction and pore size in comparison to the other two areas.
Fig. 6.46. Log normal Z distribution for HL5 (511 °C, 00d 15h 56m).

Fig. 6.47. Graph displaying the grain size and Z of every grain analysed in HL5 (511 °C, 00d 15h 56m). The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free.
Fig. 6.48. Graphs displaying the relationship between halite grain size and a) Z, b) pore size and c) porosity volume fraction in three areas of HL5 (511 °C, 00d 15h 56m).
6.6.3. 511 °C comparison

Comparing the Zener parameter vs. halite grain size data from the pre-growth phase (HL7) and the grain growth phase (HL5) shows remarkably little difference in terms of Zener parameter (Fig. 6.49). Both samples have consistently similar $Z$ values aside from some of the largest grains in HL5 which have a vastly increased Zener parameter. The observed increase in $Z$ seen in this sample is attributed to an increase in pore size. The largest grains in HL7 have a decreased Zener parameter which can be attributed to an increase in pore volume fraction. Of interest for the discussion in Chapter 7 is that despite being the longer duration test, HL5 has a consistently larger pore size and volume fraction compared to HL7.
Fig. 6.49. Graphs displaying the relationship between grain size and a) average Z, b) average pore size and c) average porosity volume fraction in the 511 °C data set. Data obtained by collating and averaging data from the three areas examined in each sample.
6.7. 600 °C

6.7.1. HP37

Note that this test was stopped as soon as temperature was reached and had a duration of <5 mins (Tab. 6.1). Three areas were examined in HP37, all of which contain visible porosity (Fig. 6.50). Pore size ranges from 0.35 µm to 7.48 µm, the average pore size is 1.7 µm. Pores are almost exclusively found along grain boundaries with pores occasionally observed as inclusions in grain interiors. Triple junction pores are common; these pores are commonly larger (approximately 3-4 µm) than those on the grain boundaries. Clustering of pores around triple junctions is observed intermittently. The normalized pore size distribution is better described as a log normal distribution than as a Weibull distribution (Fig. 6.51).
Fig. 6.50.  a) Photomicrograph of Area 4 in HP37 (600 °C, <5 min).  b) Tracings of the grain boundaries.  c) Tracings of the pores. The scale bar in a) applies to all three images.
Fig. 6.51. Pore size distributions for three areas in HP37 (600 °C, <5 min)  a) Log normal pore size distribution curves in which pore size ($d_p$) has been normalized by mean pore size ($\bar{d}_p$), b) cumulative frequency ($F$) of pores larger than $d_p / \bar{d}_p$ plotted so that it should give a straight line if well described as a Weibull distribution and c) cumulative frequency ($F$) of pores larger than $d_p / \bar{d}_p$ plotted so that it should give a straight line if well described as a log normal distribution.
Individual grains in HP37 display a range in Zener parameter \((Z = d_p/f_p)\) values of 46-7539, that are log normally distributed (Fig. 6.52). The average \(Z\) value is 1042.

The variation in \(Z\) value with halite grain size is shown in Fig. 6.53. The data is particularly scattered with a number of grains sitting below the right blue line. Of particular are those smaller grains with large \(Z\) values. Sorting this data to show average Zener parameter for halite grains of given size (Fig. 6.54) indicates that the Zener parameter increases with increasing halite grain size. Area 7 displays a large increase in \(Z\) at intermediate grain sizes which can be attributed to a decrease in the pore volume fraction. The Zener parameter in Area 4 stops increasing with grain size at the largest halite grain size, this is reflected in the pore size and volume fraction which remain approximately constant. Area 12 exhibits a sharp reduction in pore volume fraction and pore size with increasing halite grain size. This area also has a consistently higher volume fraction of pores compared to the other two areas. The reduction in pore volume fraction in Areas 7 and 4 is more gradual. Additionally, the smallest grains in these areas have a lower pore volume fraction.
Fig. 6.52. Log normal Z distribution for HP37 (600 °C, <5 min).

Fig. 6.53. Graph displaying the grain size and Z of every grain analysed in HP37 (600 °C, <5 min). The blue lines are drawn from the origin through the 5% and 95% Z grains to highlight grains that have particularly high numbers of pores around them and ones that are particularly pore free.
Fig. 6.54. Graphs displaying the relationship between halite grain size and a) Z, b) pore size and c) porosity volume fraction in three areas of HP37 (600 °C, <5 min).
7. Discussion of halite grain growth and the influence of second phase porosity

7.1. Microstructural observations

Experiments were carried out on halite powders by hot isostatic pressing at 330 °C-600 °C (0.56-0.81 \( T_m \)), where \( T_m \) is the halite melting temperature (801 °C = 1074 K), and 200 MPa confining pressure, complemented by some additional experiments at 500 °C (0.71 \( T_m \)) at 70 and 100 MPa.

Upon reaching experimental temperature, porosity was, in general, approximately 5% or less, indicating that the samples were already approaching a fully dense state. Throughout the annealing period porosity is always present (e.g., HL21, Fig. 4.4d), indicating that the halite grains, up to 511 °C, are always under pore controlled conditions and never transition into the boundary controlled regime described in Fig. 2.13. At 600 °C however, the observed change in growth controlling mechanism to interface controlled growth suggests that boundary mobility is sufficiently high to allow growth under boundary / interface controlled conditions with minimal pore influence. Pores still remain locally influential, for instance, at triple junctions, hence the continued occurrence of anomalous grain sizes at this temperature. Generally, the samples display foam-like textures with approximately equidimensional grains meeting at 120° triple junctions. Pores are located almost exclusively along grain boundaries. However, there are some, estimated at <5%, that occur as inclusions within the grain interiors. These inclusions are of similar size to the pores located along grain boundaries and at triple junctions and are randomly distributed within grains.

The initial stage of the annealing period is characterised by limited grain growth; the microstructural changes are subtle but are presumed to involve further reduction in porosity and possibly re-distribution of pores along grain boundaries. Although it is considered that this stage is primarily characterized by pore reduction through sintering processes, there is the possibility that some grain boundaries are mobile, and consequently, there may be some degree of recrystallization. However, the fact that the foam-like textures are so pervasive and that lobate grain boundaries are only rarely seen
in samples with short annealing times, it is considered unlikely that widespread recrystallization occurs.

Following this period of “conditioning”, growth begins and continues through to the longest duration experiment (HL21, 107d 23h 36m). No maximum grain size was attained at which growth stops.

The textures throughout growth are predominantly foam-like but at all temperatures there are some ‘anomalously’ large grains, suggesting that there is a tendency towards abnormal grain growth. These larger grains are more commonly encountered at 500 °C and above. Two types of anomalously large grains are present, both of which display grains larger than 1 mm: grains that possess highly lobate grain boundaries (e.g., HP14 (Fig. 5.1)), and grains within the remaining microstructure that have gently curving grain boundaries, with significant changes in curvature occurring almost exclusively at triple junctions with neighbouring grains (HL29 (Fig. 6.22)). The implication is that, in the latter group of larger grains, grain boundary migration has been towards the centre of curvature and thus they have experienced enhanced normal grain growth processes in comparison with their neighbouring grains.

Some microstructures have anomalously small grain sizes (e.g., HP21 (Fig. 5.4)), resulting from much slower coarsening. In some of these samples, there is a higher porosity volume fraction – in the case of HP21, the average pore volume fraction (0.033) is the largest observed within the suite of samples in which detailed porosity analysis was carried out.

The results present a challenging grain size data set to analyse, with significant scatter in the grain size vs. time relationship. Given the difficulties in precisely duplicating the starting microstructures, especially the pore sizes, distribution and volume fraction, and the spatial variation of that microstructure throughout the entire sample, it follows that the observed scatter is a consequence of pore-boundary interactions. Subtle variations in the local pore size and volume fraction within a given sample apparently lead to some significant intra-sample variations in grain size. Grain growth in polycrystalline halite at the conditions used here, therefore, seems to be highly sensitive to porosity, even at pore volume fractions of <0.02.
7.2. Normal grain growth kinetics

Grain size measurements were taken from regions of the sample that displayed foam-textures and which were well away from the clear anomalously large grains. This approach was taken in order to establish the kinetics of the normal grain growth processes. Note that, in selecting these areas, one cannot be entirely certain that grains in the early stages of rapid (anomalously fast) growth or grains in which growth was anomalously slow, were not incorporated into the measurements.

7.2.1. Grain growth start time and starting grain size

$t_0$ and $d_0$ were determined by first examining the data for a change in slope on a plot of $\log_{10}(d^{1/n} - d_0^{1/n})$ vs. $\log_{10}(t - t_0)$ with $n = 0.25$ and $d_0$ and $t_0$ set at their lowest conceivable values ($d_0 = 45 \mu m$, $t_0 = 10$ sec). If a change in slope could be defined, $t_0$ and $d_0$ values were taken from after the point at which the change occurred, as done for the 380 °C and 600 °C data sets. In data sets where no change in slope could be unambiguously identified (e.g., 330 °C and 511 °C), $t_0$ and $d_0$ were determined based on the $t_0$ and $d_0$ values in the adjacent data sets on the assumption of a smooth increase in $d_0$ and a smooth decrease in $t_0$ with increasing temperature.

Evaluating $t_0$ is complicated by the possibility that different areas within the sample exited the “conditioning” period and entered the growth phase at different times, that is, the onset of growth is varying spatially within samples as well as between samples at a given temperature. This is demonstrated by the occurrence of individual grains larger than 125 µm in tests with durations less than $t_0$ (e.g., HP37 (Fig. 6.50) and HL7 (Fig. 6.39)).

Confidence in the determined $t_0$ and $d_0$ values comes from the observation that each term varies smoothly with temperature and has an Arrhenius-type dependence on temperature (Fig. 7.1 and Fig. 7.2). As expected, $d_0$ increases with increasing temperature while $t_0$ decreases with increasing temperature. Also of significance is the fact that the $d_0$ values remain within the grain size range of the starting material, thus further indicating the lack of growth in the “conditioning” period.
Fig. 7.1. Graph displaying the relationship between the determined $t_0$ values and $1000/T$. The correlation co-efficient, $R^2$, of the line of best fit is shown.

Fig. 7.2. Graph displaying the relationship between the determined $d_0$ values and $1000/T$. The correlation co-efficient, $R^2$, of the line of best fit is shown.
An activation enthalpy for normal grain growth of 109 kJ/mol was obtained from $t_0$ values (Fig. 7.1). See §7.2.4 for a further discussion of the obtained kinetic values.

### 7.2.2. Grain size distributions

Grains size distributions were measured for the majority of the samples in the study from tracings of the grain boundary network generated from photomicrographs. Those samples that were not measured were either of too large a mean grain size to permit a statistically valid number of grains to be traced or the thin-sections were of insufficient quality to allow accurate tracing of the grain boundaries. The areas of sample chosen for grain size distribution analysis were selected to avoid areas of distinct abnormal grain growth. Consequently, the impact of abnormal grain growth on the distributions has not been explored.

Grain size distributions produced by normal grain growth are, by the definition of normal grain growth, quasi-stationary when grain size is normalized by mean grain size. These features are well observed in this study, that is, all normalized grain size distributions obtained at a given temperature are approximately the same (e.g., Fig. 4.6 and Fig. 4.34). At all temperatures, the most significant variation in grain size distribution between samples annealed at given temperature occurs at the smallest measured grain sizes. There is, however, no systematic variation with regards to experimental duration.

The grain size distributions are well approximated as log normal distributions, as commonly observed in grain growth studies (e.g., Feltham, 1957). In this study, the grain size distributions are better described (particularly at fine grain sizes) as Weibull distributions based on comparisons of linearity between Weibull cumulative distribution and cumulative log normal distribution plots. This too is what is observed in other normal grain growth simulations (e.g., Fayad et al., 1999; Rios, 2000).

It can be said that samples that did experience abnormal grain growth did not have anomalous grain size distributions in areas of the sample away from the larger grains. For example, HP21 (500 °C, 35d 00h 00m) displays grains with characteristic abnormal grain growth textures at the margins of the sample and also occasional larger grains within the main body of the sample which display normal grain growth textures (Fig. 5.4). Despite this, the size distribution is approximately log normal (Fig. 4.34). Abnormal grain growth
is not necessarily readily visible on a grain size distribution curve because the number of large grains is very small compared to the total number of grains, but it is potentially visible on linearized cumulative frequency plots at large grain sizes.

As stated previously, the quasi-stationary nature of the grain size distribution is a defining characteristic of normal grain growth. However, it should be noted that in this study, all distributions at all temperatures are quasi-stationary, that is, there are no apparent differences between pre-$t_0$ samples, samples with anomalous grain sizes (whether they be large or small) and those samples that are in the post-$t_0$ growth stage (compare HP37, HP48 and HP35 in the 600 °C data set Fig. 4.48). This is consistent with the observation that all samples annealed at a given temperature have foam textures that are visually indistinguishable from each other.

7.2.3. Grain growth exponent

Over the range 330 °-511 °C, the grain growth of halite is consistently well described by the normal grain growth equation (Eq. 2.8) with $n = 0.25$. At 600 °C, the data is well described by the normal grain growth equation with $n = 0.5$.

Of the three conceivable values of $n$ (0.25, 0.33 and 0.5) confidence that $n = 0.25$ is high because the value of the slope of the grain size / time data ($\log_{10}(d^{1/n} - d_0^{1/n})$ vs. $\log_{10}(t - t_0)$) is close to 1 ($m > 0.8809$ in all cases) as it must be. Likewise, the confidence in the robustness of the $n = 0.5$ value in the 600 °C data set is high for the same reason ($m = 0.9999$).

At temperatures of 330 °-511 °C, an $n$ value of 0.25 is consistent with growth being controlled by surface diffusion around pore boundaries, that is, it is the rate at which pores can be dragged along with the moving boundary that controls the rate at which the boundary moves. The presence of porosity in all samples across the range of experimental temperatures and durations supports this interpretation. At 600 °C, the change to $n = 0.5$ indicates a change of growth controlling mechanism to interface (boundary) controlled growth, however, pores remain locally influential resulting in both anomalously small and large grains.
7.2.4. Activation enthalpy for grain growth

The data from this study used to fit the normal grain growth equation are displayed in Fig. 7.3. As temperature increases, each temperature set plots at larger \( \log_{10}(d^{1/n} - d_0^{1/n}) \) values. However, there is some overlap between the 500 °C data set and the 511 °C data set. It appears that the 500 °C data set plots at slightly larger values of \( \log_{10}(d^{1/n} - d_0^{1/n}) \) when compared to the 511 °C data set. This probably reflects the resolution of the data with respect to the challenges and vagaries of the microstructural development and measurement - at this temperature the difference in grain growth kinetics as displayed on a plot like this, is very small over the temperature interval of 500 °C to 511 °C. Moreover, it is possible that, as the temperature approaches that at which the transition to interface-controlled growth occurs (511 °C-600 °C), there is an increased influence from this growth mechanism, and consequently the system becomes highly sensitive to small variations in porosity.

Some scatter also reflects the lack of reproducibility of \( d_0 \) and \( t_0 \) from sample to sample in data sets at a given temperature. Variations in the porosity characteristics of the staring material will directly impact \( d_0 \) and \( t_0 \) in individual samples which, in turn, influence the resulting grain sizes. The inclusion of grains with anomalous sizes (small and large) in the grain size measurements is also considered to be a further cause of the observed scatter.

Based on the grain size data for the 330 °C-511 °C temperature sets, an activation enthalpy \( (H) \) of 122±34 kJ/mol and a rate constant \( (k_0) \) value of \( 9.6326 \times 10^{10} \ \mu \text{m}^{1/n} \text{ s}^{-1} \) were obtained using Fig. 7.4.
Fig. 7.3. Graph displaying all halite grain size data interpreted as representing normal grain growth using an 
$n$ value of 0.25. The dashed lines represent the ideal position of each data set based upon the kinetic values 
determined from the 330 °C to 511 °C data sets. The 600 °C data are shown plotted using $n = 0.25$ for ease of 
comparison but are best described by $n = 0.5$. 

\[ \frac{d^{1/n} - d_{0}^{1/n}}{d_{0}^{1/n}} = k_{0} (t - t_{0}) \exp(\frac{H}{RT}) \]

$n = 0.25$

$H = 122 \text{ kJ/mol}$

$k_{0} = 9.6326 \times 10^{10} \mu \text{m}^{1/n} \text{s}^{-1}$
Fig. 7.4. Graph used to calculate the activation enthalpy and rate constant values for normal grain growth in halite. The 330 °C -511 °C data sets are used as the grain growth mechanism is the same in all tests, and these data sets are all described by \( n = 0.25 \). Each data point represents the average \( \ln(d_{1/n} - d_{01/n}) - \ln(t - t_0) \) for each data set. The correlation co-efficient, \( R^2 \), is also shown.

Because Cl\(^-\) is the slower diffusing of the two main ions (Na\(^+\) and Cl\(^-\)), it is considered to be rate controlling. Indeed, no halite sintering studies have cited Na\(^+\) as the principal diffusing ion during sintering in NaCl, and there is no evidence to suggest otherwise for isostatic halite grain growth. A summary of the activation enthalpy values for Cl\(^-\) diffusion and the corresponding material transport mechanism discussed in §2.5.2., together with the temperature at which they were obtained, is shown in Tab. 7.1.
Tab. 7.1. Table summarizing the activation enthalpies, and the temperatures at which they were obtained, for Cl$^-$ diffusion in NaCl discussed in §2.5.2.

<table>
<thead>
<tr>
<th></th>
<th>$H$ (kJ/mol)</th>
<th>$T$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice diffusion</td>
<td>217-227</td>
<td>588-780</td>
</tr>
<tr>
<td>Surface diffusion</td>
<td>217</td>
<td>700-750</td>
</tr>
<tr>
<td>Core diffusion</td>
<td>103-155</td>
<td>250-450</td>
</tr>
<tr>
<td>Grain boundary diffusion</td>
<td>150-155</td>
<td>365-701</td>
</tr>
<tr>
<td>Self-diffusion</td>
<td>33-260</td>
<td>227-809</td>
</tr>
</tbody>
</table>

The activation enthalpies presented in this study ($122\pm34$ kJ/mol, obtained from halite normal grain growth data, and 109 kJ/mol, obtained from the $t_0$ values) fall within the range of core diffusion (103-155 kJ/mol) and self-diffusion (33-260 kJ/mol) of the Cl$^-$ ion Tab. 7.1. However, the growth controlling mechanism of surface diffusion around pore boundaries, as indicated by $n = 0.25$, suggests that the activation enthalpies should correlate with the of Cl$^-$ surface diffusion. This is not the case, as the value for halite surface diffusion determined by Swinkels and Ashby (1981) is significantly higher than that determined here (217 kJ/mol). It should be noted that this value was obtained using data from sintering studies at higher temperatures than those used here (700 °-750 °C) but not at the pressures used in these experiments. There is also very little in the way of data for surface diffusion in halite at the elevated pressure and temperature conditions used in the present study.

The activation enthalpy determined from grain size measurements of samples considered to have experienced normal grain growth ($122\pm34$ kJ/mol) is closer to the activation enthalpy obtained for grain boundary diffusion of the Cl$^-$ ion in halite, that is, 155 kJ/mol reported by Burke (1968) and 150 kJ/mol, reported by Goodall et al. (2006) (Tab. 7.1). Both of these studies were conducted within the temperature range covered by this experiment, however, neither of these studies were conducted under elevated pressure conditions.

These activation enthalpies, although closer to those determined in this study, do not provide a satisfactory correlation. This indicates that there may be some uncertainty associated with the values calculated in this study. This could be associated with the complexity of the microstructural measurements, and the potential inclusion of grains that were undergoing anomalous grain growth within the areas used to obtain grain size measurements. Also of potential significance is the fact that Burke (1968) and Franssen
(1994) observed a change in activation enthalpy and material transport mechanism near the upper end of the temperature range used to determine the presented values (450 °-550 °C). A similar situation may be occurring in the isostatic experiments carried out in this study, as the system approaches the temperature at which the transition to interface controlled growth takes place (511 °-600 °C), the transition could be accompanied by a change in activation enthalpy which, in turn, could have influenced the values obtained here. Additionally, and perhaps more importantly, many previously determined values for diffusion in halite have come from either creep studies or sintering studies, not the isostatic high pressure high temperature tests carried out in this study. All of these issues will contribute significantly to the differences in the reported values for the activation enthalpy.

Combining the results for $n$ and $H$ in this study indicates that grain growth in halite at 330 °-511 °C is controlled by the rate of Cl$^{-}$ surface diffusion around pore boundaries, i.e., the rate at which the pores can be dragged along by the migrating boundary. At 600 °C, growth is controlled by the rate of diffusion of the Cl$^{-}$ ion across grain boundaries.

7.3. The influence of porosity

A porosity of <5% is consistently present in all samples across the entire data set. In general, the pores concentrate along grain boundaries and pore breakaway rarely happens, that is, pores are rarely found in the interior of grains. Those that are found within grains are randomly distributed, making it difficult to establish when in the growth phase breakaway occurred. Visual inspection of the optical microstructures provides the impression that pores are progressively eliminated with increasing annealing times but samples never reach full densification as is shown by the longest duration test (HL21 (Fig. 4.4d)).

An inability to achieve full densification is commonly reported in sintering studies (e.g., German, 2010), and is attributed to increasing gas pressure within the pores as sintering proceeds. In the final stages of sintering, pores become isolated, and the atmosphere within them becomes a closed system. As pores continue to shrink, pressurization of the atmosphere within them increases and eventually reaches a point where the pressure is high enough to resist further densification.
To some extent grain boundary migration can assist in eliminating porosity since pores can be regarded as large vacancies that can be consumed by moving boundaries, which can be considered as vacancy annihilation sites (Brett and Seigle, 1963; German, 2010). However, when the pores collect and perhaps coalesce at relatively stable parts of the microstructure (e.g., grain boundary triple junctions), there is much reduced scope for this pore elimination mechanism to be effective.

In this study, some experiments at different confining pressures were performed in an attempt to control porosity and therefore to investigate pore effects directly (Chapter 5). The results of these experiments indicated that varying the confining pressure exerted negligible control over the porosity, and the resulting grain size, in the specimen. As such, varying confining pressure cannot be used to control sufficiently porosity at the onset of growth, and therefore, does not allow systematic investigation of pore-boundary interactions. Instead, high resolution images were used to characterize the porosity in the 200 MPa samples and consider pore-boundary interactions at the grain scale utilising the Zener parameter \( Z = d_p / f_p \) (§2.4) where \( d_p \) is the average pore size around a given grain and \( f_p \) is the pore volume fraction around that same grain (§3.4.3.2)). Consequently, efforts were focused on measuring pore size and pore volume fraction and correlating this with halite grain size.

### 7.3.1. The influence of pore size

The mean pore size (1.34-3.35 µm) decreases extremely slowly with annealing time. For example, at 330 °C, the average pore size reduces from 1.52 µm to 1.30 µm over the course of approximately 100 days. There is no systematic change in mean pore size with increasing experimental temperature. Within individual samples, mean pore size varies from area to area. The differences in mean pore size between these areas are small (approximately 2-3 µm), but within a given area the pore size is approximately independent of halite grain size, that is, pores around large grains are generally of similar size as pores around small grains. There are unusual examples of larger grains having larger pore sizes (e.g., HL5, Area 15 (Fig. 6.48b)) which can perhaps be attributed to some pore coalescence or swelling of pressurized pores. In sintering tests it has been demonstrated that at high temperatures, pressurized pores can effectively swell resulting
in an increase in pore size (German, 2010). There is also some evidence of minor pore coalescence pre-$t_0$ in HL24 (Fig. 6.11b) where average pore size increases with average halite grain size by approximately 0.2 µm. The contribution of pore coalescence is difficult to quantify as multiple pores coalesce into one large pore, making it challenging to differentiate a large pore from one that has formed by coalescence. Although, the fact that mean pore size shows little change with growth suggests that pore coalescence is limited. A small number of pores coalescing in particular locations, e.g., at triple junctions, may have a disproportionately large effect on growth, however, these occurrences of coalescence are difficult to identify. Pore size distributions are consistently better described as a log normal distribution in contrast to the grain size distributions which are best described as a Weibull distribution.

### 7.3.2. The influence of pore volume fraction

On the whole sample scale, average pore volume fraction is generally between 0.004-0.033. As with pore size, pore volume fraction decreases slowly with annealing time (e.g., at 330 °C, the average pore volume fraction decreases from 0.009 to 0.006 over the course of approximately 100 days) and has no systematic dependence with temperature in the samples analysed.

Within individual samples, the spatial variation in pore volume fraction is generally small (<0.01) for halite grain sizes larger than 50-100 µm (e.g., HL9 (Fig. 6.21c)). At smaller grain sizes, the pore volume fraction increases with decreasing grain size, as does the disparity between subareas within samples. Since the variation in pore size is minimal with respect to grain size, it is implied that pores are swept along with the boundary as it migrates, this would result in an increase in the pore volume fraction. The fact that this is generally not observed suggests that progressive pore elimination takes place during boundary migration. In some samples (e.g., HP14, Area 17 (Fig. 6.32c)), pore volume fraction increases at the largest grain sizes on the order of 0.02-0.05. The implication in these samples is that a significant proportion of the swept pores have not been eliminated.
7.3.3. The Zener parameter and the comparative influence of its constituents

The distribution of the Zener parameter, as defined on a grain by grain basis, is log normal (e.g., Fig. 6.25). The range in mean Zener parameter between subareas of the same sample shows little variation (e.g., the difference in mean Z ranges between 129 and 386). HL5 and HP37 display a greater spatial variation with a Z range of 911 and 862 respectively.

The spatial relationship between the Zener parameter and grain size within individual areas of samples is highly complex. At grain sizes up to approximately 150 µm, the Zener parameter increases in an approximately linear fashion with increasing grain size (e.g., HL17 (Fig. 6.16a)). At larger grain sizes, a number of different behaviours are observed. In HL9 (Fig. 6.21), the linear increase in Zener parameter with halite grain size continues through to the largest measured grains in the sample. In some cases the largest measured grains have a very large Zener parameter (e.g., HL29 (Fig. 6.27)). For samples such as HL24 (Fig. 6.5a), this linear behaviour breaks down with the Zener parameter sharply decreasing at the largest grain sizes.

Comparing how the constituents of the Zener parameter (pore size and pore volume fraction) vary with halite grain size gives insight into which of the two exerts more influence during grain growth. The lack of change in pore size with increasing halite grain size, both between samples and spatially within samples, points towards the porosity volume fraction exerting the larger control on the measured grain size. The same interpretation was made by Brodhag et al. (2011) from microstructural analysis of marbles of the Adamello contact aureole. Indeed, in all samples where the Zener parameter starts decreasing at large grain sizes, it is because of an increase in pore volume fraction. Clear evidence for this can be seen in HP14, Area 17 (Fig. 6.32) where the decrease in Z is accompanied by an increase in pore volume fraction, on the order of 0.04, with minimal change in pore size. A similar scenario, although not as extreme, is observed in HL7, Area 4 (Fig. 6.43) where a sharp decrease in Z is accompanied by an increase in pore volume fraction of 0.002 with marginal pore size change. This increase in pore volume fraction can be attributed to the sweeping of pores along the moving boundary. As the grain grows it consumes the surrounding smaller grains, the pores that lie on the grain boundaries are swept and accumulated along the migrating boundary. At the same time, pores are continually being eliminated. If, as growth continues, the rate
of pore elimination is higher than the rate of pore accumulation, the Zener parameter increases; if the reverse occurs, then $Z$ decreases.

The presence of grains that have clear anomalously large sizes (e.g., the white space seen in Fig. 6.28 (HP14)), indicate that obvious abnormal grain growth is taking place. It is, however, possible that non-conventional abnormal growth is also taking place as shown by grains displaying reduced $Z$ values resulting from increasing pore volume fractions. The only way that these grains could have attained the size they have whilst increasing their pore volume fraction is by a period of abnormal growth at the onset, or shortly thereafter, of the grain growth period. During this period of abnormal growth, the grain boundaries migrate rapidly resulting in pore accumulation outpacing pore elimination, that is, the pore volume fraction increases which causes $Z$ to decrease. However, the textures displayed by these large grains with decreased $Z$ (e.g., HP14, Area 17 (Fig. 6.28)) are not those associated with typical abnormal growth. In addition, the driving forces are those associated with normal grain growth, i.e., migration of the boundary is still towards the centre of curvature, it just happens that certain grains begin their growth stage before the majority of the microstructure.

Provisionally, it seems that one of two situations takes place, both of which are intimately linked to grain boundary migration. If grain boundary migration rates are low (either at low temperatures where grain boundary mobility is low (HL24 and HL21) or at short annealing durations (HP14)) then pore elimination rates will also be low. Since boundary mobility is low, the effect of drag imposed on the grain boundaries by pores is large; therefore, any grains that do grow require larger $Z$ values than the remaining microstructure. When growth begins in these grains, pore accumulation outpaces pore elimination resulting in a locally increased pore volume fraction. This leads to a decrease in $Z$ values and rapid slowing of boundary migration. In the second situation, both grain boundary migration and pore elimination rates are high (long annealing times at high temperatures (HP21)), therefore, $Z$ increases. This is due to pore elimination being able to keep pace with pore accumulation, therefore, reducing the likelihood of the Zener parameter decreasing. HL7 can be considered a “halfway house” of sorts between these two situations, as it was conducted at high temperature but over a short duration. As a result, the sample contains grains with both large $Z$ values and reduced $Z$ values. See §2.4 for a more detailed discussion of this relationship.
Spatial variations in porosity are inevitably set up during the sample fabrication and sintering processes. This provides an explanation for the variation in porosity of different areas of a given sample. However, there are more minor spatial variations in porosity on the grain scale, that is, where the pores are located along individual grain boundaries. For instance, localization of pores to triple junctions will provide the most efficient pinning regime; therefore, a smaller number of pores will be required to produce the same pinning force as a large number of pores spread along grain boundaries. These variations in pore location will directly impact on the point at which grain boundary migration is initiated.

7.4. Model of pore-influenced grain growth

The occurrence of anomalously large grains, both those displaying clear abnormal grain growth textures and those that occur in the remainder of the microstructure that display gently curved grain boundaries and 120° triple junctions, are considered to be a result of spatial variations in porosity at the onset of grain growth. The presence of a second phase has been well documented as a cause of abnormal grain growth (e.g., Lange and Hirlinger, 1984; Srolovitz et al., 1985; Liu and Patterson, 1993). How these spatial variations evolve with increasing test duration directly impacts on halite grain size. With this in mind, a model is presented with the aim of relating halite grain size to the Zener parameter. Firstly, in situations where pore elimination is larger than pore accumulation, resulting in normal grain growth and a large Zener parameter, and secondly, in situations where pore accumulation occurs quicker than pore elimination, resulting in a spurt of early abnormal grain growth producing grains with decreased Zener parameter.

Upon the application of confining pressure, quasi-instantaneous plastic yielding occurs and is followed by densification, pore formation and subsequent pore elimination via boundary diffusion as the boundaries migrate slightly during the pre-$t_0$ “conditioning” phase (German, 2010). In both scenarios, slight grain boundary adjustments, together with continual pore elimination, occur prior to $t_0$ as shown by the presence of grains larger than the sieve fraction in HP37 (600 °C, <5 mins (Fig. 6.53)).

Once $t_0$ is reached, slow boundary migration takes place during which pores are eliminated (acting to increase $Z$), but also pores are accumulated as they are encountered
by the boundary (acting to decrease $Z$). Which of the two situations presented below then takes place is dependent upon the balance between pore elimination and pore accumulation.

7.4.1. Pore elimination > pore accumulation

Under conditions in which pore elimination exceeds pore accumulation, grain boundary migration is sufficient to overcome the dragging force exerted by the pores, resulting in grain growth throughout the majority of the microstructure (Fig. 7.5). From this point, grain growth becomes less impeded due to the reduced dragging force exerted by the pores. Eventually, sufficient porosity is eliminated so that the boundary migration is free of pore influence, this manifests as the slope change seen in Fig. 7.5. Once a grain has transitioned into "pore independent" growth, the grain boundary pores are too large, i.e., too widely spaced, or the pore volume fraction is too small to have any influence over the rate at which the boundary migrates.

The transition to pore independent growth is not directly observed from the Zener plots presented here. Although, the change to interface controlled growth at 600 °C, as demonstrated by the change in the growth exponent ($n$) from 0.25 to 0.5, suggests that pore independent growth is more prevalent than pore controlled growth at this temperature. Pores still remain influential, as demonstrated by the continued occurrence of samples with anomalous grain sizes, however, they are no longer controlling growth. There is also some evidence in the 511 °C tests (Area 7 of HL7 (Fig. 6.43) and Area 15 of HL5 (Fig. 6.48)) that the transition to pore independent growth may have occurred in the largest grains, as shown by the increased Zener parameter at the largest measured grain sizes.
Fig. 7.5. Schematic Zener plot of the proposed model of halite grain size and Z evolution in grains experiencing normal grain growth, i.e., pore elimination is greater than pore accumulation during grain boundary migration. Note that both halite grain size and Z are not to scale.

7.4.2. Pore accumulation > pore elimination

The schematic microstructural evolution of large grains with reduced Zener parameter values (e.g., HP14 (Fig. 6.31) and HL7 (Fig. 6.42)) can be seen in Fig. 7.6. It is considered that these grains are examples of a pulse of abnormal grain growth during the early stages of the growth period.

In the case where a grain undergoes rapid grain growth in comparison to the surrounding microstructure, the decreased Z (e.g., HP14 (Fig. 6.31)) arises from sweeping of pores that originally lay along the boundaries of the grains consumed by the growing grain. Since pore size remains fairly constant, the deviation of the curve to the left reflects the increase in pore volume fraction. Because the rate of pore accumulation outpaces that of pore elimination, a decrease in Z occurs. As grain size increases, the combination of reduced driving force, associated with grain size increase, and increased drag force from pore accumulation out pacing pore elimination, results in grain boundary migration
slowing to a much reduced rate in comparison to the remainder of the microstructure. As this happens, pore accumulation rates reduce allowing the relative significance of pore elimination to increase. The overall result is an increase in $Z$. As the surrounding grains grow, the microstructure resulting from the early growth pulse ceases to appear to be the product of abnormal grain growth, and the abnormally large grain becomes incorporated into the overall microstructure. This process results in any textural evidence of the initial abnormal growth spurt being either modified or lost completely, thus making these grains indistinguishable from those that have grown under normal grain growth conditions.

![Figure 7.6: Schematic Zener plot of the proposed model of halite grain size and Z evolution in grains experiencing early abnormal grain growth resulting in a reduced Zener parameter, i.e., pore accumulation is greater than pore elimination during grain boundary migration. Note that the upper section of the graph, i.e., the section in which the boundaries undergo a period of pore elimination, is highly speculative as no samples displayed this decrease in pore volume fraction after experiencing an initial increase at the largest grain sizes.](image)

It is important to bear in mind that, as shown by the Zener plots constructed for each of the samples examined here, different grains are at various points along these proposed microstructural evolution curves. In addition, it is also clear that both of these types of pattern of microstructural evolution are in operation within single samples, for example,
in HL7 where grains with large $Z$ values and reduced $Z$ values co-exist (Fig. 6.43). Also of significance is the fact that the grain size and $Z$ value at which the stages discussed above start and end vary, not only from sample to sample, but also from grain to grain. This latter case reflects the sensitivity to the location of the pores along the boundary, that is, whether they are clustered around triple junctions or spread along grain edges.

In the classical treatment of abnormal grain growth, it is considered that grains that tend towards abnormal growth possess an advantage over the surrounding grains that allows early growth to take place. In this study, the advantage is considered to be the presence of larger pores and/or small volume fraction of pores around the “abnormal” grain at the onset of growth, and hence a much reduced pore dragging force. This then raises the question of how these grains attained this advantage. A definitive reason is challenging to identify.

One potential reason could be the crystallographic orientation of these grains. Previous studies have demonstrated that grains, and even individual boundaries, can be favourably orientated crystallographically as to provide them with an advantage over the surrounding grains or boundaries, leading to abnormal growth (Srolovitz et al., 1985; Rollett et al., 1989; Frost et al., 1992; Holm et al., 2003). A large difference in crystallographic orientation between grains, or grain boundaries, effectively increases the misorientation angle between the abnormal grain and the remainder of the microstructure. This, in turn, results in these grains, or boundaries, having higher mobility relative to the remaining microstructure. This has the effect of encouraging abnormal growth (Rollett et al., 1989). It is possible that this is occurring in the halite samples examined in this study.

The contribution of this mechanism to abnormal growth cannot be quantified in the presented data. Efforts were made during the fabrication stage to not introduce a fabric into the sample during tamping of the powder. On account of minimal recrystallization taking place during the sample conditioning stage of the experiment, it is possible that any initial differences in crystallographic orientation may be preserved from the starting material. Any resulting difference in orientation may provide the advantage that the abnormal grains require in order to begin growth before the rest of the microstructure. Further microstructural analysis, through the use of EBSD mapping of samples, would reveal whether there is any difference in crystallographic orientation. This method could
also allow for the identification of anomalous grains that have experienced early abnormal growth, but have had their textures overprinted, and thus, have been included in the grain size measurements.

The most obvious cause of the variation in $Z$ is grain scale spatial variations in porosity prior to $t_0$, i.e., variations in pore size, volume fraction and distribution, originating from tiny variations during the tamping, pressurization or early sintering stages. The scatter of the grain size data in Fig. 7.3 is attributed to the influence that these small variations in porosity have on the growing halite grains.

Evidence for these variations can be seen in HP14 (Fig. 6.32) where pore size varies spatially between areas but within areas shows only minor variation. As a result, an early abnormal growth spurt appears to have taken place in Area 17 which displays the largest pore size and volume fraction. It is, therefore, considered that the largest grains in this area followed the evolution described in Fig. 7.6 where the accumulation of large numbers of large pores resulted in a decreasing $Z$ at the largest grain sizes. Area 24, on the other hand, which has lower pore size and volume fraction, displays a grain size vs. $Z$ curve more similar to that in Fig. 7.5, thus indicating that the pore elimination was able to keep pace with pore accumulation. In turn, this suggests that neither the number nor size of the pores was sufficient to initiate a reduction in $Z$.

Evidence for which grains are likely to experience, or have experienced, each of these two scenarios is shown by the Zener plots of individual grains. The occurrence of single grains with high $Z$ values and large grain sizes, such that they lie on or below the right hand blue boundary, e.g., HL29 (Fig. 6.26), indicates growth relatively unimpeded by pores, i.e., traditional abnormal growth, albeit without the typical abnormal grain growth textures. In the opposite case where the large $Z$ values occur at small grain sizes, such as in HL17 (Fig. 6.15) and HL21 (Fig. 6.9), the explanation is more complex. Based on the $Z$ values, these grains are considered to represent those most likely to experience a spurt in growth. Grains of this type are prevalent in HP37 (Fig. 6.53) (600 °C, <5 mins) as would be expected having just reached experimental temperature. Grains that have already undergone this initial spurt of growth are interpreted as those that lie above the left hand blue boundary on the single grain Zener plots, e.g., HP14 (Fig. 6.31). The lack of variation in pore size indicates that the only way such grains could attain the size and $Z$ that they
display is an increase in pore volume fraction associated with pore accumulation outpacing pore elimination during an early growth spurt.

Based on the proposed model, together with the Zener parameter data for individual grains, it is clear that by solely examining the halite grain size data, large grains that lie on the left hand side of the blue line on single grain Zener plots would be considered as simply the largest grains within the sample. Detailed porosity analysis reveals that this is not the case as the increased porosity volume fraction around these grains suggests that they experienced early abnormal growth where pore accumulation outpaced pore elimination. This resulted in the observed $Z$ reducing in the largest grains in some samples.

7.4.3. The effect of temperature

Based on the evidence presented by Herwegh and Berger (2004) (Fig. 2.14), increasing temperature should have the effect of shifting the transition point between pore controlled and pore independent growth to larger grain sizes, whilst $Z$ remains approximately constant.

From the data presented here, it is only possible to speculate on this effect due to the transition to pore independent growth not being definitively observed. The mobility of both pores and boundaries is enhanced with increasing temperature. Based on this, it is reasonable to presume that the transition point would increase in terms of grain size with increasing temperature. The relationship with regards to $Z$ is more complex. As pore elimination appears to be intimately linked to boundary migration, i.e., growth, it is possible that the value of $Z$ will show little variation with increasing temperature. However, more work is needed to investigate this further. To do this, the porosity analysis data set would have to be expanded to increase the number of samples from within two or three temperature sets.
7.5. Comparison with previous grain growth studies

Comparison with previous grain growth studies on geological materials highlights the unpredictable nature of grain growth in halite which reflects the sensitivity of halite to spatial variations in porosity.

In studies on the isostatic grain growth kinetics of calcite, both Covey-Crump (1997) and Olgaard and Evans (1988) found calcite grain growth to be influenced by porosity in a similar way to that of halite. In the case of Covey-Crump (1997), calcite grain growth data displays much less scatter, in terms of grain size, compared to the data presented here. However, the scatter that was present was attributed to the influence of a dragging force applied by the pores. Pores observed along grain boundaries displayed a distorted lenticular shape, suggesting pores were imposing a dragging force on the boundary (Olgaard and Evans, 1988). The lack of scatter results in the determination of $d_0$ and $t_0$ being more straightforward in calcite than in the present study. This suggests that halite grain growth is much more sensitive to the spatial distribution of porosity. Abnormal grain growth was also not observed in either of these calcite studies, however, Covey-Crump (1997) did observe that a small number of long duration tests displayed anomalously small grain sizes, similar to that of HP21, the cause of which was considered to be pinning of grain boundaries. This, together with a calculated $n$ value of 0.25, led the author to conclude that growth in dry calcite was controlled by the rate at which the pores can move with the boundary, i.e., the same conclusions presented here for halite. The lack of abnormal growth could suggest that either pore distribution was not sufficiently heterogeneous to allow the early growth of a small number of grains, or that calcite has a low tendency towards abnormal growth. Irrespective of the reason, this demonstrates that the behaviour of halite is somewhat unique in that it is highly sensitive to small spatial variations in pore size and distribution from grain to grain.

It has been shown, in both experimental (Azuma et al., 2012) and simulation (Roessiger et al., 2012) grain growth studies on ice, that porosity influences grain growth. Azuma et al. (2012) found that a reduction in activation enthalpy was associated with the presence of boundary porosity. In pore free ice, an activation enthalpy of 110-120 kJ/mol was determine while the presence of boundary porosity reduced the activation enthalpy to 40-70 kJ/mol. It is possible that the same behaviour is being observed in halite in that the presence of boundary porosity may be reducing the activation enthalpy. This provides a
potential explanation as to why the calculated activation enthalpy for halite grain growth is lower than would be expected based on the growth controlling mechanism indicated by $n = 0.25$. The observations made in these studies could also explain the observed increase in $n$ seen in halite between 511-600 °C. In this study, the transition is attributed to a change to interface controlled growth, i.e., boundary migration with little influence from pores. This can be equated to pore-free growth in ice which was observed to also be $n = 0.5$, the addition of porosity to the ice resulted in $n$ reducing to <0.5 (Azuma et al., 2012), as is the case with halite. Both Azuma et al., (2012) and Roessiger et al. (2012) found that, in a similar way to halite, pores exert a significant enough dragging force on the migrating boundary as to control the rate at which it moves. No abnormal grain growth was observed by Azuma et al. (2012), indicating that, unlike halite, ice appears to not have as much tendency towards abnormal growth.

Isostatic grain growth studies have been carried out on synthetic olivine samples (Karato, 1989; Ohuchi and Nakamura, 2007). Olivine is one of the few geological materials in which abnormal grain growth is observed in high temperature static grain growth experiments. Abnormal grain growth has been attributed to the presence of a significant amount of fluid-filled pores, found along the grain boundaries, restricting growth (Karato, 1989). A consequence of this is that grain boundary migration in areas free of porosity is more rapid and abnormal grain growth is the result, as is found to be the case in halite. However, olivine grain growth appears to be significantly less sensitive to porosity than halite. Karato (1989) states that pores only have a significant effect on grain growth at concentrations of more than approximately 3%. In mixtures of diopside and forsterite, Ohuchi and Nakamura (2007) observed that small amounts of porosity (<1%) had no effect on the resulting grain size nor did it influence the occurrence of abnormal grain growth. On the other hand, in this study, halite is sensitive to pore volume fractions of <1% (e.g., HL7 (Fig. 6.43)).

Both olivine (Karato, 1989) and ice (Azuma et al., 2012) display some degree of pore coalescence with increasing grain size. In the case of olivine, the pore size increased and the pore density along grain boundaries decreased. A similar situation can be observed in HL5 (Area 15 (Fig. 6.48)) where the a clear increase in pore size is accompanied by a decrease in pore volume fraction, producing a large increase in $Z$. 

266
Based on currently published grain growth studies, it is considered that the behaviour of halite is somewhat unique. As discussed above, porosity has been observed to influence grain growth in other geological materials but not to the extent seen here where the occurrence of abnormal grain growth is dependent upon spatial variations in pore size and volume fraction. Despite halite having been successfully used as an analogue for other geological materials, such as silicates in shear zones (e.g., Shimamoto and Logan, 2013), the behaviour of halite, as presented in this study, reduces its usefulness as an analogue for high temperature static grain growth in geological materials.

The results presented here further the understanding of the high temperature, high pressure static grain growth behaviour of geological materials. The results demonstrate that grain growth in geological materials can be highly sensitive to very small amounts of (<5%) porosity. In addition, variations in pore size and volume fraction on the grain scale can have a significant effect on grain size. Therefore, one must take into account the presence of porosity in geological materials exposed to high pressures and temperatures as any porosity may have influenced grain growth processes, and thus, the observed grain size.

The apparent dependence of the grain size of individual halite crystals on the presence of a pore second phase could have implications for strain localization in the lower crust/upper mantle. If a sufficient volume fraction of second phases is present in the rocks at this depth, grain growth could be restricted. This would result in smaller grain sizes in areas of high second phase concentration which, in turn, would allow deformation to be localized in these areas. However, on account of the experiments carried out in this study being isostatic, the influence that deformation may have on the ability of second phases to restrict grain growth is not considered here.
Part II:
The influence of a calcite second phase on the mechanical behaviour of two phase calcite + halite aggregates
8. Relevant background to the calcite + halite neutron diffraction tests

In Part I, the influence of a pore second phase on the high temperature isostatic grain growth of halite was examined. In this part, the influence of the spatial distribution of second phases on the low temperature mechanical behaviour of halite in two phase calcite + halite aggregates, in which calcite is the second phase, is examined. This is investigated through the use of neutron diffraction experiments.

The spatial variation between phases is significant in determining the strength of a geological material. This is especially the case when a strength contrast exists between the phases as the yield strength of the material, and any subsequent load transfer, will be dependent upon any spatial variation between phases. In order to measure the spatial variation, two topological parameters will be used; these are mean free path (mean distance between two particles of the same type) and contiguity (grain boundary area shared between particles of the same phase). It has been demonstrated, in material science, that these two parameters describe well the spatial relationship between phases (Carpinteri et al., 2009).

In traditional rock deformation tests only the bulk deformation that is introduced into the sample is known and any inferences about the response of each phase have to be made from subsequent microstructural analyses. Neutron diffraction experiments are implemented in this part of the study because they allow this limitation to be overcome. Through the constant measurement of neutrons diffracted off lattice planes in various orientations, the response of each phase to deformation to be determined throughout the experiment. This, in turn, allows the yield strength of the material to accurately be constrained and any load transfer between phases to be observed.

8.1. The strength of materials

The strength of a polyphase material in which the constituent phases are not chemically interacting is primarily controlled by the relative proportions of the constituent phases and by the grain size, mean free path and contiguity of each phase (Carpinteri et al., 2009). During intracrystalline plasticity at low homologous temperatures where diffusion
rates are relatively slow, the strength of a material increases when there is less opportunity for dislocations to move. Grain boundaries provide the ultimate barrier to dislocation movement; therefore, the strength of a material increases with smaller grain size. On a larger scale in a sample made of a weak phase and a strong phase, the distribution of the phases is significant. If grains of a weak phase are dispersed amongst grains of the strong phase, the sample will be stronger than if the weak phase has aggregated or localized into patches.

The most straightforward approach when examining the strength of polyphase materials is the rule of mixtures

$$\sigma_{agg,\alpha,\beta} = f_\alpha \sigma_\alpha + f_\beta \sigma_\beta \quad \text{Eq. 8.1}$$
$$\varepsilon_{agg,\alpha,\beta} = f_\alpha \varepsilon_\alpha + f_\beta \varepsilon_\beta \quad \text{Eq. 8.2}$$

where $\sigma_{agg,\alpha,\beta}$ and $\varepsilon_{agg,\alpha,\beta}$ are the aggregate (agg) and phase ($\alpha$ and $\beta$) specific average in situ stress and strain, and $f$ is the volume fraction (Fan et al., 1994). The rule provides a way to quantify the contribution that each phase makes to the bulk deformation of the sample. The rule of mixtures is rigorous in the sense that it expresses force balance and strain compatibility. However, it only accounts for the volume proportion of the different phases and does not take into account the spatial relationship between the two phases. The conventional way of taking into account this spatial relationship is to measure the mean free path (distance between two particles of the same phase) and contiguity (the extent to which a phase shares grain boundary area with other grains of that phase) of the phases.

8.1.1. Contiguity

The first work to focus on the role of contiguity in two phase materials was Gurland and co-workers (Gurland, 1958, 1963; Lee and Gurland, 1978; Pickens and Gurland, 1978) who defined it as the fraction of the total interface area of a phase that is in contact with grains of the same phase. It is worth noting that this is different from phase continuity, which describes the interconnectivity of a phase through the aggregate.
Contiguity is most commonly considered in terms of a system of one weak phase and one strong phase. Note that for the remainder of this chapter when $\alpha$ is used it is in reference to the weak phase and $\beta$ is in reference to the strong phase.

Contiguity ($C_\beta$) is defined using the equation

$$C_\beta = \frac{2S_{\beta\beta}}{2S_{\beta\beta} + S_{\alpha\beta}} \quad Eq. \ 8.3$$

where $S_{\beta\beta}$ is the boundary area shared by two grains of the $\beta$ phase and $S_{\alpha\beta}$ is the surface area shared between the $\alpha$ and $\beta$ phases (Underwood, 1970).

Contiguity is dependent on both the volume fraction and grain size of each phase as demonstrated by Fan and Miodownik (1993). For a two phase system of randomly distributed equiaxial $\alpha$ and $\beta$ grains

$$\frac{S_{\alpha\beta}}{S_\alpha} = \frac{S_\beta}{S_\alpha + S_\beta} \quad Eq. \ 8.4$$

where $S_\alpha$ and $S_\beta$ are the total grain boundary area of the two respective phases given by $S_\alpha = S_{\alpha\alpha} + S_{\alpha\beta}$ and $S_\beta = S_{\beta\beta} + S_{\alpha\beta}$. Combining equations Eq. 8.3 and Eq. 8.4, returns

$$C_\beta = \frac{S_\beta}{S_\alpha + S_\beta} \quad Eq. \ 8.5$$

In order to describe the effects of volume fraction and particle size, the Tomkeieff equation (Eq. 8.6) (Underwood, 1970, pp.35),

$$\frac{f_\beta}{S_\beta} = \frac{d_\beta}{4} \quad Eq. \ 8.6$$

where $f_{\alpha,\beta}$ and $d_{\alpha,\beta}$ are the volume fraction and particle size of $\alpha$ and $\beta$ respectively, can be applied to Eq. 8.5 giving

$$C_\beta = \frac{f_\beta d_\alpha}{f_\alpha d_\beta + f_\beta d_\alpha} \quad Eq. \ 8.7$$

Note that if the two phases are of equal grain size, Eq. 8.7 reduces to $C_\beta = f_\beta$. Eq. 8.7 can be used to determine contiguity from thin-sections using the measurement of grain size and volume fraction.
8.1.2. **Mean free path**

Mean free path ($\lambda$) is defined by Underwood (1970) as the mean distance between two particles of the same type and is given by

$$\lambda_\alpha = \frac{L_\beta f_\alpha}{f_\beta} \quad \text{Eq. 8.8}$$

where \(L_\beta\) is the mean intercept length between \(\beta\) particles. The mean intercept length, in this case, is defined as a line of known distance divided by the number of grains intercepted by that line, and is used as an effective measure of the grain size of the \(\beta\) phase. Although mean free path is determined from two-dimensional cuts through samples, Eq. 8.8 has been shown to provide true three-dimensional $\lambda_\alpha$ values (Underwood, 1970). Since the first derivation of this expression, however, it has been found to be too simplistic. Consequently, Gurland and co-workers (Lee and Gurland, 1978; Pickens and Gurland, 1978; Gurland, 1979) incorporated contiguity of the \(\beta\) phase into Eq. 8.8 in order to account for the impact of the \(\beta\) phase contiguity upon the \(\alpha\) phase mean free path. That is, the higher the contiguity of the \(\beta\) phase, the more localized the \(\alpha\) phase becomes; hence the mean free path decreases. The resulting expression is

$$\lambda_\alpha = \frac{L_\beta f_\alpha}{f_\beta(1-c_\beta)} \quad \text{Eq. 8.9}$$

which expresses the intimate link between mean free path and contiguity.

8.1.3. **Yield strength, load transfer and their relation to contiguity and mean free path**

The yield strength of a material is the stress at which a material begins to deform plastically. Load transfer describes the transfer of load from the weak phase to the strong phase in a two phase system during deformation, and can occur during both elastic and plastic deformation. When loading a sample containing an elastically stiff (strong) phase in contact with an elastically compliant (weak) phase, the compliant phase attempts to deform more. If slip is prevented at the interface between the two phases, then the compliant phase cannot deform any further. At this point, shear stresses are established at the interface between the two phases and load transfer from the weak to the strong phase occurs. This continues to happen after yielding has begun but it is also augmented
by the shear stresses set up as a result of the large strain gradient occurring within the thin layer of weak phase immediately adjacent to the interface.

Mean free path and contiguity both influence yield strength and the effectiveness of subsequent load transfer. Mean free path expresses the extent to which the weak phase is constrained in the way it can deform by the strong phase while the contiguity of the strong phase expresses the extent to which load can be transferred from the weak to the strong phase. Therefore, a high contiguity in the strong phase results in a lower mean free path value for the weak phase. This, in turn, results in a higher yield stress and less opportunity for load transfer due to the weak phase being constrained by the strong phase. Conversely, if particles of the strong phase are widely spaced, then they are effectively isolated within the weak phase, thus decreasing the contiguity of the strong phase and increasing the mean free path of the weak phase resulting in a less efficient load transfer and yield at lower stresses. In this situation, the weak phase can accommodate a larger proportion of the deformation; therefore, there is also less need for load transfer to occur.

There is a large body of work concerning the impact of contiguity and mean free path on the strength of materials. Clear evidence has been presented (e.g., Sigl and Fischmeister, 1988; Aldrich and Fan, 2001; Golovchan and Litoshenko, 2003; Luyckx and Love, 2006) to show that the contiguity of the weak phase decreases with increasing volume fraction of the strong phase and vice versa. In terms of yield strength, a decrease in the contiguity of the strong phase results in a decrease in strength because more grain boundary area is shared with the weak phase and hence there is greater possibility for the transfer of load from the weak phase to the strong phase. This is only valid up to a point, however, because the more connected the weak phase becomes, the easier it is for it to accommodate the deformation without constraints imposed by the strong phase. Mean free path studies (e.g. Sigl and Fischmeister, 1988; Makhele-Lekala et al., 2001; Luyckx and Love, 2003; Luyckx et al., 2007) produce similar results, where an increase in the mean free path of the weaker phase is accompanied by a decrease in strength of the material. Indeed, this has been observed in geological materials when the weaker phase has formed continuous layers within samples (Jordan, 1987; Barnhoorn et al., 2005).

While contiguity and mean free path are good quantifiable microstructural parameters, it has been found that in near pure materials, i.e., those with volume fractions near
1.00:0.00, contiguity becomes a less useful method of describing the microstructure due to the effect of phase clustering (Horvath et al., 1997). This issue was also highlighted by Luyckx and Love (2006) who found that contiguity values of 1 are not necessarily observed in systems where the volume fraction of the weak phase tends toward 0. This is attributed to coalescence and aggregation of the low volume fraction phase in the system.

Despite some of the earliest work focused on load transfer being carried out in the early 1940s (Gensamer et al., 1942), the factors that influence load transfer are still a topic of current research (e.g., Li and Langdon, 1998; Balch and Dunand, 2006; Fernández and González-Doncel, 2009; Young et al., 2009). Of particular significance to this study is the observation that the yield stress of a two phase aggregate is inversely proportional to the mean free path (Gensamer et al., 1942; Takahashi and Nagumo, 1970). That is to say, as the mean free path decreases, the yield strength increases (Fig. 8.1).

\[ \text{Fig. 8.1. Yield stress versus inverse square root mean free path of ferrite in pearlitic steel (ferrite and cementite). (Adapted from Takahashi and Nagumo, 1970).} \]
The significance of contiguity and volume fraction in strain localization within polyphase systems has been emphasised in extensive studies on geological materials (e.g., Price, 1982; Jordan, 1987; Dell'Angelo and Tullis, 1996; Barnhoorn et al., 2005; Bystricky et al., 2006). Few of these studies, however, have gone as far as to quantify mean free path and contiguity and correlate these to the strength of geological materials. Bloomfield and Covey-Crump (1993) examined the influence of contiguous calcite volume fraction, $V_{cc}$ (where $V_{cc} = C_{cc} f_{cc}$ ($C_{cc}$ is calcite contiguity and $f_{cc}$ is calcite volume fraction)), on strain partitioning in calcite + halite aggregates similar to those used in this study. Strain partitioning from the weak halite phase to the strong calcite phase was observed at $0 < C_{cc} < 1$, the extent of which is dependent upon the contiguity of the calcite phase. At $C_{cc}$ values of 0 the calcite is dispersed to the degree that the mechanical properties of the sample match those of pure halite. At $C_{cc}$ values of approximately 1 the calcite grains are in such close proximity that the sample behaves as if it were pure calcite. This same partitioning of deformation into stronger calcite was observed by Covey-Crump et al. (2013) in neutron diffraction experiments on similar synthetic calcite + halite aggregates. These two studies in particular heavily influence the approach adopted in this investigation.

8.1.4. The Hall-Petch effect

The influence of grain size on the strength of materials at relatively low homologous temperatures is empirically well described by the Hall-Petch equation (Hall, 1951; Petch, 1953),

$$\sigma_y = \sigma_0 + kd^{-1/2} \quad Eq. 8.10$$

where $\sigma_y$ is the yield strength of the material, $\sigma_0$ is frictional stress or resistance to dislocation movement, $k$ is a constant and $d$ is the mean grain size. The Hall-Petch relationship (Eq. 8.10) implies that the strength of a material will increase with decreasing grain size and vice versa.

The mechanisms which lead to the Hall-Petch relationship are poorly understood. Four different explanations have been proposed to explain the relationship (Zhu et al., 2008), involving: 1) dislocation pile-up at grain boundaries, 2) dislocation production at grain
boundaries, 3) slip distances associated with grain size and 4) geometrically necessary dislocations.

Of these four potential explanations, dislocation pile-up, first proposed by Hall (1951), is the most commonly cited cause of the Hall-Petch relationship. This proposed cause is centred upon the idea of grain boundaries acting as barriers to dislocation migration. Pile-up involves the formation of dislocations within the grains followed by migration to the boundaries where their concentration increases. As dislocations build up, a cumulative stress also develops. With the continued addition of dislocations, yield occurs when the stress at the tip of the pile-up equals the shear stress (Zhu et al., 2008). This mechanism is dependent upon the number of dislocations within a grain, and so the larger the grain, the quicker the critical value will be reached. This type of dislocation stacking results in weaker grains.

8.2. Calcite

8.2.1. Calcite crystal structure

Calcite belongs to the trigonal crystal system with a space group of \( R\overline{3}m \) and a hexagonal prism (hexagonal scalenohedral) unit cell \( (\overline{3}m) \). Typical unit cell parameters for calcite are: \( a = 4.9896 \text{ Å} \) and \( c = 17.061 \text{ Å} \), with an axial ratio \( a:c = 1:3.419 \) and unit cell volume is \( 367.85 \text{ Å}^3 \) (Chang et al., 1998). \( \text{Ca}^{2+} \) cations are octahedrally coordinated to \( \text{O}^{2-} \) ions which themselves are part of the planar \( \text{CO}_3^{2-} \) carbonate molecules (Fig. 8.2). There are 6 formula units within the \( \overline{3}m \) unit cell.

Throughout the remainder of this study, the convention of replacing \( i \) in the \( hki \) Miller-Bravais indices (where \( i = -(h + k) \)) with a dot when defining calcite lattice planes, will be adhered to. This avoids any potential confusion that could arise when \( l \) is larger than 9.
8.2.2. Relevant mechanical characteristics of calcite

The elastic stiffness tensors for calcite can be seen in Tab. 8.1. In terms of a calcite rhomb, principle slip occurs on $r = \{10.4\}(\overline{2}0.1)$ and $f = \{\overline{1}0.2\}(2\overline{2}.1)$. In this study, the calcite either remains fully elastic or undergoes twinning, which takes place on the $e = \{\overline{1}0.8\}(40.1)$ plane (Turner et al., 1954; Griggs et al., 1960).
Tab. 8.1. Table of the independent components of the calcite and halite elastic stiffness tensors \((c)\) and isotropically averaged effective elastic moduli, calculated from these tensors, used for the calculations in this study. \(K\) is the bulk modulus, \(G\) is the shear modulus, \(E\) is the Young’s modulus and \(\nu\) is the Poisson’s ratio (all given in GPa). (From Covey-Crump et al., 2013).

<table>
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<th>Calcite</th>
<th>Halite</th>
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<td>(c_{11})</td>
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<td>0.2564</td>
</tr>
</tbody>
</table>

8.3. Halite

8.3.1. Crystal structure

Halite belongs to the isometric cubic crystal system with a space group \(Fm\bar{3}m\) (class \(m\bar{3}m\)). The \(Na^+\) and \(Cl^-\) ions within halite are arranged with a face centred unit cell (Fig. 8.3). Each ion within the unit cell has a co-ordination number of 6. The halite cell parameters are: \(a = 5.6404\) Å and the unit cell volume is 179.44 Å³ (Chang et al., 1998).
8.3.2. Relevant mechanical characteristics of halite

The elastic stiffness tensors for halite can be seen in Tab. 8.1. Various slip systems are activated as halite is being deformed. Despite halite being cubic, at room temperatures it behaves anisotropically (Liu et al., 2005) and deformation preferentially takes place along the \{110\}(1\bar{1}0) slip system (Frost and Ashby, 1982; Wenk, 1999). This particular slip system only contains two stress variables, therefore, slip along additional systems, the majority of which are harder to activate, is required to produce homogeneous shape change. Frost and Ashby (1982) cite slip along the \{001\}(1\bar{1}0) and \{111\}(1\bar{1}0) planes as those that require activation. At higher temperatures, \{111\}(1\bar{1}0) remains active whilst the \{100\}(011) systems become active (Wenk and Van Houtte, 2004). Critically resolved shear stresses of 5 MPa have been determined for the \{110\}(1\bar{1}0) system and 33 MPa for the \{100\}(011) and \{111\}(1\bar{1}0) systems (Wenk et al., 1989).
9. Experimental strategy for the calcite + halite neutron diffraction tests

In order to complete successfully such a self-contained neutron diffraction study, a group approach was applied such that each of the three members of the multi-disciplinary team (J. Tant, S.J. Covey-Crump and P.F. Schofield) performed specific tasks associated with data analysis and extraction. In the following method discussion, focus will primarily be on the aspects carried out by Tant. The tasks carried out by Covey-Crump and Schofield will be described in a more summary fashion.

Samples were fabricated by Tant. All three investigators carried out the deformation experiments at ISIS. Thin-sections were made by Tant. Of the data acquisition, analysis of the single peaks and microstructures was carried out by Tant. Whole diffraction pattern fitting was done by Schofield. Recovery of the strains and stresses from the diffraction peaks was carried out by Covey-Crump and the synthesis of the mechanical and microstructural information was completed by Tant and Covey-Crump.

9.1. Principles of neutron diffraction experiments

9.1.1. The ISIS facility at the Rutherford Appleton Laboratory

The experiments were performed at the ISIS neutron spallation facility, which is part of the Rutherford Appleton Laboratory located near Chilton, United Kingdom (Fig. 9.1) (Wilson, 1995). ISIS produces both pulsed neutrons and muons that enable detailed investigations of materials at the atomic scale. The facility contains two target stations and 41 instruments which are located at varying distances from the targets (Fig. 9.1) depending upon the wavelength characteristics of the neutron beam required for the particular type of analysis. Methods as varied as muon and neutron spectroscopy, reflectometry, small angle scattering, neutron tomography, magnetic scattering, and neutron diffraction are carried out at ISIS. The ENGIN-X beam line (Daymond and Edwards, 2004) was used to carry out the experiments reported here.
9.1.2. The production of neutrons at ISIS

In order to produce the neutrons required for the diffraction analysis, H⁻ ions are accelerated in a particle accelerator and converted to protons. These protons are transferred to a synchrotron ring and are further accelerated to 800 MeV. 50 times per second a pulse of protons are released and fired at a tantalum (or tungsten) target.
located in each of the two target stations. Four in every five pulses of protons are fired at Target Station 1, and one in five pulses is fired at Target Station 2. For each pulse, collisions between the protons and the tantalum nuclei results in cascade reactions which, in turn, produce pulses of polychromatic neutrons, that is, neutrons with a range of energies (wavelengths). In order to reduce the energy of these neutrons to a useable level, they pass through a hydrogenated liquid, known as a moderator. The neutrons are then guided down beam lines toward the instruments (Fig. 9.1). The energy, or wavelength, characteristics of the polychromatic beam that enters the neutron instrument may also be refined by chopping the highest and/or lowest energy neutrons of each pulse and by varying the distance from the target.

9.1.3. The ENGIN-X beamline

ENGIN-X is a fixed geometry, non-destructive time-of-flight neutron diffractometer that allows precise in situ strain measurements of polycrystalline materials (Johnson and Daymond, 2002; Daymond and Edwards, 2004). The beam-line became available to the user community in 2003 (Daymond and Edwards, 2004). The geometry of the beam-line is designed such that a load frame can be mounted horizontally at 45° to the incoming neutron beam, with two banks of detectors positioned at ±90° to the beam (Fig. 9.2). The detector bank on one side collects neutrons from lattice planes perpendicular, and scattering vectors parallel, to the sample loading direction (axial), and the detector bank on the other side collects neutrons from lattice planes parallel, and scattering vectors perpendicular, to the sample loading direction (radial) (Fig. 9.3).
Fig. 9.2. Photograph of the ENGIN-X apparatus displaying the experimental set up. Note the 45° orientation of the Instron load frame to the beam aperture and the 90° angle between the beam aperture and the two detector banks.
Fig. 9.3. Top: Schematic diagram of the experimental set up. Bottom: More detailed diagram of the geometry of the sample demonstrating how the neutrons are diffracted to either the axial or radial detectors. Only grains containing lattice planes with scattering vectors parallel to the radial direction (A and B) will diffract neutrons towards the radial detector bank while those grains containing lattice planes with scattering vectors parallel to the axial direction (C and D) will diffract neutrons towards the axial detector bank. Note that if the orientation of the grains A and B, and likewise for grains C and D, are not the same, then the neutrons measured by the detectors will be from different lattice planes. (Adapted from Schofield et al., 2003).

ENGIN-X collects neutron time-of-flight diffraction data. To analyse the data, the \(d\)-spacing of each peak is required, and thus, conversion of the time-of-flight for each peak is necessary. The wavelength (\(\lambda\)) of the detected neutrons is given by de Broglie’s equation

\[
\lambda = \frac{h}{m v}
\]

Eq. 9.1
where $h$ is Planck’s constant, $m$ is the neutron mass, $t$ is the time-of-flight and $L$ is the length of the neutron flight paths (Santisteban et al., 2006). $\lambda$ is related to $d$-spacings through Bragg’s law

$$\lambda_{hk,l} = 2d_{hk,l} \sin \theta$$ \hspace{1cm} Eq. 9.2

where $d_{hk,l}$ is $d$-spacing of the $hk,l$ lattice plane and $\theta$ is the angle of incidence of a diffracted neutron. Combining Eq. 9.1 with Eq. 9.2 gives

$$d_{hk,l} = \frac{h}{2 \sin \theta m(L)} t_{hk,l}$$ \hspace{1cm} Eq. 9.3

Consequently, the measured diffraction data comes from a precisely defined volume within the centre of the sample (4 x 4 x 7 mm in these experiments). Within this volume, all the lattice planes that satisfy Bragg’s law will diffract neutrons towards the detectors. The geometry of the experiment is such that only neutrons diffracted from lattice planes oriented parallel or perpendicular to the loading direction will be detected (Fig. 9.3) (Schofield et al., 2003). Each individual grain does not produce an entire diffraction pattern (or spectrum) but instead will contribute either a single peak, or set of peaks, to the final diffraction pattern, depending on which lattice planes are suitably oriented. Each subset of grains that are similarly oriented will contribute similarly to the diffraction patterns. Each group of similarly oriented grains will contribute differently to the diffraction patterns than a differently oriented group of grains. When the whole volume of sample illuminated by the polychromatic neutron beam is considered, a complete powder diffraction pattern is produced (Schofield et al., 2003).

Although the diffraction data presented here are collected from a polychromatic neutron beam and measured as time-of-flight, they will be plotted as a function of $d$-spacing and referred to as diffraction patterns, a term more familiar to the general geological community.

9.1.3.1. Experimental set up on ENGIN-X

The cylindrical samples used in this study were approximately 15 mm long and 9.5 mm in diameter, and were positioned so that data is collected from the centre of the sample (Fig. 9.4). This is done in order to avoid sampling grains that are influenced by specimen
end effects (e.g., friction at the specimen/apparatus interfaces). Prior to mounting in the Instron load frame, the sample mass and dimensions were measured. This allowed the initial porosity of the sample to be calculated (see §9.3). Samples were mounted in the Instron load frame between two pistons and were deformed in uniaxial compression. In order to measure the change in length of the sample during the experiment, and hence, the axial strain, an extensometer (MTS model 632.13F-21, gauge length 10 mm) was fitted to the specimen (Fig. 9.4). After the experiment, the dimensions of the sample were also re-measured as a cross-check on the permanent axial strain experienced, and to evaluate any potential changes in porosity.

![Sample setup](image)

*Fig. 9.4. Photograph of the sample set up within the load frame on ENGIN-X.*

Samples were taken to axial loads of 65 MPa (4.69 kN) in 4 MPa steps. The samples were taken to the desired load and held at that load while neutron diffraction data were collected. Once the signal-to-noise statistics on the diffraction patterns were sufficient for the intended analyses, the load was increased and the process repeated. A total beam current of 40 µA (which equated to approximately 1 hr under the ISIS operating
conditions of the experiments) was used for each load except for ENGX5 where the count time was 50 µA per load. In test ENGX26, data were also collected at incremental loads during unloading from 65 MPa down to 25 MPa, and in test ENGX30, data were collected during two loading-unloading cycles. In order to complete the second loading-unloading cycle of ENGX30 within the allocated beamtime, neutron data collection was reduced to 15 µA (approximately 25 min) per load.

9.1.4. Sample fabrication

9.1.4.1. Volume fraction determination

The samples for the neutron diffraction experiments were fabricated from powders of calcite and halite, mixed in the desired volume proportions and isostatically hot pressed.

The halite used was the same as that used in the monomineralic halite grain growth tests (see §3.1). Reagent grade halite powder (Fisher Scientific) was crushed and sieved to collect the 38-125 µm sieve fraction used here.

Three types of calcite were used: chelometric grade calcite, Carrara marble and Solnhofen limestone. The grain sizes (mean linear intercept sizes) of these three materials are 6, 150, and 4 µm respectively. The chelometric grade calcite was purchased in powder form from the SIGMA chemical company. It is extremely pure (+99.95 %) with trace amounts of Sr, Na, K, Mg, Fe, Ba, chloride, fluoride, sulphate and heavy metal impurities, all of which have concentrations of \( \leq 100 \text{ ppm} \) (Covey-Crump, 1997). Carrara marble is an extremely pure form of natural calcite (98% CaCO\(_3\)) with occasional second phases of quartz, dolomite, epidote, white mica and pyrite (see Pieri et al., 2001 for a complete description of the impurity content). It displays a typical static recrystallization texture with a high prevalence of 120° triple junctions and little in the way of lattice or shape preferred orientations. Solnhofen limestone is also very pure (97% CaCO\(_3\)) with occasional quartz grains and organic and clay mineral impurities found along grain boundaries (Llana-Fúnez and Rutter, 2005). The microstructures display a uniform texture and grain size distribution. A weak c-axis crystallographic preferred orientation parallel to the bedding plane is present, however, this is completely modified upon the introduction of deformation to the rock (Llana-Fúnez and Rutter, 2005).
The Carrara marble and Solnhofen limestone were crushed and sieved to produce a range of clast sizes (Tab. 9.1). Crushing was carried out using two methods. For the small clast sizes (<38 µm and 50 µm), pieces of rock about 1 cm$^3$ in size were ground down to a powder in a tema mill. To obtain the larger clast sizes, pieces of rock about 1 cm$^3$ in size were smashed with a hammer and then ground by hand in a pestle and mortar in order to obtain particles of approximately the correct size. The crushed calcite was introduced into the sieves listed in Tab. 9.1 and shaken by hand for at least two hours. Periodically during the sieving process the rock in the sieve above the required fraction was removed, re-ground and re-introduced into the sieves. This was repeated until no rock remained in the upper sieve. A summary of the sieve fractions used is given in Tab. 9.1. The grain sizes of both Carrara marble and Solnhofen limestone mean that clasts from the larger sieve fractions were polycrystalline.

<table>
<thead>
<tr>
<th>Grain size fraction (µm)</th>
<th>Sieve fraction (µm)</th>
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</thead>
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<tr>
<td>&lt;38</td>
<td>&lt;38</td>
</tr>
<tr>
<td>50</td>
<td>38-64</td>
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<td>200</td>
<td>125-250</td>
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<tr>
<td>500</td>
<td>500-600</td>
</tr>
</tbody>
</table>

9.1.4.2. Pressing

For the neutron diffraction experiments, samples with a calcite + halite volume fraction of 0.60 calcite: 0.40 halite was chosen based upon the findings of Covey-Crump et al. (2013). In that study, the effect of volume fraction on the yielding behaviour of calcite + halite samples was investigated at room temperature. It was found that the best load transfer data were obtained at a composition of about 60% calcite. Since characterizing the influence of phase spatial distribution on load transfer was a key target of the present experiments, all but one of the samples were made to this composition. In order to vary the spatial distribution (spacing) of the phases, calcite clast (grain) size was varied – at
fixed composition, the larger the calcite clast size, the more widely separated the clasts are.

The crushed calcite was dried in an oven at 60 °C for at least 48 hrs while the halite was stored in sealed glass jars housed in a desiccation box containing silica gel which was changed on a weekly basis. Each mineral was weighed out in 10 g batches. The mass required to obtain the desired volume proportions of each mineral was calculated using density values of 2.7106 g cm\(^{-3}\) for calcite and 2.166 g cm\(^{-3}\) for halite resulting in 6.52 g of calcite and 3.48 g of halite being used for a 0.60:0.40 mixture.

In order to ensure that the powders were properly mixed and any clumps of halite were broken up, the mixing was done by hand using a glass plate and spatula. The powders were mixed continuously for at least 20 minutes. During this period, any clumps of powder were broken up using a razor blade thus ensuring that the powders were as evenly distributed as possible.

The copper jackets used in sample fabrication (see §3.3.1) were not annealed as they were for the halite grain growth experiments. This prevented the jacket from deforming whilst the sample is being pressed. The jacket was placed in weak hydrochloric acid to clean off any material that could potentially contaminate the sample. The exterior of the copper jacket was coated with PTFE (polytetrafluoroethylene) spray before being placed into a split-die. The spray acts as a lubricant to prevent the jacket deforming during pressing. The same procedure used for adding the powder to the jacket in the monomineralic grain growth halite tests was used here (§3.3.1). Nimonic spacers were placed at each end of the powder.

The samples were then cold pressed in a hand press (Fig. 9.5). A 30 mm long hardened steel piece was inserted into the upper open end of the jacket in order to transfer the applied axial load to the sample. The axial load was applied in four stages via an Enerpac hand pump. Initially, the sample was loaded to 10 kN (140 MPa) and left for approximately 5 minutes. The axial load was then increased to 20 kN (280 MPa), 45 kN (631 MPa) and then finally 65 kN (912 MPa). At each step, the sample was held for at least 10 minutes so as to allow the sample time to adjust to the applied load.
The final stage in sample preparation was hot pressing at 600 °C and 200 MPa confining pressure. This stage was approached in the same way as the heating phase of the pure halite tests (§3.3.2). The sample was initially pressurised in stages and then heated at 85% furnace power until the sample reached 500 °C at which point the furnaces are turned to calibrated power. The temperature was held at 600 °C for 3 hours at which point the furnaces were turned off and the samples allowed to cool to room temperature. The cooling took approximately 2½ hours.
9.2. Diffraction pattern analysis

9.2.1. The General Structure Analysis System (GSAS)

Diffraction data were fitted using the General Structure Analysis System (GSAS) and the RAWPLOT diffraction pattern plotting routine therein (Larson and Von Dreele, 2004). Whole pattern fitting was carried out by Schofield while single peak analysis was carried out by Tant. The two different analysis techniques provide slightly differing information relating to the within-phase deformation. Whole pattern fitting is used to monitor the variation of the lattice parameters (or the unit cell) as a function of load, whereas single peak fitting enables measurement of the changes to the spacing of specific lattice planes. The results of both refinement techniques are presented here.

GSAS is freely available and the most commonly utilised software package for the refinement of diffraction data. In the context of this study, it allows data such as $d$-spacing, peak intensity, peak width, lattice parameters and volume fractions of the constituent phases to be extracted from the diffraction data. Whole pattern fits were performed using the Rietveld refinement method (Rietveld, 1969; Young, 1993). In whole pattern fitting, all the diffraction peaks are modelled simultaneously. A theoretical diffraction pattern is calculated based upon a specific crystal structure model and the difference between the theoretical and actual diffraction patterns is calculated. In an attempt to minimise this difference, the crystal structure model is modified, the theoretical diffraction pattern recalculated and subsequently compared to the actual pattern. This process continues until the difference between the calculated and the actual diffraction patterns is minimised. Of particular importance to this study is that, within this approach, the geometry of the unit cell is held fixed but the dimensions of that cell are allowed to vary, e.g., a hexagonal prism stays a hexagonal prism but the dimensions of its edges may change. In reality, however, during uniaxial deformation the shape of the unit cell may become distorted due to the anisotropic elastic properties of calcite and halite. Whole pattern fitting effectively averages out these distortions, providing the average calcite and the average halite behaviour but it does not provide a rigorous description of the unit cell distortion. Single peak fitting has no such assumptions as each individual diffraction peak is analysed independently and is unconstrained by the behaviour of other peaks within the diffraction pattern. Thus, analysing single peaks provides a direct measure of the changes to the $d$-spacing of
specific lattice planes, irrespective of the overall symmetry of the unit cell. Therefore, it provides a more precise description of lattice strain than whole pattern fitting, but only for those grains oriented such that the Bragg condition is satisfied for the lattice plane of interest.

9.2.2. Whole pattern fitting

Whole pattern fitting was carried out by Schofield in a two-stage process. First, lattice parameters were obtained for each phase in both the axial and radial directions at the lowest applied load. Initial crystallographic data used to start the refinement process were obtained from Abrahams and Bernstein (1965) for halite and from Maslen et al. (1993) for calcite. For the Rietveld refinement of the lowest load data, parameters were successively incorporated into the refinements. These parameters included (in order of inclusion) 1 scale factor, 4 background parameters, 1 phase fraction parameter, 1 absorption coefficient, 1 halite and 2 calcite lattice parameters and 1 Gaussian peak broadening parameter for each phase (Covey-Crump et al., 2013). Finally, and for the refinement of the lowest load data only, the fractional coordinates and isotropic displacement factors were refined. The values for the above parameters from the completed refinement were then used as a seed-file for the refinement of diffraction patterns from each subsequent load for that sample (Covey-Crump et al., 2013). Using this seed-file as a basis, the diffraction patterns from each load were refined in turn, with only the scale factor, background parameters, phase fraction, absorption coefficient, halite and calcite lattice parameters and peak broadening parameters for each phase (12 parameters in total), refined. An example of a whole pattern fit can be seen in Fig. 9.6.
Fig. 9.6. Example of a typical fit of the whole pattern diffraction data obtained from ENGIN-X. The axial diffraction pattern of the lowest load (2 MPa) in sample ENGX28 (calcite 0.61: halite 0.39, <38 µm Carrara marble) is shown. The blue points are the diffraction data, the black line is the fit to the diffraction data, the red line is the residual to the fit and the ticks represent the position of the diffraction peaks (light blue is halite and green is calcite). The peaks that correspond to these ticks are listed in Tab. 9.2.
Tab. 9.2. Table displaying all the peaks that could be identified within the whole pattern diffraction fit seen in Fig. 9.6. Note halite is given in terms of hkl and calcite is given in terms of hk.l.

<table>
<thead>
<tr>
<th>d-spacing (Å)</th>
<th>Phase</th>
<th>hkl</th>
<th>d-spacing (Å)</th>
<th>Phase</th>
<th>hkl</th>
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The quality of the completed refinement for each diffraction pattern is first assessed visually by considering the fit between the calculated and actual diffraction patterns and also considering the final refinement parameters. Numerical / statistical measures of the whole pattern goodness-of-fit are also calculated for each refinement (Young, 1993; Schofield et al., 2003). Ideally, for a set of refinements on the same sample within a single loading experiment, these goodness-of-fit parameters should remain fairly comparable. However, when plotted as a function of load, as in Fig. 9.7 for chi-squared ($$\chi^2$$), these parameters are seen to increase systematically with increasing load. The
implication is that the refinements of the data from higher loads are statistically not as good as those of the data from lower loads. As described above, the whole pattern fits are constrained by the geometry of the unit cells of the calcite and halite. The decrease in the goodness-of-fit (increase in $\chi^2$) relates to peak shifts that are not consistent with this crystallographic constraint. While the increasing mismatch between the calculated and actual diffraction patterns is subtle, it is a clear indicator that at the highest loads the unit cell of at least one of the phases is deforming. The load at which $\chi^2$ begins to increase systematically could thus be an indicator of the onset of plastic yielding. For these calcite + halite samples, the rate of increase in $\chi^2$ with increasing load reflects the enhanced distortion of the halite unit cell as a result of plastic yielding associated with crystallographically controlled dislocation motion. The observation that the unit cells of one or both of the phases is being distorted highlights the need for combining single peak analysis with whole pattern refinements.

![Graph](image)

*Fig. 9.7. Values of Chi-squared ($\chi^2$) used as a measure of goodness of fit for ENGX26 (calcite 0.62: halite 0.38, 100 µm Carrara marble) axial data.*
9.2.3. *Single peak fitting*

Note that throughout the remainder of this study, when referring to single peaks, the prefix HL and CC will be used when referring to halite and calcite single peaks respectively.

For single peak analysis, the diffraction peaks were modelled using the RAWPLOT subroutine within GSAS. The whole pattern was broken down into time-of-flight sections: 75-40 msec, 40-28 msec, 28-22 msec and 22-18 msec and peaks fitted without any crystallographic constraint.

Initially, the intensity of the desired peaks, within the time-of-flight ranges stated above, were refined using a predefined shape, or profile, dependent upon the specific characteristics of the ENGIN-X beamline. When the difference between the calculated and the actual profiles was minimised, the \(d\)-spacing and the sample dependent Gaussian peak width values were also refined. As with the whole pattern fitting, the final refined values for the diffraction peaks from the lowest load data are used as initial seed parameters for fitting the peaks at the remaining loads.

To monitor the quality and reliability of the single peak fits, they were visually assessed at each load and the numerical goodness-of-fit parameters were checked to be consistent for that peak across the entire range of axial loads. An example of a typical fit can be seen in Fig. 9.8.
Fig. 9.8. Example single peak fit for the HL (220) peak at the lowest load (2 MPa) in ENGX28 (calcite 0.61; halite 0.39, <38 µm Carrara marble). Blue crosses are the diffraction data, the black line is the fit of the diffraction data, tick is the calculated position of the peak in d-spacing and the red line is the residual. Note that the tick does not occur at the central position of the peak. This is because the peak shapes for neutron diffraction are not symmetrical.

A significant challenge encountered during the single peak fitting process was the overlap of peaks, either one calcite peak with another, or a calcite peak with a halite peak. This issue is illustrated by the CC (21.1) (Fig. 9.9) and CC (31.4) (Fig. 9.10) peaks. In monomineralic calcite diffraction tests, these two peaks display good intensities and have also been shown to produce particularly good data (Covey-Crump and Schofield, 2009). However, the HL (222) and HL (422) peaks have very similar d-spacings. As a result, the two peaks effectively merge and make it very difficult to refine consistent values for the peak shape, intensity and d-spacing across the entire range of experimental loads. Consequently, these calcite and halite peaks are rendered un-useable. Care was taken during peak selection and fitting to ensure that the peak being analysed was well defined and it’s shape not influenced by adjacent peaks. The peaks selected for fitting are displayed in Tab. 9.3.
Fig. 9.9. Example of peak overlap between the CC (21.1) and HL (222) peaks at the lowest load (2 MPa) in ENGX28 (calcite 0.61: halite 0.39, <38 µm Carrara marble). Blue crosses are the diffraction data, the black line is the fit of the diffraction data, tick is the calculated position of the peak in d-spacing (blue for halite, green for calcite) and the red line is the residual.

Fig. 9.10. Example of peak overlap between the CC (31.4) and HL (422) peaks at the lowest load (2 MPa) in ENGX28 (calcite 0.61: halite 0.39, <38 µm Carrara marble). Blue crosses are the diffraction data, the black line is the fit of the diffraction data, ticks are the calculated position of the peaks in d-spacing (blue for halite, green for calcite) and the red line is the residual.
The peaks selected for single peak analysis (Tab. 9.3) were chosen on account of their reasonable intensity and non-overlapping nature, so that the peak is well-defined. The amount of scatter associated with the fit parameters was variable and specific to each peak. Peaks that provide minimal scatter, such as CC (10.4) (Fig. 9.11a), show well constrained trends with regards to d-spacing and increasing load, whereas, increased scatter in the parameters for other peaks, such as CC (11.6) (Fig. 9.11b), diminish the clarity of any potential trends as a function of load.

Tab. 9.3. Table displaying the calcite and halite peaks that were selected for single peak analysis. Note that in the single peak fits and plots used throughout the remainder of this study the nomenclature for {10.8} becomes (01.8), {10.2} becomes (01.2) and {21.5} becomes {12.5}.

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Fig. 9.11. Plots of aggregate stress versus d-spacing for single peaks in ENGX28 (calcite 0.61: halite 0.39, <38 µm Carrara marble). a) CC (10.4) and b) CC (11.6). Note that a) CC (10.4), is an extreme example where zero load lattice parameters, as indicated by the axial and radial detectors, differ. This primarily reflects residual stresses remaining after sample fabrication.

Equal angle stereograms showing the positions of the analysed peaks in relation to the variations in directional Young’s modulus of calcite and halite have been plotted by
Covey-Crump (Fig. 9.12). The selection of single peaks analysed was influenced by a desire to cover grains with a range of stiffnesses, e.g., relatively compliant calcite grains such as those with CC (10.4) parallel to the direction of loading, and relatively stiff calcite grains such as those with CC (10.$\bar{2}$) parallel to the direction of loading.
Sectors of equal angle stereograms (other sectors obtained from these by symmetry) showing the orientation of the single peaks analysed in this study (i.e., the orientation of the pole to the indicated lattice plane) for calcite (top left) and halite (bottom left). The variation in directional Young’s modulus with orientation is shown on an equal angle stereogram for calcite (top right) and against an orientation parameter $\Gamma_{hkl} = (h^2 + k^2 + l^2)^{2}/(h^2 + k^2 + l^2)$ for halite (bottom right). For calcite, the directional Young’s modulus is obtained from the single crystal elastic stiffness tensor and so is equivalent to that obtained by a polycrystalline sample deforming under conditions of homogeneous stress. The real variation of directional Young’s modulus in an isotropic polycrystal of calcite has the same shape as this variation, but the variation is of smaller magnitude. For halite, the directional Young’s modulus is the self-consistent value for an isotropic polycrystal of halite as given by the equations of de Wit (1997). For further details, see §9.4.3 and note that the difference between the values determined by de Wit are slightly different (<0.1 GPa) than those actually used in this study, which used Kröner’s self-consistent formulation. Plots constructed by Covey-Crump.
9.3. Porosity and volume fraction determination

Porosity ($\Phi$) was determined from

$$\Phi = 1 - \left( \frac{\rho_{obs}}{\rho_{th}} \right) \quad \text{Eq. 9.4}$$

where the observed and theoretical densities ($\rho_{obs} / \rho_{th}$) are given by

$$\rho_{obs} = \frac{m}{\pi r_0^2 L_0} \quad ; \quad \rho_{th} = f_{cc} \rho_{cc} + f_{hl} \rho_{hl} \quad \text{Eq. 9.5}$$

in which $m$ is the sample mass, $r_0$ and $L_0$ are the sample radius and length before deformation, $f_{cc}$ and $f_{hl}$ are the volume fractions of calcite and halite respectively, and $\rho_{cc} = 2.7106 \ \text{gcm}^{-3}$ and $\rho_{hl} = 2.166 \ \text{gcm}^{-3}$ are the densities of calcite and halite respectively.

The volume fractions of the phases was set by the volume proportions in which the calcite and halite powders were mixed (§9.1.4.1). However, the actual volume fractions stated throughout the remainder of this text are the volume fractions obtained from the whole pattern fitting since these represent the volume fractions in the actual volume of sample illuminated by the neutrons. The difference between the intended volume fractions and those given by the whole pattern fitting is very small, approximately $\pm4\%$. This close correspondence highlights the well-mixed nature of the powders.

The neutron diffraction volume fractions are actually only those of the solid part of the sample, that is, they do not account for porosity. Strictly, if the sample is treated as three phases (calcite + halite + porosity), the true volume proportions are given by;

$$f_{cc} = (1 - \Phi) f_{cc}^{\text{neutron}} \quad \text{Eq. 9.6}$$

$$f_{hl} = 1 - f_{cc} - \Phi \quad \text{Eq. 9.7}$$

where $f_{cc}^{\text{neutron}}$ is the calcite volume fraction determined from the neutron data.
9.4. Stress and strain analysis

9.4.1. Axial stress applied to the sample

Axial stress applied to the sample ($\sigma_{agg}$) is given by applied axial load divided by the initial cross-sectional area of the sample. No correction for cross-sectional area change with deformation is applied. Any change in cross-sectional area would be very small (smaller than the uncertainty of the initial cross-sectional area obtained from the measurements of sample dimensions) because the axial strains are very small (mostly <1%).

9.4.2. Calculation of strains

The primary data recovered from the neutron diffraction experiments are the lattice parameters as a function of the axial stress applied to the sample. The deformation variable that these lattice parameters are most directly converted into is elastic strain. The average elastic strain experienced by each phase is obtained from

$$\varepsilon_V = -(1/3) \ln(V/V_0) \quad Eq. \ 9.8$$

where $V$ is the apparent volume of the unit cell calculated using the unit cell dimensions obtained from the whole pattern fit at a given load, and $V_0$ is the volume of the unit cell of the same phase at zero load. The presence of the $(1/3)$ term is used to make the resulting $\varepsilon_V$ values linear, thus allowing comparison with directional strains. The minus sign is used so that contractional strains are positive. Note that $\varepsilon_V$ values are determined for each phase in both the axial (parallel to the direction of loading) and radial (perpendicular to the loading direction) directions.

The linear elastic strain in a given lattice direction, $\varepsilon_{hk.l}$ ($\varepsilon_{hkl}$ for halite), is given by

$$\varepsilon_{hk.l} = - \ln\left(\frac{d_{hk.l}}{d_{0,hk.l}}\right) \quad Eq. \ 9.9$$

where $d_{hk.l}$ is the $d$-spacing of the $hk.l$ plane obtained from a single peak fit at a given axial load, and $d_{0,hk.l}$ is $d$-spacing of the that lattice plane at zero load. Again, note that $\varepsilon_{hk.l}$ values were calculated for each peak in both the axial and radial directions.
In the experimental set-up, it is not possible to take measurements at zero load, and so zero load values of $V$ and $d_{hk,l}$ were obtained by extrapolating polynomial fits of $V$ vs. axial load and $d_{hk,l}$ vs. axial load (respectively) to zero axial load. Generally only data from the lowest seven loads were used for these fits so as to avoid the changing relationship of $V$ and $d_{hk,l}$ with load after halite yielding had occurred.

There is often a small difference in the zero load lattice parameters in the axial and radial directions (e.g., Fig. 9.11a). Primarily, this probably reflects anisotropic residual stresses remaining after sample fabrication (which includes a high-stress axial compression step associated with the initial cold pressing stage). A contributing factor may also be uncertainties in the experimental set-up, either from calibrations for each detector bank (carried out by the instrument scientist on ENGIN-X), or fractionally non-perfect centring of the sample with respect to the beamline geometry.

Whole pattern derived elastic strain data is shown here as plots of $\sigma_{agg}$ vs. $(\varepsilon_{V,hl})_{ax}$ and $(\varepsilon_{V,cc})_{ax}$, and of $(\varepsilon_{V,cc})_{ax}$ vs. $(\varepsilon_{V,hl})_{ax}$ (Fig. 9.13); single peak derived elastic strain data are reported in terms of $\sigma_{agg}$ vs. $\varepsilon_{hk,l}$ (Fig. 9.14). To re-emphasize: all strains are elastic strains even after yielding of the halite; total strains (elastic + plastic) may be recovered from the data using the axial strain measurements of the sample (recorded by the extensometer) and the rule of mixtures (Eq. 8.1 and Eq. 8.2, see Covey-Crump et al., 2013) but this not relevant for the particular aims of the study reported here. In this study, of central interest is to establish the onset of plastic yielding of the halite and to correlate this with microstructural variables. Plastic yielding of the halite is seen most clearly in the halite strains recovered from the whole pattern fits (e.g., Fig. 9.13). It is also visible as changes in the rate of peak broadening with increasing axial load Fig. 9.15, and as mentioned in §9.2.2, also potentially from the systematic increase with load in the $\chi^2$ values for the whole pattern fits. Among the contributing factors to peak width are lattice distortions, these amplify after plastic yielding due to dislocation generation. The effects of halite yielding on the halite single peak data is more subtle and is visible for some peaks but not others depending on the activated slip system (Fig. 9.14).

The significant advantage of these deformation tests compared to conventional laboratory deformation experiments is the high strain resolution. This allows the onset of yielding (departure from linearity on a stress vs. strain plot) to be precisely located.
Fig. 9.13. Plots of aggregate stress vs. halite elastic strain and calcite elastic strain (top) and calcite elastic strain vs. halite elastic strain (bottom) for whole pattern data in ENGX28 (calcite 0.61: halite 0.39, <38 µm Carrara marble). In the top plot, plastic yielding of the halite is highlighted by a change in slope of the halite data at $\varepsilon_{Y,H} = 780 \mu \varepsilon$; the calcite remains linear elastic throughout. In the lower plot, it can be seen that the yielding in the halite leads to an increase in the rate at which elastic strain (and hence stress) accumulates in the calcite, that is, halite yield leads to enhanced load transfer from the halite to the calcite. On energetic grounds, the pre-yield data must lie between the homogeneous stress and homogeneous strain boundaries. The data should also lie within even tighter bounds based on minimizing potential energy and complementary potential energy (the Hashin and Shtrikman boundaries, HS+ and HS-; (Hashin and Shtrikman, 1963) Plots constructed by Covey-Crump.
Fig. 9.14. Example of the elastic strain vs. aggregate stress for the HL (200) peak (left) and the HL (311) peak (right) in ENGX28 (calcite 0.61: halite 0.39, <38 µm Carrara marble). Yielding of the halite is picked out very well by a change in slope of the axial data at 37 MPa. This is particularly the case in the HL (200) peak but less so in the HL (311). Plot constructed by Covey-Crump.

Fig. 9.15. Example of peak broadening as shown by halite elastic strain vs. halite normalized peak width in ENGX28 (calcite 0.61: halite 0.39, <38 µm Carrara marble). Derived from a whole pattern fit; the peak width parameter is normalized by the value of that parameter at the lowest load. Yielding of the halite is picked out in both axial and radial data by an increase in the rate of peak broadening with load. Plot constructed by Covey-Crump.
9.4.3. Calculation of stresses

Although the primary data recovered from the diffraction patterns is in terms of strain, it is conceptually easier to interpret the results in terms of stress. For the uniaxial approximation (radial stress is zero), then the axial stress in the halite and in the calcite is given by

\[ \sigma_{hl} = E_{hl} \varepsilon_{V,hl} \]  \hspace{1cm} Eq. 9.10

\[ \sigma_{cc} = E_{cc} \varepsilon_{V,cc} \]  \hspace{1cm} Eq. 9.11

where \( E \) is the Young’s modulus.

More rigorously, the uniaxial approximation should not be made because although the overall deformation is uniaxial (there is no confining pressure), within the sample each phase acts as a constraint on the other, and hence experiences a triaxial state of stress. In this case, the triaxial version of Hooke’s law is needed:

\[ \sigma_{ax} = \frac{E}{(1-2v)(1+v)} [(1 - v) \varepsilon_{ax} + 2v \varepsilon_{rad}] \]  \hspace{1cm} Eq. 9.12

\[ \sigma_{rad} = \frac{E}{(1-2v)(1+v)} [\varepsilon_{rad} + v \varepsilon_{ax}] \]  \hspace{1cm} Eq. 9.13

where \( v \) is the Poisson’s ratio (0.3199 for calcite and 0.2564 for halite (Tab. 9.4)), again, the strains are elastic strains for the given phase in the indicated direction. The axial and radial stresses in the calcite and in the halite as calculated using Eqs. 9.10-9.11, are very similar to those using Eqs. 9.12-9.13 indicating that the uniaxial approximation is a good one for the experiments reported here, particularly up to the point of halite yielding (Fig. 9.16). However, given the extra rigour of the triaxial equations, Eqs. 9.12-9.13 are used to calculate all the stresses reported in this study. Comparison of the stresses in the calcite and halite is most completely done through the use of von Mises equivalent stress, \( \sigma_{eq} \), which for \( \sigma_1 = \sigma_{ax} \) and \( \sigma_2 = \sigma_3 = \sigma_{rad} \) where

\[ \sigma_{eq} = \left\{ \left[ (\sigma_{ax} - \sigma_{rad})^2 + (\sigma_{rad} - \sigma_{ax})^2 \right]/2 \right\}^{1/2} = (\sigma_{ax} - \sigma_{rad}) \]  \hspace{1cm} Eq. 9.14

Examples of the plots resulting from the stress calculations for whole pattern fits can be seen in Fig. 9.16.
Fig. 9.16. Examples of the graphs used to display whole pattern stress data obtained from strain data for ENGX28 (calcite 0.61: halite 0.39, <38 µm Carrara marble). Top left: Axial and radial stresses in the calcite vs. axial stress applied to the sample. Top right: Axial and radial stresses in the halite vs. axial stress applied to the sample. Note that the stresses are well described using the uniaxial approximation (dashed lines (Eqs. 9.10-9.11)) up until the halite yields but that after yielding this approximation is less good. Bottom left: von Mises equivalent stresses in the calcite and halite vs. axial stress applied to the sample, clearly showing the yield point of halite. Bottom right: Calcite axial stress vs. halite axial stress, again clearly showing the yield point of halite, and the subsequent enhanced load transfer from halite to calcite. Plots constructed by Covey-Crump.

For the single peak data, Eqs. 9.12 and 9.13 also apply but the directional Young’s modulus ($E_{hk,l}$) and Poisson’s ratio ($v_{hk,l}$) for the specific peak in question must be used:

$$\sigma_{hk,l,ax} = \frac{E_{hk,l}}{(1-2v_{hk,l})(1+v_{hk,l})} \left[ (1 - v_{hk,l})\varepsilon_{hk,l,ax} + 2v_{hk,l}\varepsilon_{hk,l,rad} \right]$$  \hspace{1cm} \text{Eq. 9.15}

$$\sigma_{hk,l,rad} = \frac{E_{hk,l}}{(1-2v_{hk,l})(1+v_{hk,l})} \left[ (1 - v_{hk,l})\varepsilon_{hk,l,rad} + 2v_{hk,l}\varepsilon_{hk,l,ax} \right]$$  \hspace{1cm} \text{Eq. 9.16}

The directional elastic constants are obtained (for a diffraction experiment) by averaging the elastic properties over all the grains which satisfy the Bragg condition for the direction
(peak) of interest, where the averaging is carried out subject to some assumption about the stress and/or strain distribution between grains (e.g., homogeneous stress, homogeneous strain, or some kind of middle ground between these two such as that given by the self-consistent approximation). In this study, self-consistent values obtained using the formulation of Kröner (1958) were used. For cubic phases (i.e., halite), these are easily obtained from the components of the elastic compliance tensor using straightforward formulae (e.g., Bollenrath et al., 1967). For lower crystal symmetries, the calculations are more complex but have been implemented in the IsoDec software of (Gnaupel-Herold, 2012), which was used here to recover the calcite values. The self-consistent directional elastic constants for the peaks analysed in this study are tabulated in Tab. 9.4.

**Tab. 9.4.** Table of directional Young’s modulus ($E_{hk,l}$) and directional Poisson’s ratio ($\nu_{hk,l}$) for the single peaks analysed in this study. These are self-consistent values obtained using the formulation of Kröner (1958). Table compiled by Covey-Crump.

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Examples of the plots resulting from the stress calculations for single peak fits can be seen in Fig. 9.17. The onset of yielding in the halite is apparent in the stress plots together with the enhancement of the load transfer from the halite to the calcite once yielding occurs,
as shown by the departure from the homogeneous stress line (1:1). In addition, the way in which the deformation is accommodated within differently oriented grains of given phase is also highlighted. Plotting of the stress values above the homogeneous stress line indicates that the lattice plane in question sees more deformation, whilst plotting of the stress values below the line indicates that the lattice plane sees less stress.

![Graphs showing stress values](image)

Fig. 9.17. Examples of the graphs used to display single peak stress values obtained from strain data for ENGX28 (calcite 61: halite 39, <38 µm Carrara marble). The position of the data below the 1:1 line on the right hand side plot indicates that the grains providing the data for CC (10.4) single peak are under less stress than the average calcite grain. Plots constructed by Covey-Crump.

9.5. Microstructural analysis

Thin-sections were made using the same technique used for the monomineralic halite tests discussed in §3.3.4. Due to the contrast in hardness between the two phases, thin-section polishing was finished by hand. Although not as time-efficient as using a rotary polisher, hand polishing allows thin-sections of more even thickness to be produced and reduces the damage done to the samples. Despite the care taken during the creation of the sections, the hardness contrast between the two phases resulted in a small degree of plucking of the halite.

Full analysis of the microstructure in these samples required the determination of halite mean free path ($\lambda_{hl}$) and calcite contiguity ($C_{cc}$).
9.5.1. Measuring calcite contiguity

As noted previously (§8.1.1), contiguity is defined as the fraction of the total internal surface area that a given phase shares with other grains of that phase. In terms of the present system where the α phase is halite and the β phase is calcite, calcite contiguity \( C_{cc} \), from Eq. 8.3, becomes

\[
C_{cc} = \frac{2S_{cc-cc}}{(2S_{cc-cc} + S_{hl-cc})} \tag{Eq. 9.17}
\]

where \( S_{cc-cc} \) is the shared area of the boundary between calcite grains and \( S_{hl-cc} \) is the boundary area shared by calcite and halite grains. Using the relationship

\[
S_{cc-cc} = 2P_{cc-cc} \tag{Eq. 9.18}
\]

where \( P \) is the number of boundaries, of the type indicated by its subscript, that are intercepted per unit length of a line across a planar section through the aggregate (Underwood, 1970), Eq. 9.17 becomes

\[
C_{cc} = \frac{4P_{cc-cc}}{(4P_{cc-cc} + 2P_{hl-cc})} \tag{Eq. 9.19}
\]

Hence, calcite contiguity can be estimated from counts of different types of boundaries intercepted along transects across a thin-section. In practical terms, obtaining \( P_{hl-cc} \) is straight-forward. Obtaining \( P_{cc-cc} \) is more challenging because sharp imaging of calcite-calcite grain boundaries is difficult on a thin section that has been prepared in such a way as to allow precise imaging of the halite grain boundaries. The problem is particularly severe in the fine calcite clast size experiments (6 and <38 µm) where calcite size is on the order of a few microns. Consequently, Eq. 9.19 is expressed in terms of \( P_{hl-cc} \), \( f_{cc} \) and mean calcite clast linear intercept length \( L_{cc} \) which is a measurement of the calcite clast size and, in a single phase material, is given by

\[
L_{cc} = \frac{1}{N_{cc}} \tag{Eq. 9.20}
\]

where \( N_{cc} \) is the number of grains or clasts per µm. In a two phase material the volume fraction of the phase becomes significant, hence

\[
L_{cc} = f_{cc}/N_{cc} \tag{Eq. 9.21}
\]

\( N_{cc} \) in a two phase system is given by
\[ N_{cc} = \frac{(2P_{cc-cc}+P_{ht-cc})}{2} \quad \text{Eq. 9.22} \]

Substituting Eq. 9.21 into Eq. 9.22 gives

\[ L_{cc} = \frac{2f_{cc}}{(2P_{cc-cc}+P_{ht-cc})} \quad \text{Eq. 9.23} \]

From Eq. 9.19, it can be shown that

\[ (1 - C_{cc}) = \frac{P_{ht-cc}}{(2P_{cc-cc}+P_{ht-cc})} \quad \text{Eq. 9.24} \]

Substituting Eq. 9.23 into Eq. 9.24 and rearranging gives Eq. 9.25 (derived in Bloomfield and Covey-Crump (1993))

\[ C_{cc} = 1 - \left[ \frac{L_{cc}P_{ht-cc}}{(2f_{cc})} \right] \quad \text{Eq. 9.25} \]

To measure \( P_{ht-cc} \), photomicrographs orientated parallel to the direction of loading were taken into Adobe Illustrator CS3 and a grid consisting of 10 transects orientated parallel to the loading direction was superimposed over the image (Fig. 9.18). Multiple images representative of the overall microstructure were analysed for each sample in order to obtain a statistically valid number of intercepts. The number of intersections between calcite and halite along these transects was counted (red ticks). Since the transect length is known, the number of boundaries intersected per \( \mu \text{m} \) can be determined. Aside from samples RUT49 (207 intercepts) and ENGX14 (270 intercepts), at least 330 intercepts were used to obtain values of \( P_{ht-cc} \) by dividing the total number of halite-calcite intercepts by the total line length occupied by halite.
Fig. 9.18. Photomicrograph of ENGX26 (calcite 0.62: halite 0.38, 100 µm Carrara marble) displaying the transects across which the mean free path and contiguity were calculated. The vertical red lines represent the boundaries between calcite (heavier relief phase) and halite (low relief phase) and were used to determine \( P_{hl-cc} \). The loading direction is parallel to the transect lines.

In order to obtain \( l_{cc} \), Eq. 9.20 was used. To measure \( N_{cc} \), two approaches were required owing to the range of calcite grain sizes. At small calcite clast sizes (6-50 µm), photomicrographs were examined for clusters of calcite that displayed clearly defined grain boundaries. The number of calcite-calcite boundaries was then counted parallel to the direction of loading. In 6 µm samples at least 210 intercepts were measured, in the <38 µm sample 351 intercepts were measured and in the 50 µm sample 112 intercepts were measured.

At larger calcite clast sizes, the clasts are polycrystalline, and as a result, more care is needed when measuring \( N_{cc} \) as one needs to be sure that clast-clast boundaries are being measured and not grain-grain boundaries. At calcite sizes of 100 µm and 200 µm, transects orientated parallel to the loading direction, similar to those in Fig. 9.18, were randomly placed over photomicrographs and examined for clear calcite-calcite clast boundaries, the numbers of which were counted. 534 intercepts were measured in the
100 µm sample and at least 195 intercepts measured in the 200 µm samples. At the largest sizes (500 µm) the same transect approach was taken, however, only one or two clasts may lie along each transect. To address this, single clast sizes are repeatedly measured along the transects until the mean size remains approximately constant, this occurred after measuring 125 clasts.

The nature of placing random transects across the photomicrographs means that transects do not always go through the centre of the clasts. This was allowed for given that the number of measured clasts off-sets any influence of measuring clast margins.

9.5.2. Measuring halite mean free path

The mean spacing between calcite clasts, that is, the halite mean free path \( \lambda_{\text{hl}} \) is given via two definitions

\[
\lambda_{\text{hl,}U} = \frac{l_{\text{cecl}}}{{f_{\text{cc}}}} \quad \text{Eq. 9.26}
\]

\[
\lambda_{\text{hl,}G} = \frac{L_{\text{cecl}}}{(f_{\text{cc}}(1-c_{\text{cc}}))} \quad \text{Eq. 9.27}
\]

Eq. 9.26 and Eq. 9.27 were derived by Underwood \( \lambda_{\text{hl,}U} \) (1970) and Gurland \( \lambda_{\text{hl,}G} \) (Lee and Gurland, 1978; Pickens and Gurland, 1978) respectively. In order to determine which of these two expressions provides the best description of \( \lambda_{\text{hl}} \), the mean linear intercept spacing between calcite clasts was measured along transects in the 100 µm, 200 µm and 500 µm samples \( \lambda_{\text{hl,m}} \). The expression that gives the highest confidence is the one that gives a \( \lambda_{\text{hl}} \) value closest to \( \lambda_{\text{hl,m}} \).

Of the two equations used to describe mean free path, the expression used by Gurland is most commonly used. It has been demonstrated by Kim (2004) that, when comparing mean free path values produced by Eqs. 9.26 and 9.27 with those values measured directly from samples, Gurland’s expression gives more representative values. The same is observed in this study (Fig. 9.19) where the values calculated using Gurland’s expression are consistently closer to \( \lambda_{\text{hl,m}} \), and as such, is the more appropriate expression. When halite mean free path \( \lambda_{\text{hl}} \) is referred to throughout the remainder of the study, it is the value calculated from the Gurland expression that is implied.
Fig. 9.19. Plot comparing the measured values of halite mean free path vs. values of halite mean free path calculated using the Underwood (Eq. 9.26) and Gurland (Eq. 9.27) definitions.

9.5.3. Confidence in the mean free path equation variables

Confidence in the microstructural results is dependent upon confidence in the measurements of $f_{cc}$, $L_{cc}$ and $P_{hl-cc}$ that are used in Eq. 9.25 and Eq. 9.27.

The values of $f_{cc}$ are well constrained as all samples have $f_{cc}$ determined from diffraction data close to the mixture volume fraction. There is high confidence in the value of $P_{hl-cc}$ as the calcite-halite boundaries are very well defined (e.g., Fig. 9.18). The most significant challenge when obtaining the $P_{hl-cc}$ measurements was to ensure that they were taken from areas representative of the overall sample microstructure. By obtaining $P_{hl-cc}$ from multiple areas within the sample, in addition to the number of intercepts used in the measurements in any one area, representativeness was ensured. Confidence in $L_{cc}$ is secured as the determined values, when multiplied by a factor of 1.4 to 1.5,
approximately match the sieve fraction of the starting material, as would be expected for equant clasts (Han and Kim, 1995).
In this section, a selection of plots are shown that best illustrate the results of the neutron diffraction experiments. The entire neutron diffraction experiment dataset is tabulated in Appendix 14.5, together with a full suite of plots showing the stress and strain results (tables and figures compiled by Covey-Crump). The plots presented in this section have been re-drawn by Tant.

A summary of the experiments is given in Tab. 10.1. This includes several samples (labelled RUT) that were made by Covey-Crump in a previous study, but which were microstructurally analysed for the first time as part of this study. The ENGX samples were the samples used in the eight neutron diffraction experiments of this study. Note that from here on, the mean calcite clast linear intercept sizes ($L_{cc}$ in Tab. 10.1) will be used when stating calcite clast size. To keep consistency with Part I of this thesis, the notation $d_{cc}$ will be used when referring to mean calcite clast linear intercept size. For the sake of simplicity, the RUT tests, and ENGX tests 20 and 23, are considered to have clast sizes of 6 µm. Tab. 10.1 also lists the powder volume fraction of the starting material ($f_{\text{powder}}$), the volume fraction obtained from the whole pattern fit ($f_{\text{whole pattern}}$) and the volume fraction corrected using Eq. 9.6 and Eq. 9.7 to take into account porosity ($f_{\text{true}}$). Note that the differences between $f_{\text{whole pattern}}$ and $f_{\text{true}}$ are minimal. Throughout the remainder of this study, the volume fraction obtained from the whole pattern fit ($f_{\text{whole pattern}}$) will be used.
Tab. 10.1. Table summarizing the microstructural and mechanical results for the neutron diffraction tests carried out for this study. \( f_{\text{powder}} \) is the volume fraction of the calcite:halite powders measured during sample preparation. \( f_{\text{whole pattern}} \) is the volume fraction determined from the whole pattern fit. \( f_{\text{true}} \) is the volume fraction corrected using Eq. 9.6 and Eq. 9.7 to take into account porosity, hence they do not equal 1. Uncertainties associated with the volume fractions are estimated from those of the Rietveld refinements to be ±0.001. \( d_{\text{cc start}} \) is the calcite clast size fraction used in the sample preparation stage and \( L_{\text{cc}} \) is the mean calcite intercept length and is a measure of calcite clast size in thin-section.

<table>
<thead>
<tr>
<th>Calcite type</th>
<th>Test</th>
<th>( \Phi )</th>
<th>( f_{\text{powder}} )</th>
<th>( f_{\text{whole pattern}} )</th>
<th>( f_{\text{true}} )</th>
<th>( d_{\text{cc start}} )</th>
<th>( L_{\text{cc}} ) (µm)</th>
<th>( P_{\text{cc-hl}} ) (µm(^{-2}))</th>
<th>( C_{\text{CC}} \lambda_{\text{hl}} ) (µm)</th>
<th>Axial stress at halite yield point (MPa)</th>
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</thead>
<tbody>
<tr>
<td>Reagent grade and chelometric calcite</td>
<td>RUT34</td>
<td>0.10:0.90</td>
<td>5</td>
<td>6</td>
<td>0.0249</td>
<td>0.201</td>
<td>58</td>
<td>72</td>
<td></td>
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<tr>
<td></td>
<td>RUT39</td>
<td>0.21:0.79</td>
<td>5</td>
<td>5</td>
<td>0.0285</td>
<td>0.627</td>
<td>21</td>
<td>56</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>ENGX20</td>
<td>0.012</td>
<td>0.40:0.60</td>
<td>0.37:0.63</td>
<td>0.37:0.62</td>
<td>6</td>
<td>7</td>
<td>0.0167</td>
<td>0.843</td>
<td>12</td>
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<td>RUT57</td>
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<td>6</td>
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<td>0.932</td>
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<td>92</td>
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<td>ENGX23</td>
<td>0.021</td>
<td>0.60:0.40</td>
<td>0.62:0.48</td>
<td>0.61:0.37</td>
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<td>0.923</td>
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<td>RUT56</td>
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<td>7</td>
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<td>0.962</td>
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<td>7</td>
<td>0.0047</td>
<td>0.983</td>
<td>1</td>
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<td>Carrara marble</td>
<td>ENGX28</td>
<td>0.016</td>
<td>0.60:0.40</td>
<td>0.61:0.39</td>
<td>0.60:0.38</td>
<td>&lt;38</td>
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<td>0.0119</td>
<td>0.825</td>
<td>12</td>
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<td>ENGX5</td>
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<td>0.61:0.39</td>
<td>0.60:0.38</td>
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<td>0.729</td>
<td>20</td>
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<td>ENGX26</td>
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<td>0.60:0.40</td>
<td>0.62:0.38</td>
<td>0.61:0.37</td>
<td>100</td>
<td>57</td>
<td>0.0076</td>
<td>0.650</td>
<td>35</td>
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<td>ENGX9</td>
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<td>0.64:0.36</td>
<td>0.61:0.35</td>
<td>200</td>
<td>130</td>
<td>0.0063</td>
<td>0.357</td>
<td>73</td>
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<td></td>
<td>ENGX14</td>
<td>0.021</td>
<td>0.60:0.40</td>
<td>0.67:0.33</td>
<td>0.66:0.32</td>
<td>500</td>
<td>361</td>
<td>0.0024</td>
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<td>178</td>
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<td>Solnhofen limestone</td>
<td>ENGX30</td>
<td>0.036</td>
<td>0.60:0.40</td>
<td>0.64:0.36</td>
<td>0.62:0.35</td>
<td>200</td>
<td>141</td>
<td>0.0078</td>
<td>0.137</td>
<td>79</td>
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Axial stress at halite yield point (MPa)

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<th>( \sigma_{\text{agg}} )</th>
<th>( \sigma_{\text{ax.hl}} )</th>
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Axial stress at halite yield point (MPa)

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<th>( \sigma_{\text{agg}} )</th>
<th>( \sigma_{\text{ax.hl}} )</th>
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Axial stress at halite yield point (MPa)
10.1. Contiguity and mean free path results

10.1.1. Contiguity and mean free path as a result of calcite volume fraction

In a previous study (Covey-Crump et al., 2013) numerous calcite + halite samples were fabricated in addition to the samples used in the neutron diffraction experiments reported in that study. These were made using the same halite powders as used in this study. The calcite used was reagent grade (+98%) calcite but had the same particle size (approximately 5 µm) as the chelometric grade calcite used in this study. Sample fabrication followed the same cold pressing and hot isostatic pressing procedures used in this study (cold pressed at approximately 900 MPa, followed by hot isostatic pressing for 3 hrs at 600 °C and 200 MPa confining pressure) with the exception that one sample (RUT34) was cold pressed at 575 MPa, and another (RUT49) was hot pressed for over 4 hrs, both for reasons that were important for the Covey-Crump et al. (2013) experiments.

The samples were fabricated with a range of volume fraction calcite, and so together with ENGX20 and ENGX23, microstructural analysis of these samples was carried out in this study to establish the variation of calcite contiguity and mean free path as a function of volume fraction in samples of constant calcite grain size.

10.1.1.1. Microstructural observations

After hot isostatic pressing, the grain size (mean linear intercept size) of both phases was similar to the particle size of the starting powders. That is, the calcite had a grain size of about 6 µm, and the halite had a grain size in the range of the original 38-125 µm sieve fraction.

The changing microstructure associated with changing volume fraction is shown in Fig. 10.1. At fractions of 0.10 calcite, small clusters of calcite grains can be seen resulting in heterogeneous distribution of calcite (Fig. 10.1a). Single isolated calcite grains lie along the halite grain boundaries. Increasing the calcite volume fraction to 0.20 results in increased clustering and calcite heterogeneity leading to an increase in the size of the calcite clusters (Fig. 10.1b). There is also a higher occurrence of strings of calcite grains lying along halite grain boundaries creating “haloes” around the halite. Despite rigorous
mixing during the sample preparation stage, clustering of the halite into lenses still occurred (Fig. 10.1c). At calcite volume fractions of 0.37, calcite grains form larger clusters. Some clusters become connected so that individual halite grains are isolated (at least they are on the 2D section through the microstructure). At equal volume fractions of calcite and halite, halite grains are further isolated (Fig. 10.1d). At greater calcite volume fractions, the halite becomes increasingly localised to clusters or isolated as single grains (Fig. 10.1e, f and g).
10.1.1.2. Calcite contiguity observations

It is expected that as calcite volume fraction increases, calcite contiguity increases, that is, the calcite shares more of its grain boundary area with other calcite grains. However, the details of this relationship will be sensitive to how well intermixed the phases are.

The samples display a smooth non-linear trend of increasing contiguity with increasing calcite volume fraction (Fig. 10.2). Contiguity increases rapidly with calcite volume fraction up to approximately 0.40. Contiguity then approaches its maximum value of 1, thus becoming approximately constant and, therefore, insensitive to changes in calcite volume fraction.

![Calcite volume fraction vs. calcite contiguity in constant calcite clast size tests](image)

**Fig. 10.2.** Plot displaying the relationship between calcite volume fraction and calcite contiguity in constant calcite grain size (6 µm) tests.
10.1.1.3. **Mean free path observations**

It is expected that as calcite volume fraction increases, the separation of calcite grains should decrease, that is, the halite mean free path should decrease, although these trends will be sensitive to how well intermixed the two phases are.

A decrease in mean free path (as defined by Gurland, Eq. 9.27) with increasing calcite volume fraction is indeed observed (Fig. 10.3). At intermediate volume fractions (0.25-0.55 calcite), there is, however, considerable variability in the mean free path. Undoubtedly, this reflects poor intermixing of the phases at these compositions, e.g., clustering of the halite grains into lenses (Fig. 10.1c), which does not occur at larger calcite volume fractions because the halite occurs as single grains (Fig. 10.1g). It is noteworthy that this confirms the speculation given by Covey-Crump *et al.* (2013) that the very weak behaviour of their intermediate composition samples reflected clustering of the phases, and in particular, the effects of stress concentration in the relatively narrow calcite bridges between patches of deforming halite. It also highlights the motivation behind attempting to correlate sample strength with mean free path rather than volume fraction.
Fig. 10.3. Plot displaying the relationship between calcite volume fraction and halite mean free path in constant calcite grain size (6 µm) tests.

10.1.2. Contiguity and mean free path as a function of calcite size

A total of seven samples were fabricated with compositions of approximately 0.60 calcite: 0.40 halite, but with different calcite clast sizes so as to vary calcite contiguity and halite mean free path (Tab. 10.1). Five of these used Carrara marble, one Solnhofen limestone (ENGX30) and one chelometric calcite (ENGX23).

10.1.2.1. Microstructural observations

In the sample containing 6 µm chelometric grade calcite (ENGX23), the halite is not fully intermixed with the calcite, that is, there are clusters of halite grains. In places, calcite grains form “necklaces” around the halite grains. (Fig. 10.4a).

In the samples containing Carrara marble, at calcite grain sizes of 18 µm, clustering of halite still occurs (Fig. 10.4b). However, the calcite-halite boundaries are better defined and less lobate. Large (approximately 75-100 µm) single crystals of halite are also present. These are considered to be larger clasts that contaminated the halite sieve fraction.
In the 31 µm sample, there are large anomalous (>500 µm) lenses of halite with their long axes oriented perpendicular to the long axis of the sample, the tip of one of these lenses can be seen in Fig. 10.4c. By treating the sample as consisting of “lenses” and “non-lenses” and using the same technique used to determine $P_{ht-c}$ (§9.5.1), a lens volume fraction of approximately 0.2 was determined. These lenses were probably formed during cold pressing. Halite grain sizes within the lenses are significantly larger (>150 µm) than halite located in the surrounding calcite, which remain in the range of the starting material (38-125 µm) indicating that some halite grain growth took place within the lenses during the hot pressing. Smaller (approximately 100 µm) halite clusters, together with single <50 µm halite grains, are seen in the remainder of the sample which is more representative of the overall microstructure. As a result, the lenses were not included in the mean free path and contiguity calculations.

In the 57 µm calcite experiment, a transition occurs in which halite begins to form strands around the calcite grains (Fig. 10.4d). Isolated areas of halite still occur but are less common than in previously described samples. Increasing calcite clast size to 130 µm results in a further increase the size of interstitial halite patches (Fig. 10.4e). At this clast size, the clasts are similar in size to the mean grain size of Carrara marble (150 µm). Note that the calcite in this sample appears to be composed of single large Carrara marble grains approximately 130 µm in size and what appear to be aggregates of smaller Carrara marble fragments. However, it is challenging to distinguish individual calcite grain boundaries within these clasts.

At the largest calcite sizes examined (361 µm), large areas (>500 µm) of halite occur between calcite clasts in addition to thinner halite bands that occur between more closely spaced calcite clasts (Fig. 10.4f). Within the halite patches, the grain size is larger (>100 µm) than within the other samples. However, in areas where the gap between calcite clasts is small, the halite grain size is smaller (approximately 50 µm).
A similar microstructure to that containing 130 µm Carrara marble clasts is observed in the sample containing 141 µm clasts of Solnhofen limestone (Fig. 10.5). However, the small grain size of Solnhofen limestone (4 µm) means that the clasts are polycrystalline. The Solnhofen limestone clasts are more angular (Fig. 10.5) than the Carrara marble clasts.
Clasts also appear to be better sorted, that is, small (<50 µm) Solnhofen limestone clasts are rarely observed (Fig. 10.5a). The presence of such angular clasts is likely due to smaller Solnhofen limestone fragments clumping together during the crushing, grinding and sieving process. Halite forms thin strands around calcite clasts together with larger interstitial patches, as observed in the corresponding Carrara marble bearing sample, but the size of the interstitial halite areas is smaller. Halite grain size is in the range of the starting material (38-125 µm).

Fig. 10.5. Photomicrographs of ENGX30 (141 µm clasts, 0.64 calcite: 0.36 halite). The calcite (dark phase) is Solnhofen limestone. The sample has been uniaxially deformed to an axial strain of approximately 0.8% (loading direction is left/right parallel). Note that the Solnhofen limestone clasts have a weak shape fabric, induced during cold pressing.
10.1.2.2. *Contiguity observations*

It is expected that at constant volume fraction, as calcite clast size increases, calcite clast contiguity should decrease because the calcite is less dispersed, that is, the calcite is contained within increasingly large patches. Again, the details of this relationship will be sensitive to how well intermixed the phases are. Note that in the samples containing polycrystalline calcite clasts, it is the contiguity of the clasts that is of principal interest here, not the contiguity of the individual calcite grains. The potential influence of grain size on how the deformation is accommodated within the calcite clasts forms the rationale for why an experiment using Solnhofen limestone was performed. This is particularly important at high temperatures where calcite deformation is strongly grain size sensitive (Edwards, 2009), but these matters are only touched upon in this study (§10.2.2).

The expected results are observed as calcite contiguity decreases non-linearly with increasing clast size (Fig. 10.6). The Solnhofen limestone sample exhibits a lower contiguity than would be expected given the contiguity of the Carrara marble sample of the same approximate clast size. This variation indicates that the clasts in the Solnhofen limestone sample are better dispersed than in the Carrara marble sample. Note that the uncertainty in clast contiguity increases at larger clast sizes because fewer calcite-calcite boundaries are encountered, therefore, the number of clasts from which measurements can be taken, decreases.
Fig. 10.6. Plot displaying the relationship between calcite clast size and calcite contiguity in constant calcite volume fraction (approximately 0.60 calcite: 0.40 halite) tests. Red dots represent the Carrara marble tests, the blue dot represents the Solnhofen limestone test.

10.1.2.3. Mean free path observations

One expects that at constant volume fraction, as calcite clast size increases, the separation of calcite clasts should increase, that is, the halite mean free path should increase. Again, these trends will be sensitive to how well intermixed the two phases are.

An increase in halite mean free path (as defined by Gurland, Eq. 9.27) with calcite clast size is indeed observed (Fig. 10.7). In the two samples in which the calcite clast size is approximately 150 µm, the slightly more dispersed nature of the Solnhofen limestone clasts is reflected by the lower halite mean free path.
Fig. 10.7. Plot displaying the relationship between halite mean free path and calcite clast size in the constant volume fraction (approximately 0.60 calcite: 0.40 halite) tests. Red dots represent the Carrara marble tests, the blue dot represents the Solnhofen limestone test.

10.2. Mechanical results

Eight calcite + halite samples were deformed in uniaxial compression at room temperature (Table 4.1). The composition of seven of these was approximately 0.60 calcite : 0.40 halite; the composition of the other (ENGX20) was approximately 0.40 calcite : 0.60 halite. A full set of mechanical results is seen Appendix 14.5.

10.2.1. General description of the deformation response

The general response of the samples to deformation is exemplified by ENGX26 (Fig. 10.8). During the initial stages of loading both phases behave linear elastically as shown by the linear nature of the data (Fig. 10.8 top left). The partitioning of strain between the phases falls within, or close to, the Hashin-Shtrikman bounds for an isotropic two phase aggregate (Fig. 10.8 top right), as previously demonstrated by Covey-Crump et al. (2001) for a two phase system deforming elastically. The fact that, at small stresses, the data lies within these bounds further increases confidence in the strain resolution of the experiments.
In all eight tests, halite yield begins at aggregate axial stresses of 20-37 MPa and halite axial stresses of 16-30 MPa while the calcite remains fully elastic throughout. Post halite yield, elastic strain (and hence stress) continues to increase in the halite with increasing applied load but at a smaller rate compared to pre halite yield (Fig. 10.8. middle right), while the rate of increase of elastic strain in the calcite with increasing applied load remains unchanged (Fig. 10.8. middle left). In other words, after yielding, slope of the post-yield data ($\Delta\sigma_{ax,cc}/\Delta\sigma_{ax,hl}$) increases with increasing applied load (Fig. 10.8. bottom right). The slope of the post-yield data is approximately constant. Upon unloading from an aggregate stress of 65 MPa, the strain in the calcite is fully recovered, while in the halite the axial stress is fully offloaded by an aggregate stress of approximately 20 MPa (e.g. Fig. 10.8. top left / bottom left) and, with further unloading, this halite axial stress becomes tensile.
Fig. 10.8. Plots displaying the general response of the samples to deformation in ENGX26 (0.62 calcite: 0.38 halite, 57 µm Carrara marble). Top left: Aggregate stress vs. elastic strain in each phase. Top right: Calcite axial elastic strain vs. halite axial elastic strain. Middle left: Calcite stress vs. aggregate stress. Middle right: Halite stress vs. aggregate stress. Bottom left: Equivalent stress vs. aggregate stress. Bottom right: Calcite axial stress vs. halite axial stress. The uncertainty in the stress and strain data is about the same size as the symbols. Unloading data (represented by the purple symbols) was collected from 65 MPa down to 25 MPa.
From examination of the calcite single peak data, it is apparent that all ten of the analysed peaks show linear elastic behaviour throughout loading (Fig. 10.9). The grains in elastically stiff orientations (peaks CC (01.2) and CC (12.5)) are more highly stressed than the average stress in the calcite (Fig. 10.9 (01.2) right); grains in elastically compliant directions (peaks CC (10.4) and CC (21.7)) are less highly stressed than the average stress in the calcite (Fig. 10.9 CC (10.4) right); grains in intermediate stiffness directions (all other peaks analysed) experience stresses close to the phase average (Fig. 10.9 CC (00.6) right). This indicates that the behaviour of the calcite is in agreement with its single crystal elastic properties (see Fig. 9.12) without the complication of twinning or crystallographically controlled microfracturing.

An examination of the halite single peak data reveals that four of the five peaks analysed (typified by HL (311) in Fig. 10.9) show little change in the rate of elastic strain increase as the applied load is increased, even after the halite yields. However, yielding leads to a strong decrease in the rate at which elastic strain accumulates in the HL (200) planes with increasing applied load. Some preliminary viscoplastic modelling of the effect of slip on the elastic strains recorded by the five analysed peaks demonstrates good agreement with that predicted for slip on the \{110\} <110> system when using approximate values for the critical resolved shear stresses of the slip systems of halite (pers. comm. Covey-Crump). This slip system is by far the weakest in halite at room temperature (§8.3.2).
ENGX26 calcite single peak data

(00.6)

(01.2)

(10.4)
Fig. 10.9. Example plots of aggregate stress vs. elastic strain (left) and h.k.l stress vs. phase equivalent stress (right) for calcite single peaks (previous page) and halite single peaks (this page) in ENGX26 (0.62 calcite: 0.38 halite, 57 µm Carrara marble). The bracketed numbers represent the single peak in question. The small black arrows indicate the point of halite yield. The purple lines indicate the unloading behaviour. The lines either side of the key symbols represent the uncertainties associated with the strain calculations. If no lines can be seen, the errors are of the same approximate size as the symbols.

10.2.2. Variation of the mechanical response with calcite contiguity and mean free path

The key aim of the analysis of this mechanical data in this study is to establish if the yield stress, and the extent of the subsequent enhanced load transfer from halite to calcite, correlate with the calcite contiguity and mean free path measurements reported in the previous section.
Compilations of the axial elastic strain partitioning between the calcite and halite, and the corresponding axial stress partitioning between the phases, are shown in Fig. 10.10 and Fig. 10.11. On both of these figures, there is a general sense that the data follow paths that shift to the right with increasing halite mean free path / decreasing calcite contiguity, i.e., samples with larger calcite clasts are more to the right. Note that there is a marginal difference in terms of yield stress between the two samples with calcite clast sizes of approximately 200 µm, i.e., ENGX9 (Carrara marble) and ENGX30 (Solnhofen limestone). This suggests that the same style of deformation took place in each calcite type and, therefore, no twinning took place in the Carrara marble clasts.

Compilations of the single peak data (Fig. 10.12) show small differences of this type between tests. Fig. 10.12 indicates that deformation is preferentially partitioned onto the stiffer calcite planes, i.e., CC (01.2) (Fig. 10.12c), while the weaker planes see less deformation, i.e., CC (10.4) (Fig. 10.12d) and the c-axis direction sees approximately homogeneous stress. The fact that the data in these weaker lattice planes remain linear indicates, again, that the calcite remains elastic and that the observed reduction in stress can be explained by the differing elastic properties of each plane.
Fig. 10.10. Plot of halite volumetric strain vs. calcite volumetric strain, both in the axial direction. The arrows indicate the onset of yielding in each experiment. The predicated pre-yield elastic strain partitioning is shown for the cases of homogeneous stress (Reuss), homogenous strain (Voigt) and the Hashin-Shtrikman (HS) upper and lower boundaries.

Fig. 10.11. Plot of halite vs. calcite axial stresses. Arrows represent the values of halite axial stress at which yielding begins. The homogeneous stress line is included; deviation from this line indicates partitioning of deformation into the calcite.
Fig. 10.12.  Plots of phase equivalent stress vs. hk.l equivalent stress for single peak data. Top left) CC (00.6); top right) HL (200); bottom left) CC (01.2); bottom right) CC (10.4). Note the different y-axis scales on the HL (200) and CC (01.2) and the different scale on the x-axis on the HL (200). The 1:1 line represents the point at which no partitioning of the deformation on to the specific crystallographic plane takes place. The key applies to all plots.

10.2.2.1. Correlation of yield stress with calcite contiguity and mean free path

It is expected that decreasing yield stress should be accompanied by increasing halite mean free path and decreasing calcite contiguity. This is attributed to the fact that, because it is the halite that yields, the larger the mean free path and the smaller the calcite contiguity, the easier it is for yielding to take place as the behaviour is less constrained by the calcite.
There is a general trend of decreasing halite yield stress with increasing mean free path as expected (Tab. 10.2 and Fig. 10.13a). The only sample that does not follow this pattern is ENGX5 which exhibits a lower than expected yield aggregate stress and axial strain. Picking out an unambiguous trend in the equivalent plot for contiguity is more challenging due to the scatter of the data (Fig. 10.13b). The scatter reflects variations in the local microstructure, and hence local mean free path and contiguity, within the sample.

It should be noted that distinguishing the variation of mean free path and contiguity with aggregate stress at the point of halite yield is slightly artificial due to the relative consistency of the sample volume fractions. However, Eq. 9.27 implies that if there is correlation between yield stress and mean free path, as there is, then the same correlation should be present with regards to calcite contiguity.

Tab. 10.2. Table summarizing the contiguity, mean free path and axial stress at the point of halite yield results.

<table>
<thead>
<tr>
<th>Calcite type</th>
<th>Test</th>
<th>$C_{CC}$</th>
<th>$\lambda_{hl} (\mu m)$</th>
<th>$\sigma_{agg}$ (MPa)</th>
<th>$\sigma_{ax.hl}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chelometric calcite</td>
<td>ENGX20</td>
<td>0.843</td>
<td>75</td>
<td>28</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>ENGX23</td>
<td>0.923</td>
<td>55</td>
<td>34</td>
<td>30</td>
</tr>
<tr>
<td>Carrara marble</td>
<td>ENGX28</td>
<td>0.825</td>
<td>66</td>
<td>37</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>ENGX5</td>
<td>0.729</td>
<td>73</td>
<td>21</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>ENGX26</td>
<td>0.650</td>
<td>100</td>
<td>25</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>ENGX9</td>
<td>0.357</td>
<td>114</td>
<td>26</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>ENGX14</td>
<td>0.356</td>
<td>276</td>
<td>20</td>
<td>16</td>
</tr>
<tr>
<td>Solnhofen limestone</td>
<td>ENGX30</td>
<td>0.137</td>
<td>92</td>
<td>26</td>
<td>24</td>
</tr>
</tbody>
</table>
Fig. 10.13. Plot displaying the relationship between a) halite mean free path and the aggregate stress at the point of halite yield and b) calcite contiguity and aggregate stress at the point of halite yield in the constant volume fraction (approximately 0.60 calcite: 0.40 halite) tests. Red dots represent the Carrara marble tests, the blue dot represents the Solnhofen limestone test and the green dot represents ENGX20 (6 µm chelometric grade calcite, 0.37 calcite: 0.62 halite).
10.2.2.2. Correlation of post-yield load transfer with calcite contiguity and mean free path

Two scenarios potentially arise from this data. On one hand, the effectiveness of load transfer increases with decreasing calcite contiguity, as high calcite contiguity results in less shared boundary area with halite, and therefore, less opportunity for load transfer to occur. Conversely, if the clasts are widely spaced, then the clasts effectively “float” in the halite resulting in less efficient load transfer – in this case, the effectiveness of load transfer decreases with increasing mean free path.

Plots of the post-yield slope vs. mean free path and vs. calcite contiguity are shown in Fig. 10.14 with the data summarized in Tab. 10.3. The extent of load transfer is quantified by the slope of the data after halite yielding \( \Delta \sigma_{ax,cc} / \Delta \sigma_{ax,hl} \), the larger the value, the higher the degree of load transfer. It should be noted that these slopes have been fitted, by eye, by Covey-Crump.

The slope of the post-yield axial data decreases with increasing mean free path and decreasing contiguity (Fig. 10.14). This suggests that of the two scenarios outlined above, the latter best describes the present results. The scatter associated with the data can be attributed to spatial variations in the local microstructure within the sample, and thus, in the mean free path and contiguity.

Tab. 10.3. Table summarizing the contiguity, mean free path and axial halite stress at the point of halite yield data results.

<table>
<thead>
<tr>
<th>Calcite type</th>
<th>Test</th>
<th>( C_{cc} )</th>
<th>( \lambda_{hl} ) (( \mu )m)</th>
<th>Pre-yield</th>
<th>Yield</th>
<th>Post yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chelometric calcite</td>
<td>ENGX20</td>
<td>0.843</td>
<td>75</td>
<td>1.5</td>
<td>21</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>ENGX23</td>
<td>0.923</td>
<td>55</td>
<td>1.1</td>
<td>30</td>
<td>5.3</td>
</tr>
<tr>
<td>Carrara marble</td>
<td>ENGX28</td>
<td>0.825</td>
<td>66</td>
<td>1.4</td>
<td>29</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>ENGX5</td>
<td>0.729</td>
<td>73</td>
<td>1.4</td>
<td>19</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>ENGX26</td>
<td>0.650</td>
<td>100</td>
<td>1.2</td>
<td>24</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>ENGX9</td>
<td>0.357</td>
<td>114</td>
<td>1.3</td>
<td>22</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>ENGX14</td>
<td>0.356</td>
<td>276</td>
<td>1.0</td>
<td>16</td>
<td>1.6</td>
</tr>
<tr>
<td>Solnhofen limestone</td>
<td>ENGX30</td>
<td>0.137</td>
<td>92</td>
<td>1.5</td>
<td>24</td>
<td>3.4</td>
</tr>
</tbody>
</table>
Fig. 10.14. Plot displaying the relationship between a) halite mean free path and the slope of the post-yield axial stress and b) calcite contiguity and slope of the post yield axial stress in the constant volume fraction (approximately 0.60 calcite: 0.40 halite) tests. Red dots represent the Carrara marble tests, the blue dot represents the Solnhofen limestone test and the green dot represents ENGX20 (chelometric grade calcite, 0.37 calcite: 0.62 halite).
11. Discussion of the calcite + halite neutron diffraction tests

11.1. Summary of key findings

Measurements of calcite contiguity and mean free path show the expected trends with varying calcite volume fraction in samples with the same calcite clast size (Fig. 10.2 and Fig. 10.3), that is, calcite contiguity increases and mean free path decreases with increasing calcite volume fraction. As the calcite volume fraction increases, the halite becomes progressively more isolated into small pockets. The change in mean free path with calcite volume fraction is noisy at intermediate calcite compositions (0.20-0.60) (Fig. 10.3). At those compositions, mean free path measurements are particularly sensitive to how well intermixed the two phases are. This is an unavoidable issue, especially at low phase volume fractions where phase clustering tends to occur regardless of the thoroughness of the mixing (Luyckx and Love, 2006). This situation can be seen, to some degree, in RUT39 (0.20 calcite: 0.80 halite (Fig. 10.1b)) where there is a lack of calcite along halite grain boundaries and clustering of calcite is taking place (compare the calcite distribution on the left-hand side to the right-hand side of Fig. 10.1b). In this sample, the calcite distribution is reducing the mean free path, whereas in RUT57 (0.50 calcite: 0.50 halite (Fig. 10.1d)), the increase in calcite volume fraction has resulted in clustering of the halite, therefore, increasing the halite mean free path. At calcite volume fractions of 0.60 and above, the amount of mixing appears to be sufficient to break-up the halite and prevent excessive clustering as shown by the smooth trend of decreasing mean free path with increasing calcite volume fraction (Fig. 10.3).

Measurements of calcite contiguity and halite mean free path also show the expected trends with calcite clast size in samples with constant calcite volume fraction (Fig. 10.6 and Fig. 10.7), that is, calcite contiguity decreases and mean free path increases with increasing calcite clast size. This corresponds with increasing localization of the calcite with increasing clast size (compare Fig. 10.4a and Fig. 10.4f). The data scatter is quite small, although it is present indicating that there is some variability in the degree of phase intermixing between the samples. Note that, because of the way mean free path is defined (Eq. 9.27), at constant composition, a smooth decrease in calcite contiguity with
increasing clast size should be reflected by a corresponding smooth increase in mean free path.

The yield stress of the samples in uniaxial compression decreases with mean free path, and increases with calcite contiguity, although the trend is more defined in the mean free path data (Fig. 10.13). Since all but one of the samples used in this study were of approximately the same composition, the effect of mean free path and calcite contiguity are not easily decoupled. Once yield had occurred, the rate of enhanced load transfer from halite to calcite ($\Delta\sigma_{ax,cc} / \Delta\sigma_{ax,hl}$) with increasing applied load increases with decreasing halite mean free path and increasing calcite contiguity (Fig. 10.14). The calcite remains elastic at all loads.

Ultimately, one of the aims of this analysis is to fit the Hall-Petch equation to the constant volume fraction tests and assess the validity of this relationship within this study.

11.2. The effect of mean free path and calcite contiguity on halite yielding

Intuitively, one expects the sample yield stress to decrease with halite mean free path because, as the distance between the calcite clasts increases, the mechanical response of the halite is less constrained by the calcite. Based on this logic, mean free path, not calcite contiguity is the key variable in determining material strength. This is the behaviour seen in the data in Fig. 10.13a, where there is a clear increase in yield stress with decreasing halite mean free path.

The effect on yielding will be highly sensitive to how well intermixed the phases are. For example, if there is a patch of sample with anomalously large mean free path, then it rather than the whole sample mean free path potentially controls overall yielding behaviour at the very small strains (<0.5%) examined in this study. ENGX5 (31 µm, Carrara marble) provides an example of such behaviour as it has a lower than expected yield strength given the yield stress of ENGX28 (18 µm, Carrara marble) and ENGX26 (57 µm, Carrara marble). The halite lenses in ENGX5 (Fig. 10.4c) represent areas with larger halite mean free path distances, and consequently, may well control yielding.
Combining ENGX20 with the approximately 0.60 calcite: 0.40 halite tests (excluding ENGX5, which contains halite lenses), the Hall-Petch relationship has been determined using halite mean free path and aggregate stress at the point of halite yield (Fig. 11.1). A frictional stress ($\sigma_0$) of 5.86 MPa and a Hall-Petch slope ($k$) of 212 MPa/µm$^{1/2}$ has been calculated. The fit of the relationship is good, indicating that the smaller the halite mean free path, the higher the stress at which yield takes place in the halite, that is, the sample is stronger.
Fig. 11.1. Hall-Petch relationship between halite mean free path and aggregate stress at the point of halite yield. Plotted using ENGX20 in addition to the constant volume fraction (0.60 calcite: 0.40 halite) tests. Note that ENGX5 has been excluded from the fit but is shown on the graph as a cross.

11.3. The effect of mean free path and calcite contiguity on load transfer after halite yield

Partitioning of deformation between the calcite and the halite takes place in the variable calcite clast size experiments as shown by the clear change in the slope of the data in Fig. 10.10 and Fig. 10.11. The effect of mean free path and calcite contiguity on the rate of load transfer (with increasing load) from halite to calcite after yielding is more difficult to predict. The expected behaviour is that the rate of load transfer will increase with decreasing calcite contiguity (increasing clast size in the present experiments) because the amount of boundary area that the calcite shares with the halite then increases and the mechanical response of the halite is less constrained by the calcite. However, if the mean free path is large, less load transfer is required to accommodate the deformation, i.e., the deformation is essentially accomplished by the halite and the calcite clasts are
'carried along' within the halite. In this case, one expects the rate of load transfer to decrease with increasing mean free path (increasing clast size in the present experiments), that is, the opposite trend to that predicted by the calcite contiguity logic.

In the data described here, the rate of load transfer decreases with mean free path and increases with calcite contiguity (Fig. 10.14), therefore, it is the mean free path logic that applies, not the calcite contiguity logic. This suggests that the halite is sufficiently continuous in those parts of the samples that are controlling the deformation response at these low strains (<1%) to effectively “grease” the boundaries of the calcite clasts so that stress does not build up rapidly in the calcite after the halite has yielded. There is the possibility that some frictional sliding may take place which is helping to accommodate the deformation, however, the fact that the single peak data indicates that halite is yielding plastically (Fig. 10.9) and the microstructural data shows no evidence of brittle deformation suggests that this isn’t the case.
Part III:

Summary
12. Conclusions and future work

This study has investigated the impact of a pore second phase on the microstructural evolution of halite during grain growth (Part I) and the influence of a calcite second phase on the mechanical behaviour of two phase calcite + halite aggregates (Part II).

12.1. Conclusions

In Part I, grain sizes were obtained from 62 experiments carried out on halite powders by hot isostatic pressing at 330 °C-600 °C (0.56-0.81 $T_m$) at 200 MPa confining pressure, these were complemented by 6 additional experiments at 500 °C (0.71 $T_m$) at either 70 or 100 MPa.

In summary;

- Grain growth in halite is well described by the normal grain growth equation with $n = 0.25$ for temperatures up to 511 °C and $n = 0.5$ at 600 °C. This indicates that between 330 °C and 511 °C growth is controlled by surface diffusion around pore boundaries, but that between 511 °C and 600 °C a transition to interface controlled growth takes place.

- $d_0$ and $t_0$ were determined by using four pre-defined constraints. Each term varies smoothly with temperature and has an Arrhenius-type dependence on temperature with $d_0$ increasing as temperature increases, while $t_0$ decreases as temperature increases. Based on the $t_0$ values, a diffusion activation enthalpy value of 109 kJ/mol was obtained for halite. Using the 330 °C-511 °C data sets, an activation enthalpy ($H$) of 122±34 kJ/mol and rate constant ($k_0$) of $9.6326 \times 10^{10}$ $\mu$m$^{1/n}$ s$^{-1}$ were calculated for normal grain growth in halite.

- Scatter observed for the grain size data limits the resolution with which the temperature dependence can be observed. This is due to small spatial variations in porosity size and volume fraction.
• Grain size distributions are consistently log normal but are best described as a Weibull distribution. Pore size distributions, on the other hand, are best described as log normal distributions.

• By imaging the pores in halite samples, the Zener parameter \( Z = d_p/f_p \) was determined for individual grains. Pore size and volume fraction vary spatially between samples but also between the grains within separate areas of the same sample. Of the two constituents of the Zener parameter, pore volume fraction exerts the greater control over halite grain size.

• A general trend of increasing \( Z \) with increasing grain size is observed, indicating that pore elimination keeps pace with pore accumulation in the growing grains. In some samples, the largest grains display a decrease in the Zener parameter that corresponds with an increase in pore volume fraction. These grains are interpreted as having experienced a short lived phase of abnormal growth shortly after \( t_0 \) during which pore accumulation outpaced pore elimination.

• A model of pore controlled grain growth is proposed in which pore accumulation along grain boundaries during growth out paces pore elimination resulting in an increase in pore volume fraction. Consequently, the Zener parameter decreases with boundary migration. This model can be applied to other systems in which a pore second phase is present, e.g., ice.

• When compared with grain growth studies of other geological materials (e.g., calcite, ice and olivine), halite appears to be uniquely sensitive to spatial variations in porosity and has a tendency towards abnormal growth. Despite having been used previously as an analogue for other geological materials (e.g., silicates and MgO), these factors reduce the applicability of halite as an analogue for high temperature, high pressure static grain growth in geological materials.

• The study has highlighted the importance of accounting for the Zener parameter in systems with small (<5%) volume fractions of second phases.
This study has provided a unique opportunity to investigate pore controlled grain growth, and subsequent abnormal grain growth, in geological materials. The results enhance the understanding of high temperature grain growth in geological materials.

In Part II, eight neutron diffraction experiments were carried out, seven on samples with constant volume fraction (approximately 0.60 calcite: 0.40 halite) but with calcite clast sizes varying from 6 µm to 361 µm. To explore the effect of volume fraction at constant clast size, one test had a volume fraction of 0.37 calcite: 0.63 halite and a calcite clast size of 6 µm. In addition, as part of this study six samples that were made by Covey-Crump in a previous study were microstructurally analysed for the first time.

In summary;

- In constant calcite clast size tests (6 µm chelometric calcite), halite mean free path has been shown to decrease and calcite contiguity increases with increasing calcite volume fraction.

- In constant volume fraction tests (approximately 0.60 calcite: 0.40 halite), halite mean free path increases and calcite contiguity decreases with increasing calcite clast size. This reflects isolation of the calcite clasts as they increase in size.

- During the initial stages of loading, both calcite and halite are elastic. The halite then yields at aggregate axial stresses of 20-37 MPa and halite axial stresses of 16-30 MPa while the calcite remains fully elastic throughout. Once halite yield had occurred, the rate of enhanced load transfer from halite to calcite, with increasing applied load, decreases with mean free path and increases with calcite contiguity. This suggests that the halite is sufficiently continuous in those parts of the samples that are controlling the deformation response at these low strains (<1%) to effectively lubricate the boundaries of the calcite clasts so that stress does not build up rapidly in the calcite after the halite has yielded.
Deformation is preferentially partitioned onto the stiffer calcite planes such as CC (01.2), while the weaker planes such as CC (10.4) see less deformation. The c-axis direction sees approximately homogeneous stress.

A Hall-Petch relationship between halite mean free path and aggregate yield stress is observed with a frictional stress of 5.86 MPa and a Hall-Petch slope of 212 MPa/µm$^{1/2}$.

The results presented here help further the understanding of how the yielding, and subsequent load transfer, takes place in a two phase geological system composed a strong phase and a weak phase. This provides insight into how localization of deformation may take place in two phase systems.

12.2. Future work

There are numerous different avenues that future work, building upon the data presented here, could take.

Part I:

- The next stage in this work is to expand the detailed porosity analysis samples that would facilitate a greater understanding of the variation in Z with temperature and experimental duration specifically. The effect of temperature has only been touched on here so this would be a logical step in the analysis. Analysing all the samples from three temperature sets would allow greater understanding of how Z evolves with increasing test duration and increasing temperature.

- Systematically investigate the spatial variation in pore size and volume fraction around individual grains. The main aim of this analysis would be to determine the m factor (Eq. 2.23) for individual grains therefore allowing the Zener parameter calculation to take account of the location of the pores, for example, at triple junctions and along grain boundaries.
• Systematic analysis of the size and distribution of pores as inclusions. This is aimed at establishing the point after $t_0$ at which the migrating boundary brakes away from the pore. This would allow for more rigorous constraint of the grains that underwent early abnormal grain growth.

• Modelling of grain boundary energies and grain boundary migration would complement the experimental study presented here. The data presented here, with the addition of measurements of pore geometry, could be applied to previously existing models of grain boundary migration in the presence of pores (e.g., Yu and Suo, 1999). This would allow the mobility of halite grain boundaries to be quantified in addition to quantifying the mobility and driving force required for pore breakaway to take place.

• Investigate the potential for variation in the crystallographic orientation of grain boundaries, and the orientation of the grains themselves, to be the cause of the observed abnormal grain growth. This would be done through the use of EBSD to map the orientations of the grains. In addition, the interiors of the biggest abnormal grains could be examined for subgrains. This would be a substantial expansion to the work presented here and as such would be appropriate as a separate project.

Part II:

• In a similar fashion to the RUT tests, the calcite clast size could be fixed, for example, at 200 or 500 µm, and the volume fraction varied. This would allow the yield behaviour of halite, calcite contiguity and halite mean free path to be investigated as a function of varying volume fraction at a larger calcite clast size.

• The same constant volume fraction experiments carried out in this study should be repeated with both larger, and smaller, halite grain sizes in order to investigate what, if any, impact a change in halite grain size has on the yield behaviour. Another method of varying the halite grain size would be to hot-press the samples
for durations longer than 3 hours, thus allowing more halite grain growth to take place.

- The 100, 200 and 500 µm calcite clast size constant volume fraction experiments could be repeated at elevated temperature in order to attempt to induce twinning in the calcite. The effect of calcite twinning on the yield stress of the halite and the degree of subsequent load transfer could then be investigated.
13. References


14. Appendix – On disk

All appendices on disk

14.1. Plots used to determine the most appropriate growth exponent for each temperature set

14.2. List of experiments carried out during this study

14.3. Tracings used to determine grain size distributions

14.4. Grain boundary and pore tracings from SEM images used to determine the pore size distributions and the Zener parameter

14.5. Full tabulations and plots for ENGX tests