THE CRYSTAL GROWTH OF SODALITE ZINCOPHOSPHATE OBSERVED USING IN SITU ATOMIC FORCE MICROSCOPY

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Abstract

Atomic Force Microscopy (AFM) was used in order to investigate the crystal growth of sodalite zincophosphate (SOD-ZnPO). For the first time, in situ growth experiments studying an inorganic zeotype were performed.

On the \{100\} face of SOD-ZnPO, an interlaced spiral growth mechanism was observed that was a consequence of a difference in condensation rates between the phosphorus and zinc species adding at the crystal edge. It was found that zinc condensation was slower, and therefore rate limiting. Growth rates on this face were found to be directly influenced by solution stoichiometry, and the importance of solution ageing was also determined.

On the \{111\} face, the importance of extra-framework cations in the growth process was investigated. Monolayer terraces that were propagated by through-extra-framework species bonding were observed as well as bilayers that grew by through-framework bonding. That the cation assisted mechanism was observed suggested the importance of extra-framework species in the growth of nanoporous materials.

Lateral Force Microscopy (LFM) was used to investigate the friction of growing terraces and step edges on the \{100\} face of SOD-ZnPO. On terraces, anisotropic friction was observed that was related to the anisotropic growth. It was found that scanning across rows of zinc atoms on a crystal surface caused an enhanced friction compared to scanning along rows of phosphorus, due to the different friction experienced scanning the different T units. At step edges, enhanced energy was imparted to the tip as a direct result of an increase in growth rate. This was attributed to an increase in shear strength due to increased kink density at higher growth rates.
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Chapter 1

An Introduction to Nanoporous Materials and Crystal Growth
1.1 Aims and Objectives

The aim of this thesis is to study the crystal growth of the sodalite zincophosphate zeotype by *in situ* atomic force microscopy. These zeotypes have been selected for analysis since they are isostructural to aluminosilicate zeolites, whilst having mild synthetic conditions (room temperature and pressure). The motivation for studying the crystal growth of these materials is that by understanding the fundamental aspects of the growth, a greater control over synthetic products can be achieved. This could lead to more selective syntheses, with greater control over the morphology, size and occurrences of defects in the crystal.\(^1\)

In Chapter 1, nanoporous materials will be introduced, describing the structures, synthesis and mechanisms of growth in particular for the zincophosphate family of materials. This chapter will also introduce the key concepts in crystal growth that will be drawn upon throughout this thesis.
1.2 Nanoporous materials

1.2.1 Zeolites

Zeolites are the most well-known examples of nanoporous materials. These are crystalline aluminosilicate materials joined together through corner sharing tetrahedra, creating infinite 3D frameworks. The frameworks are generally very open and contain channels (pores) and cavities in which cations and water molecules are located. These cations and water molecules have a high degree of mobility, leading to facile ion exchange and the ready loss and gain of water molecules. This a key feature of zeolites, and leads to one of their industrial applications, which is ion exchange. As well as ion exchange, zeolites exhibit many other features that makes them ideal for use in industry. These include the ‘molecular sieve’ properties, in which the pore size of the zeolite can cause separation of molecules based on size and shape. Other industrial applications of zeolites include catalysis, adsorption and gas separation. Due to the many applications of zeolites, there has been great interest in the study of them over the past half a century.

Zeolites were first reported in 1756 by A. F. Crönstedt, upon the discovery of stilbite. The name zeolite means boiling stone, and is derived from the Greek zein meaning to boil and lithos meaning stone. This name comes from the visible loss of water noted when natural zeolites are heated, which illustrated their ready loss of water. This property of zeolites is known as intumescence.

The first synthetic studies on zeolites were carried out by Richard Barrer and Robert Milton, commencing in the late 1940’s. Barrer’s initial investigations involved the heating of known mineral phases at high temperatures under the action of strong salts, and resulted in the formation of a material with the KFI framework, the first synthetic framework unknown as a natural mineral. Meanwhile, Milton discovered zeolites A and X, two industrially important zeolites. These syntheses were performed under milder conditions than those Barrer was working with, made possible by using more reactive precursors such as freshly precipitated aluminosilicate gels.
Zeolites occur both naturally and synthetically. Natural zeolites can be formed in a variety of geological environments, mainly forming by hydrothermal alteration of volcanic deposits. These natural syntheses tend to take place over times ranging from 50 - 5000 years. There are over 40 natural zeolites known, and over 200 synthetic zeolites known with new discoveries occurring frequently. Although syntheses in the laboratory can attempt to mimic the conditions of natural zeolite formation, the timescale of formation for natural zeolites cannot be replicated.

Zeolites that can be synthesised tend to be industrially more viable, since natural zeolites contain impurities such as quartz, other zeolite phases and amorphous glass, whereas synthetic zeolites are relatively pure. These synthetic zeolites can have structures that are analogous to natural zeolites, and also structures not found in nature, for example the industrially important zeolite A.

1.2.1.1 Zeolite Structures
Zeolites are microporous framework materials. This means that they have a pore size below 20Å. Materials with pore sizes between 20Å and 500Å are described as mesoporous, whilst those with pore sizes greater than 500Å are described as macroporous. Although many framework structures have been discovered, the definition of them as being microporous relies on the removal of the templating amines, leaving clear pore structures. In the case of some zeolite and zeotype materials, the removal of a template, typically an amine, by calcination collapses this pore network, and therefore the material cannot be described as microporous. True microporous materials are those that have shown some reversible adsorption and desorption behaviour.

Zeolites are open-framework materials, made up of TO₄ units (T = tetrahedral atom) linked together through T-O-T bonds to create an infinite 3D network. Due to the connectivity involved, this means that for every T atom present there will be 2 O atoms, giving an overall structural formula of M⁺ₓₙ(ₓAlO₂ySiO₂)ₓH₂O, where M⁺ is a cation present in the pores / channels of the zeolite that balances the negative framework charge created by the presence of Al. There are a large variety of
zeolite structures that can be formed. This structural complexity arises from the way in which the T groups are linked through the bridging oxygen bonds.\(^7\) In order to classify zeolites, designations of the zeolites based on their framework types are used. This is expressed by three capital letters, for example SOD represents materials with the sodalite framework type.\(^{10}\) This definition does not take into account symmetry, framework composition or cell dimensions.\(^3,7\)

The primary building units (PBU’s) of zeolites are the \([\text{SiO}_4]^4-\) and \([\text{AlO}_4]^5-\) T units. The common structural units that combine to make zeolite frameworks are called secondary building units (SBU’s). These are finite units which contain up to 16 T-atoms. Although particular SBU’s may commonly be observed in structures, this does not mean that they are present in the solution as building units for growth; instead they are a way of identifying common structural features of some zeolites. Figure 1.1 shows the SBU’s of zeolites.\(^{10}\) In the figure, the numbers represent the number of T atoms in the SBU.\(^{10}\)
As well as these units, composite building units (CBU’s) can also be used to describe zeolite frameworks. These represent units, such as cancrinite cages, that appear in multiple different frameworks. These differ from SBU’s, since they are not required to be achiral, and they cannot necessarily be used to build a whole framework. Often, frameworks cannot be built up without some of these units sharing edges, corners or faces. They are, however, useful for describing similarities between framework types. An example of this is shown in Figure 1.2, using the sodalite CBU, also known as the β-cage, which is common for the structures of sodalite (SOD), faujasite (FAU), EMT and zeolite A (LTA).
Figure 1.2: Four different zeolite frameworks all containing the same CBU (sodalite cage).\textsuperscript{7}

In zeolite frameworks, a variety of Si / Al ratios are possible, and these can be altered depending on the synthetic conditions.\textsuperscript{3} For frameworks purely made up from Si, there is no associated charge on the framework. However, substitution of $[\text{SiO}_4]^{4-}$ tetrahedra with $[\text{AlO}_4]^{5-}$ tetrahedra leads to a negative framework charge. Therefore, for every Al substituted into the framework, an associated cation will be required in order to balance the charge of the framework.\textsuperscript{3}

1.2.2 Zeotypes
Zeotypes are porous crystalline materials with ‘zeolitic’ properties, but which contain coordination polyhedra of elements other than silicon and aluminium.\textsuperscript{2} These materials have come to prominence ever since the discovery of the aluminophosphate (AlPO$_4$) class of zeotype 1982.\textsuperscript{15} Since these materials were discovered, many new crystalline materials with open-framework architectures
have been discovered, including several types of metal phosphate (MePO) and titanosilicates. In the AlPO₄ systems, there is no overall framework charge. This is because the Al and P exist in a strict 1:1 ratio. For every [AlO₄]⁵⁻ contributing a 1⁻ charge, there is a [PO₄]³⁻ contributing a 1+ charge, making the overall system charge neutral. The use of different elements in the coordination polyhedra has led to many interesting properties to arise, such as the existence of mixed octahedral/tetrahedral coordination observed in the titanosilicates. Many novel framework structures have been produced with zeotypes, for which there are no aluminosilicate analogues.

12.2.1 Zincophosphates
The zincophosphate zeotype materials are a type of metal phosphate that were first synthesised by Gier and Stucky in the early 1990’s. Originally, framework analogues of aluminosilicate materials were reported, such as the faujasite (FAU), sodalite (SOD) and LiA (ABW) frameworks. However, it was soon found that many new framework structures could also be produced that had no aluminosilicate analogues. These included frameworks that exhibited interesting properties, such as the chiral zincophosphate framework (CZP), frameworks with large 24 T pore structures, and frameworks containing helical channels.

Whilst the AIPO frameworks have a neutral framework, the zincophosphate frameworks have a negative overall charge due to the replacement of [AlO₄]⁵⁻ with [ZnO₄]⁶⁻ T units. Therefore, a 2⁻ charge is provided by each zinc tetrahedron, whilst the phosphorus provides a 1+ charge, leading to an overall 1⁻ charge per ZnPO₄ unit. This negative charge is compensated for by the presence of associated cations, which can be from a variety of sources including sodium, lithium and templating amines.

The structures of the zincophosphates in many cases contain a strict 1 : 1 alternation of zinc and phosphorus within the framework. However, zincophosphates have also been synthesised containing Zn-O-Zn linkages. Other unusual structural features observed in zincophosphates include tetrahedral
oxygen atom centred $\text{OZn}_4$ units. These structures have resulted in a $\text{Zn} : \text{P}$ ratio of less than 1, and are unusual due to the tetrahedral environment of the zinc in these $\text{Zn–O–Zn}$ units. For other metals, such as aluminium, Al-O-Al bonds cannot form unless the metal coordination is increased to 5 or 6.

1.2.3 Synthesis of open-framework materials

1.2.3.1 Zeolite synthesis

Generally, the starting point for zeolite synthesis is crystallisation from inhomogeneous gels, created from silica and alumina sources, combined with water under high pH conditions. The majority of synthetic zeolites are formed under non-equilibrium conditions, which can lead to formation of metastable phases. Upon changing framework elements, the conditions for synthesis also change.

The typical synthetic conditions required for zeolite synthesis are high temperatures (80 - 200°C) and pressures. For aluminosilicate synthesis, a high pH is also required, since Si becomes less soluble with lower pH. In the case of AlPO synthesis, however, a more neutral or slightly acidic pH is required. For the zincophosphates, a wide range of pH’s can produce zeotype materials, mainly at neutral to high pH.

The mechanisms of zeolite formation are complex, due to the amount of reactions, equilibria and solubility variables occurring in the synthesis mixture. The nucleation process seems to be kinetically rather than thermodynamically controlled. The kinetic variables that will therefore determine the products obtained include the treatment of reactants prior to crystallisation, as well as their chemical and physical nature.

1.2.3.2 Zincophosphate syntheses

The syntheses of the zincophosphates first reported were typically gel based syntheses performed under much milder conditions compared to zeolite conditions, with a temperature range of 4 - 70°C, as opposed to the typically
>100°C temperatures for zeolites.\textsuperscript{24} The pH of reaction can vary, typically from neutral to more basic pH (ca. 10).\textsuperscript{29} In general, these syntheses incorporate structure directing amines, although some such as sodalite could be achieved without an organic template.\textsuperscript{17} The zincophosphates are generally thermally unstable, and removal of amines from frameworks has also proven to be difficult, resulting in collapse of the framework.\textsuperscript{12} There have, however, been some reports of zincophosphate frameworks that have similar thermal stabilities to the zeolites\textsuperscript{26, 30} and several frameworks have now been achieved under hydrothermal conditions.\textsuperscript{31}

As well as typical gel reactions, zincophosphates have also been synthesised by a solid state conversion that involved grinding of the reactants.\textsuperscript{32, 33} As well as this, reverse micelles have been used in order to perform controlled growth. These experiments were performed on FAU and SOD zincophosphates, which were analogues of well-known zeolites.\textsuperscript{34-38}

1.2.3.3 The mechanism of metal phosphate syntheses

Several mechanisms have been proposed in order to explain the formation of phosphate based microporous materials.\textsuperscript{30} For alumino- and gallophosphates, Férey found that for a wide range of oxyfluorinated phosphates, the structures were described by very few secondary building units (tetramers, hexamers and octamers).\textsuperscript{39} It was suggested that the reaction was governed by the action of the amines, in particular their charge density. This would act to determine the size and charge of the oligomeric building units in the solution, which would grow until they matched the amine charge density. Once the ammonium-SBU pair formed it could infinitely condense, with steric effects and amine flexibility then influencing the structure formed.\textsuperscript{39}

Investigations into the growth of ZnAPO-34 used the simultaneous use of multiple \textit{in situ} techniques in order to probe the mechanism of growth.\textsuperscript{40} By using several techniques together, a wealth of information about the solution chemistry of growth was obtained. For hydrothermal growth from a gel, it was found that the
initial gel was heterogeneous, ranging from simple cationic species up to polymeric gel species. Upon heating, the gel became more homogeneous, suggesting this is possibly a pre-condition for crystallisation.\textsuperscript{40} It was also found that zinc played a nucleating role in the synthesis, as evidenced by the production of more crystalline material with increasing amounts of Zn\textsuperscript{2+}.\textsuperscript{40}

For aluminophosphates, the isolation of several 1D chain and 2D porous layer type materials has suggested that these could be precursors to the 3D frameworks.\textsuperscript{41} For growth of CoAPO-5, a multi-technique \textit{in situ} measurement approach was taken to investigate the growth.\textsuperscript{42} This led to a mechanism being proposed whereby Al – O – P chains with a poorly ordered structure separated by template molecules would begin to condensate from an initial amorphous gel, followed by reorganisation into the 3D AFI structure.\textsuperscript{42}

Studies into zincophosphate syntheses have led to the isolation of several 2D materials, 1D laddered materials, 1D layered materials, and 0D monomers, suggesting that these may be similar precursors as in the AlPO\textsubscript{4} syntheses.\textsuperscript{12, 43-46} These materials have been used to try to understand the mechanism resulting in the formation of the intricate 3D structures produced in the hydrothermal syntheses. It has been shown that interconversions of these materials can be performed, such as the transformation of one-dimensional ladder zinc phosphates to 2D and 3D structures. From this, it was suggested that open framework structures are built from conversion of these simpler sub-units.\textsuperscript{47}

In all of the zincophosphate investigations, organic structure directing templates were used. In some cases, amines were replaced with the corresponding amine phosphates. Neeraj \textit{et al.} found that use of these amine phosphates allowed the more complex structures to form, often having a strong structural resemblance to the initial amine phosphate.\textsuperscript{48} From this work, it was suggested that amine phosphates are intermediates in the synthesis of zincophosphates.\textsuperscript{48}
1.3 Crystallisation

Crystallisation is the process in which randomly organised molecules, atoms or ions come together, forming an ordered 3D molecular array. These processes are influenced by many factors including reactant concentration, temperature, pressure and impurities. The understanding of the mechanism of crystallisation is of importance, since this would allow the control and optimisation of crystal properties. This could lead to control over the size and shape of crystals produced, as well as control over defect concentration. All of these factors will affect performance in industry, and so an understanding of the crystallisation process is important.\textsuperscript{49-53}

1.2.1 Driving Force

For any chemical process to occur there must be a driving force. The driving force for crystallisation is the difference in chemical potential of growth units in the solution and crystalline phase, $\Delta \mu$, which is defined in Equation 1.1:

$$\Delta \mu = \mu_s - \mu_c$$  \hspace{1cm} (1.1)

Where $\mu_s$ is the chemical potential of the solution phase, and $\mu_c$ is the chemical potential of the bulk of the crystalline phase. Since any change in a system must lead to a decrease in free energy, this difference in chemical potential becomes a driving force for crystal growth when $\Delta \mu > 0$. At this point, the solution is described as supersaturated. In the case of $\Delta \mu < 0$ the solution is described as undersaturated, whilst for $\Delta \mu = 0$, the solution is described as saturated and is in equilibrium with respect to the crystals. The driving force can be described by the following:

$$\Delta \mu = kT \ln S$$  \hspace{1cm} (1.2)

Where $k$ is the Boltzmann constant (J K$^{-1}$), $T$ is the absolute temperature (K), The term $S$ is the supersaturation ratio. For nucleation from solutions, this is defined as:
\[ S = \frac{\prod a_i^n_i}{\prod a_{le}^{n_i}} \]  

(1.3)

Where \( n_i \) is the number of \( i \)th ions in the molecule of the crystal, and \( a_i \) and \( a_{le} \) are the actual and equilibrium activities of the \( i \)th molecule in the crystal.\(^{54}\) A typical approximation for solution growth involves using the actual and equilibrium concentrations rather than activities of the ions to describe the supersaturation ratio \( \{S\} \).\(^{49}\) This allows the solubility to be used in order to calculate the supersaturation of the solution. Figure 1.3 shows a hypothetical solubility curve. In this case, the solid line represents the equilibrium concentration of the ions in solution, or saturation \( (c_{eq}) \). At this point the chemical potential \( (\Delta \mu) = 0. \)\(^{52}\) Below this line, the solution is said to be undersaturated, and in this case dissolution will occur. Above this line, the solution is supersaturated and the conditions for crystallisation and growth are met. The metastable region, indicated on the graph as the region in between the solid and dashed line, is the region in which the solution is slightly supersaturated, but no nucleation is observed.

In Figure 1.3, there are two ways in which a supersaturated solution can be created from point \( x \). In one case, moving along the black line to point \( a \), a decrease in the temperature, or undercooling, creates a supersaturated solution.\(^{49}\) The other way to create a supersaturated solution is by increasing the concentration, which can achieved by evaporation of solvent.\(^{52}\)
Nucleation

The first stage of crystallisation is the nucleation phase. Gibbs observed that this process required the formation of clusters of building units within the supersaturated ambient phase. Out of the many clusters formed in the solution, some of these will be of or above the critical size (radius), \( r_c \), and will go on to the growth stage (Figure 1.4).\(^5^5\) Those clusters below this size will re-dissolve into solution. In order for nucleation to occur, the local environments must be under high supersaturation; otherwise the clusters will be unstable and dissolution will occur. Once clusters reach this critical size, growth will continue even under normal supersaturation conditions.\(^4^9\)

The classical nucleation theory, originating from the work of Gibbs, is based on condensation of a vapour phase to a liquid phase. This theory can be transferred to nucleation of solids from solutions.\(^5^6\) A simplification made by this theory is the assumption of spherical nuclei. This theory is valid at small or moderate supersaturation; however it is less applicable at higher supersaturation.\(^5^5\)

The critical size of a nucleus is the point at which enough matter has come together in order that the volume excess free energy of formation of the bulk solid...
offsets the entropically unfavourable formation of a surface, known as the surface excess free energy. This surface energy is unfavourable as molecules are moved into a much more ordered environment. The surface excess free energy is given by:\textsuperscript{52}

\[ \Delta G_s = 4\pi r^2 \gamma \]  

(1.4)

Where \( \Delta G_s \) is the surface excess free energy, \( r \) is the radius of the nucleus and \( \gamma \) is the surface energy of the nuclei. The volume excess free energy, \( \Delta G_v \), represents the free energy of formation of the bulk solid and is proportional to nuclear volume. This is given by:

\[ \Delta G_v = \frac{4}{3} \pi \frac{r^3}{V} \Delta \mu \]  

(1.5)

Where \( V \) is the volume of the nucleus. Combining these two equations gives the total Gibbs free energy for the process, \( \Delta G \):

\[ \Delta G = -\frac{4}{3} \pi \frac{r^3}{V} \Delta \mu + 4\pi r^2 \gamma \]  

(1.6)

At equilibrium, both of these terms will be equal. The size of the nucleus at this point defines the critical nucleus size, \( r_c \).\textsuperscript{57}
Figure 1.4 shows a plot of the free energy, $\Delta G$, as a function of the radius of the nucleus, $r$. As the size of the nucleus increases, $\Delta G_s$ will increase (unfavourable) due to the increased surface size contributing to this term. Meanwhile $\Delta G_v$ will decrease (favourable) as more bulk solid is formed. On the combined curve describing the overall free energy (dashed line), the critical nucleus size $r_c$ is marked. If the nucleus size is less than $r_c$ then the only way to decrease free energy is by dissolution. Above the critical size, a decrease in free energy is obtained through growth of the nuclei. Since the solution is in dynamic equilibrium, there will be moments in which nucleation processes will become temporarily favourable. Coupled to this, nucleation can be assisted by foreign particles or impurities, a process known as heterogeneous nucleation. If nucleation is unaided by impurities in the solution, then it is known as homogeneous nucleation.\(^7\) Heterogeneous nucleation will reduce the free energy for the reaction, since the surface interaction between the nucleus and the particle will reduce $\Delta G_s$.\(^{55}\) This effect is enhanced when the particle has a better match with the nucleus, meaning that it is most influential when the particle and the nucleus are the same structure. This is known as secondary nucleation, and gives the lowest energy barrier for nucleation.\(^{54}\)
The size of the critical nuclei is related to the supersaturation of the reactant solution. This is shown in Figure 1.5, where the Gibbs free energy for nucleation is plotted against the radius of the nucleus, or cluster size. The red line represents a high supersaturation solution, whilst the blue line represents a low supersaturation solution. As well as a smaller critical nucleus size, increasing supersaturation also decreases the free energy barrier for nucleation.\textsuperscript{49,57}

\[ \Delta G \]

\[ f_c \]

\[ r \]

\[ \text{Figure 1.5: The effect of supersaturation on the critical nucleus size. The red line shows high supersaturation compared to the low supersaturation represented by the blue line.} \]

The nucleation rate, \( J \), is the number of viable nuclei formed per unit of time. For thermally activated processes, this can be described by the Arrhenius equation:

\[ J = Ae^{\left(\frac{-\Delta G^*}{kT}\right)} \]  \hspace{1cm} (1.7)

where \( k \) is the Boltzmann constant (1.38 x 10\(^{-23}\) J K\(^{-1}\)), \( T \) is the temperature and \( \Delta G^* \) is the free energy barrier that must be surpassed for nucleation. This is the free energy at \( r_c \). The rate of nucleation is therefore affected by degree of supersaturation, since this has an effect on the size of \( \Delta G^* \). A plot showing this relationship between nucleation rate, \( J \), and supersaturation is shown in Figure 1.6.\textsuperscript{54,58} This figure shows that there is no nucleation for supersaturation conditions up to \( \Delta \mu_c \), which is known as the critical supersaturation for nucleation.
The region below this supersaturation represents the metastable zone that was shown in the solubility curve earlier (Figure 1.3).

![Figure 1.6: The dependence of nucleation rate on supersaturation. $\mu_c$ gives the critical supersaturation.](image)

1.3.2.1 Induction Time

The induction time related the elapsed time between the achievement of a supersaturated solution and the observation of nucleated crystals. This period of time is influenced by a variety of factors including supersaturation, solution stirring and viscosity.\(^{57}\)

1.3.2.2 Nucleation of zeolites

The process of nucleation for zeolites is thought to follow the same pattern as described above, even though the precursors are more complex than for simple ionic systems.\(^{7}\) It has been predicted that the critical nucleus size for zeolite synthesis has been estimated at 1 – 8 unit cells,\(^{59}\) however this will be influenced by the structure being formed and experimental conditions.\(^{8}\)

1.3.3 Crystal Growth

Crystal growth is the second part of crystallisation, in which the nuclei formed continue to grow by incorporating further growth species into the crystal surface. For crystal growth, the species that add to the surface can be atoms, molecules or large clusters, which attach to the crystal at different types of sites.\(^{53}\) The processes that govern crystal growth can be split into two parts. The first is surface
processes, which include the attachment of atoms to the surface and their subsequent diffusion and attachment to the crystal surface. The second is related to transport, and is related to the movement of growth species in solution. These processes are shown schematically in Figure 1.7a. The associated energy changes and barriers associated with the processes are shown in Figure 1.7b. In general, the overall rate of crystal growth will be dominated by whichever of these processes is rate limiting.60

1.3.3.1 Energies involved in crystal growth
In solution growth, mass transfer plays a crucial role in the overall growth rate.51 When nucleation occurs, there will be a decrease in concentration in the surrounding area as growth species are incorporated into the crystal. To compensate for this, bulk diffusion occurs in order to balance the concentrations. Since constant incorporation of growth species into the crystal will maintain a reduced concentration directly surrounding the crystal, there will be a permanent sharp diffusion gradient between this low concentration area and the bulk solution. This region is known as the diffusion boundary layer.51 This region is important for crystal growth. The driving force for diffusion is considered to be the difference, and its gradient, between the concentration at the outer region of the boundary diffusion layer and the concentration at the surface (surface supersaturation).51 If diffusion across this boundary layer is slow, then this process will affect the supersaturation on the surface. The energy change related to the diffusion boundary layer is shown in Figure 1.7b, labelled (2).

The other energies showed in Figure 1.7b are for the diffusion processes, both at step edges and on the crystal surface, the energy for incorporation to the crystal and the energy for adsorption and desorption on the surface. Following the energy profile, it can be seen that during adsorption onto the surface (energy barrier 3), the overall energy decreases. This positive free energy process is related to the entropic contribution of partial desolvation of the adsorbed species.51 The opposite is true for desorption. For incorporation to a step edge, then fully into the crystal, further desolvation will occur which will cause a decrease in free
energy. These desolvation processes are represented in the schematic representation by the black arrows on white solvent circles. Unlike for the other processes, surface diffusion does not lead to a change in the overall free energy.

Figure 1.7: a) Schematic representation of the processes involved in crystal growth and b) the associated energy changes for these processes. The processes are 1) Transport of growth species, 2) diffusion through the boundary layer, 3) adsorption onto the surface, 4) surface diffusion, 4*) surface desorption, 5) attachment to a step edge, 6) diffusion along the step edge, 7) addition to a kink site or an edge site.

1.3.3.2 Introduction to the Kossel Model

On a smooth crystal surface, there exist different types of sites to which atoms may attach. One simplification used in order to describe a crystal surface is the Kossel model. This treats the growth units of a material as cubes, simplifying the site types that exist on a crystal surface. This model is shown in Figure 1.8.
Depending on the type of sites on the surface, different numbers of bonds will be formed between the cube and the surface. An atom binding to the surface will only make connection on one side, whereas in edge sites there will be two, in kink sites there will be three and for U sites there will be four bonds to the surface. This means that for addition to these different sites, there will be different free energies associated. The free energy associated with attachment to surface sites will be the lowest, whilst edge vacancy attachment will result in the largest excess free energy making this process most favourable. In general, kink, edge and surface sites are typically considered since these are the most common types of site.

1.3.3.3 Growth Mechanisms on a smooth surface

For crystal growth to occur on a surface, when defects are not considered, a layer-by-layer growth mechanism is required. As growth units diffuse on the surface, these will be incorporated into kink sites more favourably, leading to the advance of existing layers, or terraces. This process is shown in Figure 1.9a and 1.9b. When growth units do not incorporate into sites at a step edge, they can either undergo desorption back into solution or join other growth units on the surface, forming islands or two dimensional (2D) nuclei. The circumference of these nuclei will then provide sites onto which attachment can occur, which leads to growth of these new layers laterally across the surface. A 2D nucleus is shown forming between figure 1.9b and Figure 1.9c, resulting in the generation of a new layer. The rate of
nucleation of new 2D nuclei depends on the supersaturation of the solution. When supersaturation is high enough such that nuclei are able to form in several places, and on top of each other, this is known as birth and spread growth.  

Figure 1.9: Representation of birth and spread growth. In a), a growth unit is diffusing on the crystal surface, preferentially adding to kink sites. In b), the layer is advanced through subsequent additions to kink sites. In c), a 2D nucleation event is required to continue growth normal to the crystal surface.

When the crystal surface being grown is not perfect, it will contain outcropping screw dislocations. In this case a spiral growth mechanism can also occur. For this mechanism 2D nucleation is not required in order to continue growth normal to the crystal surface, since the defect creates a never ending supply of edge and kink sites. Since no 2D nucleation is required, these spiral growth centres will grow at lower supersaturations than those crystals that require 2D nucleation upon the completion of a growth layer. Figure 1.10 shows how a spiral centre evolves from a screw dislocation.
1.3.3.4 Dependence of growth mechanism on supersaturation

The mechanism by which a crystal grows is related to the supersaturation. As mentioned, at low supersaturations crystal growth will occur by a spiral growth, while at higher supersaturation growth will occur by a birth and spread mechanism. This is shown in Figure 1.11. So far, these considerations have considered growth on a smooth surface. However, at even higher supersaturations, the surface will become rough and the growth mechanism will change to an adhesive type growth.\textsuperscript{51} For this type of growth, attachment energetics are not direction dependent, leading to crystals bound by round non-crystallographic faces.\textsuperscript{54}
Figure 1.11: Graph showing the different growth mechanisms on a crystal surface as a function of supersaturation.

1.3.4 Batch gel crystallisation

For batch crystallisation of syntheses that include amorphous precursors, such as nanoporous material growth from gels in closed vessels, there are three main stages that describe the growth process, shown in Figure 1.12. The first stage represents the induction period and initial crystal growth, where growth species are becoming exponentially available in the solution. This period includes the induction time explained in 1.3.2.1. In stage two, the supersaturation remains at a constant high and linear growth of crystals is observed. The supersaturation is maintained as gel dissolution replenishes species incorporated into the growing crystal, creating steady-state. Finally, for stage three, nutrient depletion is observed, meaning supersaturation falls. When this happens, crystal size remains relatively constant.
Figure 1.12: Showing the three stages of growth observed in batch syntheses for gel growth.

1.3.5 Crystal Morphology

Crystal morphology is primarily influenced by the point group symmetry of the unit cell.\(^{64}\) This dictates a range of morphologies that are possible for a crystal of that symmetry. The actual morphology observed then depends on the growth rates of the different crystallographic faces.\(^{57}\) For example, in Figure 1.13 four possible morphologies of a cubic crystal are shown. In Figure 1.13a, the morphology of a crystal bound by the \{100\} face is shown, giving a cubic morphology. In Figures 1.13b and 1.13c, the morphologies of crystals bound by the \{110\} and \{111\} faces are shown giving rhombic dodecahedral and octahedral morphologies respectively. Finally, a crystal expressing all three crystal faces is shown in Figure 1.13d.

The faces that have the largest effect on the morphology are those that grow the slowest. Overall, the growth rate of each face is determined by the energetics of molecule attachment / detachment processes.\(^{49}\) The growth rate of a crystal face can therefore be influenced by environmental conditions such as temperature, solvent and supersaturation, as well as crystal structure factors including the presence of defects.\(^{57}\) The final morphology of crystals that are synthesised may
not necessarily reflect the equilibrium morphology, which relates to a minimisation of the surface free energy of the crystal. During growth, the morphology observed can instead be dominated by the kinetics of growth.49

Figure 1.13: Four different morphologies from a cubic point group, with crystals bound by a) the \{100\} face (cube), b) the \{110\} face (rhombic dodecahedron), c) the \{111\} face (octahedra) and d) the \{100\}, \{110\} and \{111\} faces.

Since the growth rates of different crystal faces determine the overall morphology, then by influencing these rates morphology can be controlled. In the synthesis of nanoporous materials, different additives can affect the growth rates of specific faces, acting as habit modifiers. For example, in Zeolite L synthesis, 21-crown-7 addition acts to poison growth in the ‘c’ direction, whilst increasing growth in the ‘a’ direction.65 This leads to the shortening of these hexagonal cylinder shaped crystals. In a 1D pore system such as Zeolite L, this type of habit modification is particularly important, since the diffusion path-length into the pores will be shortened by shortening the ‘c’ direction, leading to improved effectiveness in industrial processes.65
As well as controlling the shape of crystals, the size can also be influenced depending upon growth rates. Crystal size is important in industrial applications, with different processes requiring different crystal dimensions. For example, shape-selective catalysis requires large crystals, whilst smaller crystals provide a large surface area, making them more efficient in catalysis. The size of crystals that are produced is related to the ratio between crystal nucleation and growth. At higher supersaturations, the ratio will move in favour of nucleation, meaning smaller crystal size, whilst at low supersaturations larger crystals will grow. Since the supersaturation in gel growth is more complex, several factors will influence the supersaturation, such as the rate of gel dissolution and other factors including seeding and whether or not the synthesis is stirred.

1.3.5.1 Crystal Twinning

Intergrowth is a phenomenon whereby two or more crystals interact and coalesce. Twinning is a special type of intergrowth. Crystals can be defined as twins as long as all of the crystallographic orientations of the two crystals are related by either a mirror plane of symmetry (the twin plane), a 2-fold plane of symmetry (twin rotation) or a centre of symmetry (twin centre). Depending on the type of symmetry that relates the intergrowth twins, they can be described as either reflection twins, rotation twins or centrosymmetric twins. As well as defining the twins by symmetry, they can also be related by the spatial relationship, which is defined by the way they are intergrown. There are two different types of spatial relationship; contact twins or penetration twins. For contact twins, the crystals are attached on a specific plane (composition plane), and that by cutting along this plane the two crystals could be separated. Penetration twins, meanwhile, are defined as twins for which no compositional plane exists that cutting along would end with the clean separation of the two crystals.

In Figure 1.14a a contact twin is shown, whilst Figure 1.14b and 1.14c show penetration twins. If crystals aggregate with their crystallographic axes mutually parallel then this is called a parallel growth. In this case, the altered morphology still represents a single crystal, since the same internal structure is maintained.
throughout the specimen.\textsuperscript{58} An example of parallel growth is shown in Figure 1.14d.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{example.png}
\caption{Schematic examples of a) a contact twin, b + c) penetration twins and d) parallel growth. Separate crystals are coloured differently in each example.}
\end{figure}

The occurrence of crystal twins increases with increasing supersaturation of the precursor solution, as this provides the driving force to overcome the interface energy. This interface energy is the energy required to overcome the mismatch at the point of twinning. The degree of mismatch is also important, with closer framework alignment of twins leading to a lower interface energy.\textsuperscript{51}

The consideration of crystal twinning is of importance for nanoporous materials, since this intergrowth could potentially affect crystal properties. For example, one of the most widely used zeolites in catalysis is ZSM-5.\textsuperscript{27} Crystals of ZSM-5 only exist as twins,\textsuperscript{69} which results in two different barriers for molecular diffusion in crystals; one on the surface and one relating to 90 °mismatch in structure.\textsuperscript{70}
1.4 References

55. D. Kashchiev and G. M. van Rosmalen, *Crystal Research and Technology*, 2003, **38**, 555-574.
Chapter 2

Synthesis and Characterisation of Sodalite

Zincophosphate
2.1 Aims and Objectives

The aim of this chapter was to explore the synthesis of Sodalite Zincophosphate. More specifically, the aims were to:

- Synthesise sodalite crystals of a suitable size for AFM investigations
- Explore the effects of pH, temperature, water content and Zn : P ratio on the sodalite synthesis
- Investigate substitutions of cations and framework substituents in this system
- Investigate the long term stability of sodalite zincophosphate
- Understand the morphology of sodalite zincophosphate
2.2 Introduction

2.2.1 Sodalite

The sodalite framework (SOD) is comprised of truncated octahedral cages known as sodalite cages, or β-cages, that are fused together through 4-rings (or 6-rings) to create the framework. The structure of this framework was initially determined by Pauling using the aluminosilicate version of this material, \( \text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NaCl})_2 \). Sodalite materials can occur naturally, and can also be synthesised. Although initial syntheses gave Si : Al of 1, it has since been shown that high silica forms of sodalite can also be synthesised, up to and including the all silica framework. Unusually for zeolites, a Si:Al ratio < 1 is also possible. The Al – O – Al linkages that must exist for this arrangement are typically considered highly unfavourable, as stated by Lowenstein’s rule. However, there have been several exceptions to this rule. There also exists a purely aluminate sodalite. Both natural and synthetic versions can accommodate a large variety of compositional variation, with framework atom substitutions including Be, Ga, Ge, P, Zn and As. As well as this, many different types of guest species can be accommodated within the sodalite cage itself. The type of guest species present will depend on the framework substituents. For example, if the framework is aluminosilicate, then a cation will be required to balance the charge for every aluminium present.

Sodalite framework materials have been of interest owing to potential applications in a range of processes, such as storage of hydrogen, storage of the nuclear waste product \(^{85}\text{Kr}\), photochromism and removal of water / small molecules in industry. The study of sodalite is also important, since the sodalite cage, or β-cage, is a common structural unit in a variety of other frameworks, such as LTA, EMT and FAU.
2.2.1.1 Sodalite Zincophosphate

Sodalite zincophosphate (SOD-ZnPO) was first discovered in 1991 by Nenoff et al. This is isostructural to aluminosilicate sodalite, both of which require cations in order to balance a negative charge, and has overall stoichiometry of Na$_6$(ZnPO$_4$)$_6$.8H$_2$O. For zinc phosphate sodalite, a strict 1:1 alternation of Zn and P is observed, whereas in the aluminosilicate sodalite the Si:Al ratio does not necessarily have to be 1:1. For this reason, the space groups differ, with aluminosilicate sodalite having Im$ar{3}$m space group, whilst the zincophosphate has P$ar{4}$3n space group. The unit cell is the sodalite cage, which has a truncated octahedral shape, and is shown in Figure 2.1. In Figure 2.1a the structure is shown including the bridging oxygens (gold). However, the inclusion of the bridging oxygens makes the figure complex. Therefore, in order to simplify this, oxygen atoms will typically be omitted from structural diagrams. The same sodalite structure is shown in Figure 2.1b, but with oxygens omitted. Coupled to this, the positions of the extra-framework cations (pink spheres) are also displayed. The unit cell length, $a$, has been reported as 0.8824 nm. From thermogravimetric analysis, SOD-ZnPO has been found to be relatively unstable. At 142°C, it loses all 8 water molecules (11.5 % weight loss), converting into a hexagonal phase.

![Figure 2.1: a) Structural diagram of SOD-ZnPO showing the unit cell, with Zn coloured red, P coloured blue and oxygen coloured gold (cations omitted for clarity), and b) Structural diagram of SOD-ZnPO showing the unit cell, including extraframework cation positions in the cage. Oxygen atoms are omitted here for clarity.](image-url)
There have been several different methods developed for the synthesis of SOD-ZnPO. As well as the initial solution-based synthesis, a method was introduced whereby the reaction could be performed by grinding the substrate crystals.\textsuperscript{18, 19} This relied on one of the substrates containing the crystallisation water, and could be useful for encapsulation of compounds within the cages, as shown by the encapsulation of CdS, hydroquinone and pyridine. Within these syntheses, the ratios of Zn : P : Na were kept similar to those used in the solution method.

Another method of synthesising SOD-ZnPO was by using reverse micelles.\textsuperscript{20, 21} In this method, the zinc and phosphate species were introduced to the aqueous centre of separate micelles dispersed in an organic solvent. This meant that the crystallisation was controlled by the kinetics of the collisions and exchange of these micelles. These crystals nucleated on the surfactant – water interface, and were small (several hundred nm). As well as small crystal size, different morphologies were observed compared to crystals synthesised in solution, with crystals bound by the \{111\} face. Unlike the typical syntheses, the reverse micelle method did not proceed via an amorphous phase. By performing this type of synthesis, the authors reported more control over crystal growth kinetics due to changes in pH.\textsuperscript{22}

\subsection*{2.2.2 Experimental Techniques}

\subsubsection*{2.2.2.1 Powder X-ray Diffraction}

Powder X-ray diffraction is a powerful technique that can be used to identify samples. This technique measures x-rays as they are diffracted from a sample. In ordered solids, diffraction occurs at regular spacing (d-spacing) related to the unit cell of the solid.

In order to produce x-rays, copper is bombarded with high energy electrons, releasing Cu $K_\alpha$ radiation that is used as the x-ray source. This is generated when the bombardment of the Cu with electrons is able to displace electrons in the $K$ shell ($n = 1$) of the Cu, creating an excited state. As electrons relax from the $L$ ($n = 2$) and $M$ ($n = 3$) shells into the $K$ shell, the excess energy of this process is released...
as an x-ray photon. The x-rays emitted from relaxation from the M shell to the K shell are described as $K_{\beta}$, whilst the emission from relaxation from the L shell to the K shell is described as $K_{\alpha}$ radiation. For Cu $K_{\alpha}$, the wavelength of the x-rays is 0.154 nm. This x-ray source is used, since the wavelengths are required to be of the order of interatomic spacing in order to produce interference.\textsuperscript{23}

Once generated, the x-rays are scattered off the sample to be probed at specific angles. Peaks will occur when two waves interfere constructively with each other, as shown in Figure 2.2. If the waves are not in phase, their interaction is destructive and no peak is observed. The x-rays diffract from the periodic arrangements of atoms in a crystal, as with visible light diffracting from a grating. The diffraction from a crystal can be represented by Bragg’s law, shown in equation 2.1.\textsuperscript{24}

\begin{equation}
    n\lambda = 2d \sin \theta 
\end{equation}

Where $n$ is the order of the reflection, $\lambda$ is x-ray wavelength, $d$ is the d-spacing (spacing between planes in the atomic lattice) and $\theta$ is the angle of incidence, as shown more clearly in Figure 2.3. For a given d-spacing, a peak will occur in the diffractogram when the angle of incidence is such that constructive interference occurs between scattered x-rays. By probing the sample over a range of angles, a pattern will arise corresponding to the angles at which constructive interference is achieved for different d-spacings within the sample. This pattern will be unique to the material being studied, and can thus be used to “fingerprint” in order to identify new samples by comparison to reference patterns.\textsuperscript{24}
Figure 2.2: a) constructive interference between two waves that are in phase and b) destructive interference between two waves that are out of phase.

Figure 2.3: Bragg’s law reflection. When the difference between path 1 and path 2 is an integer number of wavelengths, the diffracted x-ray will experience constructive interference.

2.2.2.2 Scanning Electron Microscopy

The first Scanning Electron Microscope (SEM) was invented by von Ardenne in 1938, when the electron beam of a transmission electron microscope was rastered, essentially creating a scanning transmission electron microscope. Since then, microscopes for imaging bulk samples were introduced by Zworkin in 1942, whilst commercially available microscopes have been available since 1965.
The operation of the SEM is achieved by applying a voltage between a conducting sample and a filament, resulting in electron emission from the filament to the sample. The electrons are then guided to the sample through a series of electromagnetic lenses in the electron column. A typical SEM schematic is shown in Figure 2.4. The beam current and spot size are controlled by one or more condenser lenses and the probe-forming objective lenses.25

![Figure 2.4: Typical schematic of an SEM, from reference 26](image)

The beam interacts with the sample, leading to electrons being emitted from the sample, primarily as secondary electrons and backscattered electrons. It is usually the signal generated by secondary electrons that is observed. These secondary electrons are produced as a result of interactions between the electron beam and the weakly bound electrons in the conduction band of the sample. Some energy is
transferred to these from the beam, providing the energy for their escape as secondary electrons. These are low energy electrons (<50 eV) and therefore only those formed in the first few nanometres of the sample surface have enough energy to escape and be detected.

The escaping electrons are typically detected by an Everhart-Thornley detector. The resulting image is formed from the intensity of the secondary electron emission from the sample at each x, y data point during rastering of the electron beam across the surface.

In order to perform chemical analysis of the sample, emergent x-rays are measured. These are element specific allowing quantification of the specimen elemental composition. This technique is known as energy dispersive x-ray spectroscopy (EDS).
2.3 Experimental

2.3.1 Synthetic procedures

**Standard Gier and Stucky synthesis and temperature variation:** Zn(NO$_3$)$_2$·6H$_2$O (3.57 g, 0.012 mol), was added to NaBr (1.03 g, 0.02 mol) and 85 % H$_3$PO$_4$ (1.73 g, 0.015 mol) in H$_2$O (15 g), and mixed until clear (molar Zn : P is 0.8 : 1). A second solution was also prepared, mixing NaOH (1.68 g, 0.042 mol) with H$_2$O (21 g). These two solutions were combined and shaken until a homogeneous white gel was produced. After 1 day, the crystals were recovered by filtration and washed using H$_2$O (1 dm$^3$), followed by drying at 50 °C. For temperature variation experiments, the bottles were transferred either into the oven or refrigerator once the homogeneous gel was formed. The temperatures tested were 4°C, 15°C (± 5), 25°C, 35°C, 45°C, 55°C, 65°C and 70°C.

**Diluted synthesis:** The masses used in the diluted synthesis were the same for all constituents except H$_2$O. For this, the total masses used were 36 g (no dilution) 74 g (50 %) 92 g (40 %) 99 g (30 %) and 145 g (20 %). These were then split into solution A and B in the same ratio as in the initial experiment. The synthesis was performed over 1 week at room temperature. Crystals were recovered and washed using H$_2$O (1 dm$^3$), followed by drying at 50 °C.

**pH variation:** Zn(NO$_3$)$_2$·6H$_2$O (3.57 g, 0.012 mol), was added to NaBr (1.03 g, 0.02 mol) and 85 % H$_3$PO$_4$ (1.73 g, 0.015 mol) in H$_2$O (15 g), and mixed until clear. HNO$_3$ was then added to this solution if necessary (up to 0.08 g, 0.001 mol). A second solution was also created, mixing NaOH (1.68 – 1.8 g, 0.042 – 0.045 mol) with H$_2$O (21 g). These two solutions were combined and shaken until a homogeneous white gel was produced. By adjustment of the amount of HNO$_3$ added, a pH range of 2 – 7 was investigated. Meanwhile, to reach higher pH, the amount of NaOH was increased, so that a pH range of 7 – 10 was investigated. The syntheses were performed at room temperature for between 1 day and 6 months. Upon completion, crystals were recovered and washed using H$_2$O (1 dm$^3$), followed by drying at 50 °C.
**Zn:P variation:** a) 1.5 : 1 ratio: $\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$ (6.7 g, 0.022 mol), was added to NaBr (1.03 g, 0.01 mol) and $\text{H}_3\text{PO}_4$ (1.729 g, 0.015 mol) in $\text{H}_2\text{O}$ (15 g), and mixed until clear. A second solution was also created, mixing NaOH (1.85 g, 0.046 mol) with $\text{H}_2\text{O}$ (21 g). These two solutions were then combined and shaken until a homogeneous white gel was produced. The gel pH was 7 ± 0.4. After 1 month at room temperature (ca. 23 °C), the sample was recovered by filtration and washed using $\text{H}_2\text{O}$ (1 dm$^3$), followed by drying at 50 °C.

b) 1 : 1 ratio: $\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$ (4.462 g, 0.015 mol), was added to NaBr (1.03 g, 0.01 mol) and $\text{H}_3\text{PO}_4$ (1.729 g, 0.015 mol) in $\text{H}_2\text{O}$ (15 g), and mixed until clear. A second solution was also created, mixing NaOH (1.72 g, 0.043 mol) with $\text{H}_2\text{O}$ (21 g). These two solutions were then combined and shaken until a homogeneous white gel was produced. The gel pH was 7 ± 0.5. After 1 week at room temperature (ca. 23 °C), the sample was recovered by filtration and washed using $\text{H}_2\text{O}$ (1 dm$^3$), followed by drying at 50 °C.

c) 1 : 1.5 ratio: $\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$ (2.96 g, 0.01 mol), was added to NaBr (1.03 g, 0.01 mol) and $\text{H}_3\text{PO}_4$ (1.729 g, 0.015 mol) in $\text{H}_2\text{O}$ (15 g), and mixed until clear. A second solution was also created, mixing NaOH (1.55 g, 0.039 mol) with $\text{H}_2\text{O}$ (21 g). These two solutions were then combined and shaken until a homogeneous white gel was produced. The gel pH was 7 ± 0.7. After 1 day at room temperature (ca. 23 °C), the sample was recovered by filtration and washed using $\text{H}_2\text{O}$ (1 dm$^3$), followed by drying at 50 °C.

**Cobalt Substitution:** This synthesis was performed in the same way as the original paper synthesis. However some $\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$ was replaced with $\text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$ at different ratios. For example, in the 10 % substituted synthesis $\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$ (3.21 g, 0.011 mol) and $\text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$ (0.35 g, 0.001 mol). Where seed crystals were used these were obtained from a previous standard synthesis and placed into solution 1 second before mixing to form the gel. Gel pH was 6.8 ± 0.4
Cation Substitution: For K⁺ substitution, KBr (1.19 g, 0.01 mol) replaced NaBr and KOH (2.42 g, 0.044 mol) replaced NaOH. For Li⁺ substitution, LiCl (0.3 g, 0.007 mol) replaced NaBr and LiOH, (1.861 g, 0.077 mol) replaced NaOH. For K⁺ substitution the pH was 6.5 ± 0.5, and for Li substitution it was 6.8 ± 0.7.

Stability of SOD: This experiment was created to investigate the stability of the SOD crystals under the solution conditions required for AFM. This involved two different methods for investigating the stability. Method 1) One large batch of SOD was synthesised following the method of Gier and Stucky, then once the gel had formed it was split into 4 containers. These were then placed at 5°C (refrigerated room), 25 °C (water bath), 45°C (oven) and 65°C (oven). All samples were rotated throughout. Samples of the crystals were removed periodically and analysed using SEM and XRD. After 6 months, the crystals were retrieved by filtration, then washed with H₂O (1 dm³) and dried.

Method 2) This method investigated the stability of SOD in solutions that did not contain any zinc. Solution preparation was as follows: 1 dm³ of sodium phosphate solution was prepared as follows: H₃PO₄ (11.2 g, 0.097 mol) was added to NaBr (82.3 g, 0.8 mol) in H₂O (800 g) in a 1 dm³ volumetric flask. This was then adjusted to pH 7 ± 0.1 using dropwise additions of a 0.5 M NaOH solution. The solution was then filled to 1 dm³ using deionised water. 0.1 dm³ portions were then used per experiment. For a single experiment, 1 g SOD crystals obtained from a previous synthesis were added to the base solution. These were then placed at 5°C (refrigerated room), 25 °C (water bath), 45°C (oven) and 65°C (oven). All samples were rotated throughout. Samples of the crystals were removed periodically and analysed using SEM and XRD. After 6 months, the crystals were retrieved by filtration, then washed with H₂O (1 dm³) and dried.
2.3.2 Analytical techniques

Powder X-ray diffraction patterns were collected on a Philips X’Pert PRO diffraction system, using the X’Pert Data Collector software. The data were collected in the 2θ range from 2° to 60° at 0.032767°s⁻¹. Data processing was performed using Philips X’Pert HighScore Plus software.

Scanning electron micrographs were taken using an FEI Quanta 200 ESEM operating in high vacuum mode. Samples were prepared by application of crystals to double sided carbon tape, mounting on an aluminium microscope holder then sputter coating with a thin layer of gold.

Energy dispersive spectroscopy (EDS) was used to determine the approximate chemical composition of the crystals. This was carried out using an EDAX EDS detector attached to the SEM operating in high vacuum mode.
2.4 Results and Discussion

2.4.1 Gier and Stucky synthesis

Initial syntheses of sodalite were performed following the standard recipe of Gier and Stucky. From these syntheses, white powders were retrieved, which were analysed by powder XRD and SEM. The powder XRD pattern retrieved is shown in Figure 2.5. By comparison of the 2θ values and peak intensities of the reference pattern and this pattern, the phase could be identified as being SOD-ZnPO.

Figure 2.5: Powder XRD pattern showing synthesised SOD-ZnPO.

Since sodalite is from a cubic space group, the powder pattern can be indexed using the cubic indexing equation shown below (Equation 2.2) in combination with Bragg’s law (Equation 2.1) in order to assign h k l values to the set of planes giving rise to each diffraction peak and calculate the lattice parameters, a.

\[ a^2 = (h^2 + k^2 + l^2) d^2 \]  

(2.2)

Where \( d \) is the d-spacing (distance between planes), \( a \) is the unit cell length and \( h, k \) and \( l \) are the miller indices. This was performed for SOD-ZnPO\(_4\), as shown in Table 2.1 below. For the first row, the \( h k l \) values were guessed, then \( a \) was calculated. Using this \( a \) value and the \( d \) values, the rest of the \( h k l \) values could then be calculated. The first guess, (100), was incorrect since it did not give an integer for all \( h^2 + k^2 + l^2 \). Therefore, (110) was used as first reflection, which gave
the correct results. From Table 3.1, the value of a calculated from the powder pattern retrieved, 8.82 ± 0.01 Å, is very close to the reported value of 8.82805 ± 0.00012 Å, again suggesting the synthesis was successful.

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Table 3.1: Indexing of powder XRD pattern obtained from the synthesis of SOD-ZnPO following the recipe of Gier and Stucky.

As well as powder XRD, the sodalite samples were also investigated by SEM in order to see the morphology of the crystals produced. As can be seen in Figure 2.6, the crystals tend to cluster together forming intergrowth, rather than single crystals growing separately. These crystal agglomerations form due to a high degree of nucleation in the sample, meaning that many crystals nucleate close to
each other. Twinning has also been observed in these crystals. Occasionally, some faceted single crystals that had a lower degree of intergrowth did exist in the sample, such as in Figure 2.6b. From these crystals it can be seen that the most visible face is the {100} face. This suggests that this is the slowest growing facet of SOD-ZnPO, since the slowest growing face defines the morphology of a crystal.  

Figure 2.6: SEM micrographs showing SOD-ZnPO crystals grown following the recipe of Gier and Stucky at room temperature.

From the morphology of the crystals seen with SEM, some observations about the crystal growth of ZnPO-SOD can be made. From Figure 2.6b it can be seen that for ZnPO-SOD only four corners have {111} facets present, whereas the other four corners are defined either by the corner of a cube or by the joining of three {110} faces. This observation shows that there is anisotropic growth between the [111] and [111̅] directions. In one direction, the growth is faster and therefore the face grows out and so cannot be observed. Conversely, the direction growing slowest will not grow out, and it is these four faces that are observed.

In order to discover the cause of this anisotropic growth, the connectivity of the (111) face was investigated. Figures 2.7a shows the (111) face of the ZnPO-SOD (O atoms have been omitted for clarity). The crystallographic information file (CIF), created from the Reitveld analysis performed by Nenoff et al., was used to identify atom positions. The (111) face is made up of 6-rings, which are joined to lower layers through 4-ring connections in an ABC stacking arrangement. Upon observing the frameworks on both the (111) and (111̅) faces, no obvious crystallographic differences could be seen. Therefore, the positions of the cations
and water molecules that are contained in the sodalite cages were investigated. It was observed that the Na\(^+\) cations in the cages occupy tetrahedral positions, with 75\% site occupancy. These tetrahedra are oriented such that the vertex of the tetrahedra points in one direction (either [111] or [\bar{1}\bar{1}\bar{1}]), whilst the base points in the other direction. This is shown in Figures 2.7b and 2.7c, where the Na\(^+\) cations at the base of the tetrahedra are coloured in pink. These atoms have been joined together to highlight the tetrahedral configuration, and the cation at the head of this tetrahedra has been coloured in black to further emphasise this effect. The arrangement of cations in the cages is therefore an obvious difference between the two growth directions, and so could cause a difference in growth rates. The reason that the tetrahedra will be oriented in the same direction in the \{111\} direction is due to the cation occupancy in adjacent cages. If the tetrahedral arrangement was not adhered to, this would leave Na\(^+\) cations in adjacent cages both occupying the same 6 – ring. The reason that sodium cation orientation differences in the [111] and [\bar{1}\bar{1}\bar{1}] can affect the growth rates of the faces is because the growing surface will be decorated with cations. This decoration will be different on the \{111\} and \{\bar{1}\bar{1}\bar{1}\} faces, which will affect the interactions between incoming growth species. With regards to the water inside the cage, this occupies a similar tetrahedral arrangement, this time in the opposing direction. Therefore, the same argument will apply for water as well, but with directions reversed (Figure 2.7e). Inside the cage, the water and cations interact to form a cubane type geometry, shown in Figure 2.7d.\(^{17,28}\)
Figure 2.7: a) Structural diagram showing the \{111\} face of SOD-ZnPO. Oxygens are omitted for clarity, b) view of the \{111\} face showing tetrahedral cation position occupancy, c) view showing the tetrahedral occupancy of Na\(^+\) cations, with the apex pointing in the [111] direction and the base pointing in the [\bar{1}\bar{1}\bar{1}] direction, e) structural diagram showing the geometry of water / cation occupancy, with O and Na joined together for clarity, e) Figure showing the water and cations in opposing tetrahedral within the sodalite cage.

After performing the synthesis following the literature example,\(^7\) various other syntheses were investigated by varying different experimental conditions. The reason for this was to attempt to produce non-intergrowth crystals that would be amenable to AFM studies, as well as investigate the conditions in which SOD and
other zinc phosphate phases grew. To that end, the effects of dilution, temperature, pH and Zn:P ratio were investigated, the results of which are shown below.

2.4.2 Effect of dilution

By performing the standard Gier and Stucky synthesis at room temperature, the produced crystals have a lot of intergrowth, as shown in Figure 2.6a. These crystals were also small (width ca. 2 μm, maximum 5 μm) in terms of crystals amenable to AFM. Therefore, ways to synthesise larger crystals were investigated. One of these was by diluting the initial gel used to synthesise the crystals by adding extra water. This has previously been suggested as a method to form larger crystals. By using dilution, it was expected that the lower supersaturation conditions would lead to less nucleation in the vessel. This would be lead to fewer crystals overall, as well as reduce the amount of intergrowth. The dilutions that were attempted were performed using the initial reactant mass, but excess water. Dilution by 50, 60, 70 and 80 % of the initial reactant concentration was performed.

In Figure 2.8a, the powder XRD patterns retrieved for the 60% and 50% experiments are shown. It can be seen that for the 60% dilution synthesis the product was amorphous (bottom). This was also the case for the 70% and 80% dilutions. This is further demonstrated by the SEM micrograph in Figure 2.8b. However, the product from the 50% synthesis is crystalline, and by fingerprinting was found to be pure SOD-ZnPO. From the SEM micrographs in Figures 2.8c and 2.8d, the morphology of the crystals is clear since there is less intergrowth than for the standard synthesis. Nevertheless, the intergrowth of the crystals has not been entirely eliminated as can be seen in Figure 2.8d. As well as reduced intergrowth, the crystal size has increased slightly, from a maximum crystal size (width) of 5 μm to a maximum size of 15 μm. Therefore, larger crystals with less intergrowth could be achieved by synthesising SOD-ZnPO from more dilute solutions, however if the solution was too dilute the product was amorphous. The morphology of these crystals produced was cubic, with the \{100\} face expressed to the highest degree.
The \{111\} face was also present in several cases, whilst the presence of the \{110\} face was much reduced in these conditions.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{a) Powder XRD patterns showing the results of syntheses with 50\% (top) and 80\% (bottom) of reactant masses used compared to Gier and Stucky recipe, b) SEM image showing amorphous product from 80\% synthesis, c-d) SEM micrographs showing crystals obtained from 50\% synthesis.}
\end{figure}

### 2.4.3 Effect of Temperature

The temperature of the standard recipe for SOD-ZnPO synthesis was 25 °C. In order to investigate the effect of temperature, syntheses were performed at both lower temperatures (0 and 4 °C), and also higher temperatures, up to 50 °C. These covered the ranges available to the AFM used throughout these studies. Initial observations found that the synthesis time was vastly affected by the temperature, with low temperature syntheses taking between 1 week and 1 month to perform, whilst high temperature syntheses were complete within 30 minutes. At higher temperatures, SOD was still formed and the morphology of the crystals was very similar to those from the literature synthesis. This is shown in
Figures 2.9a and 2.9b, which shows a) room temperature SOD crystals and b) 50 °C crystals.

![Figure 2.9: SOD crystals synthesised at a) room temperature and b) 50 °C.](image)

The effect of lowering the temperature was more pronounced. Here, the size of the SOD crystals was vastly changed, with much larger crystals formed. The average crystal size was now ca. 10 μm, whilst the largest crystal observed was 40 μm. The crystals also tended to have less intergrowth. This is shown in Figure 2.10a. This figure also shows a representation of a crystal with the same space group as SOD-ZnPO using WinXmorph software (Figure 2.10b). In this case, the crystals also have visible {110} faces. Although larger crystals were synthesised, there was still large variation in the sample, with different facets expressed to different degrees throughout the sample, for example in Figure 2.10c. Although larger crystals with less intergrowth were synthesised, the sample was still not homogeneous. This could have arisen because the synthesis was static for the week it took to complete. Therefore, there could have been local variations in supersaturation, leading to different growth rates of the faces relative to each other, and thus the observed morphology variation. Observing individual crystals, there were many examples where crystals grew in a non-regular fashion, which suggests this type of transport controlled mechanism results in different supersaturation conditions for different faces. It could also be that the growth rates of different faces were distorted due to defects. In order to achieve a more
homogeneous sample, the reaction could be stirred in order to keep a constant nutrient concentration throughout.

The other effect of lowering the temperature was that another phase grew alongside the SOD. This can be seen more clearly in Figure 2.10d from SEM images, and in Figure 2.10e, where the XRD pattern of SOD only (top) and SOD and this new phase (bottom) are shown. This phase was identified as the Chiral Zincophosphate phase (CZP), first reported by Rajic et al.\textsuperscript{29} and Harrison et al.\textsuperscript{30} in 1995. Since the morphology of the crystals was much different to SOD, the presence of these crystals would not affect their suitability for AFM investigations, as the SOD crystals could be selected easily under the optical microscope. In all cooled experiments, these two phases were observed, however only the results obtained at 0 °C are presented here. The reason that the SOD crystals in this experiment were much larger could be due to the slower rate of reaction that was observed. If the rate of nucleation was much lower, then this would mean that fewer crystals would form and that those that did would subsequently grow larger. Another reason may be that because of the presence of a second phase, CZP, the SOD crystals did not nucleate as rapidly. This would allow the crystals that had nucleated to grow larger. This could also be the reason for the reduced amount of intergrowth present. Since crystals would be less likely to form in the same region, this could reduce the frequency of intergrowth. Nevertheless, the sample does contain some intergrowth, with some crystal twinning. For example, in Figure 2.10a, the crystal in the top right of the image has formed a penetration twin. This type of effect was observed for all samples and could not be removed; however in creating larger crystals the effect was also reduced.
Figure 2.10: a) SEM image of SOD-ZnPO crystals synthesised at low temperature, b) simulation of a crystal with the same space group as SOD-ZnPO, c) SEM images of more SOD crystals from this sample, d) SEM image showing CZP phase also present from this synthesis, and e) XRD patterns of pure SOD (top), and SOD with CZP (bottom).
The morphology of the CZP crystals is shown in Figure 2.11. In most cases, such as that shown in Figure 2.10d and 2.11d, the crystals seem to have a lot of intergrowth creating long needle like shapes. For KAl(SO$_4$)$_2$.12H$_2$O crystals, a similar type of morphology is observed. Although it seems as if these needles are made of several crystals intergrown, they are in fact a single crystal because the same internal structure is maintained throughout the specimen. This is known as parallel growth (Chapter 1.3.4.1). Some non-needle like single crystals were also observed such as that shown in Figure 2.11a. This morphology was reproduced in WinXMorph, with the crystal bound by the {110} face. In Figure 2.11c, a synthesis of CZP was stopped early. This allowed several of these non-needle like single crystals of CZP to be observed before the parallel growth that was typical.

Figure 2.11: a) SEM image showing a single CZP crystal, b) WinXMorph image reproducing this morphology, c) SEM image of CZP crystals within an amorphous gel through early reaction termination, d) SEM image showing the typical morphologies observed for CZP crystals.
2.4.4 Effect of pH

In the work of Kowalak et al., the pH of the synthesis when performed by grinding solid reactants made a large difference to the products obtained, with pH 7 being favourable for SOD.\textsuperscript{18, 19} In order to observe this influence on the SOD synthesis, and compare the solid state formation with that in solution, experiments were set up in order to investigate the formation of SOD under various pH conditions. To investigate the effect of pH, the Gier and Stucky recipe was modified by the addition of HNO\textsubscript{3} in order to lower the pH whilst maintaining the Zn : P ratio. This was used as NO\textsubscript{3}\textsuperscript{-} was already present in the synthesis mixture as part of the Zn source. The pH of both the initial gel and the final mother liquor was 7 when following the initial synthesis. A higher pH was also attempted, by addition of more NaOH. When lowering the pH, a new phase began to grow. At pH 4 - 6, both ZnPO-SOD and this phase grew together, however at lower pH only this phase was present. By using powder XRD, the second phase was identified as hopeite.\textsuperscript{31} In Figure 2.12, crystals obtained from a synthesis performed at pH 4.65 are shown, which gives mixed phase SOD and hopeite. Hopeite crystals had both plate like and needle like morphologies.\textsuperscript{32} The SOD crystals that were produced in the mixed phase synthesis were large single crystals. These had an average size of ca. 20 μm and a maximum size of 60 μm was observed. These crystals were bound by the \{100\}, \{110\} and \{111\} faces. In this case, the large crystals were formed despite the rapid rate of reaction. The reason that larger crystals formed in this case could be because of the hopeite phase that grew alongside the SOD. By having competitive nucleation between the two phases, the number of SOD crystals would be reduced. This would mean that those that did form would grow larger. Again, the larger crystals also seem to have less intergrowth, which could be related to their separation in the reaction vessel due to the lower nucleation rate.
Figure 2.12: SEM images of crystals formed at pH 4.65, achieved by addition of nitric acid. Two phases are present; sodalite and hopeite.

A third phase was also observed on several occasions, with the same morphology as hopeite. This was found to be the dehydrated form of hopeite. This was likely due to the temperature of the drying oven used in these investigations, which was set at ca. 60°C, however was not strictly controlled. In previous reports, it was found that hopeite dehydration began at 80°C. When drying time was reduced, this phase did not form, whilst this form was the only one present if the product was left drying for over 2 weeks. Figure 2.13 shows the powder XRD pattern of the three phases observed; hopeite, dehydrated hopeite and ZnPO-SOD, as well as an SEM micrograph showing the similar morphology of hopeite and the dehydrated version.
At lower pH, the reaction time was greatly reduced. Again, large single SOD crystals were achieved. The time taken for a pH 3 synthesis was near 1 minute, whilst pH 7 syntheses would take 24 hours. The completion time in this case was when the gel had been used up, so only clear mother liquor and crystals were left. When the pH was raised using extra sodium hydroxide, the reaction time increased. Up to pH 8.5, SOD crystals were still produced as a single phase, however there was still intergrowth observed. By increasing the pH further the product was initially amorphous. This was after 1 month of synthesis, at which point a large mother liquor layer was present with this amorphous product. In one case, this reaction was left for over 1 year at pH 9. After this time, large CZP crystals were formed as a single phase. These crystals obtained are shown in

Figure 2.13: a) XRD patterns showing the dehydrated hopeite only (top) and a mixture of both hopeite and the dehydration product of hopeite (bottom), b) SEM image showing the morphology of the dehydration product, c) SEM image of hopeite.
Figure 2.14. The large size is likely due to the very slow nucleation time, which is why the product appeared amorphous after 1 month. Again, the morphology of the crystals shows a high degree of intergrowth.

Figure 2.14: a and b) SEM images of CZP crystals obtained at pH 9 after 1 year synthesis time.

2.4.5 The effect of the Zn : P ratio on synthesis

In the original synthesis of ZnPO-SOD, the amount of zinc was less than that of phosphorus (0.8 Zn : 1 P). Therefore, there was a large excess of phosphorus present in the mother liquor at the end of the synthesis. This was measured by ICP-MS to be ca. 3000 ppm (0.097 mol dm$^{-3}$), compared to a zinc concentration that was less than 10 ppm (0.0002 mol dm$^{-3}$).

In order to investigate the importance of the ratio of Zn and P in the synthesis, a range of ratios were investigated. This ratio was achieved both by increasing the amount of zinc nitrate in the initial synthesis, and also by reducing the amount of phosphoric acid. In the latter case, the amount of NaOH was adjusted to maintain the gel at pH 7. When the pH was not maintained at 7 the results of the syntheses followed those of the pH adjustment experiments. In Figure 2.15, two syntheses are shown that were performed by increasing amounts of phosphoric acid but with no change to the amount of NaOH added. When the amount of phosphoric acid was slightly increased (2 g, pH 5.66), both ZnPO-SOD and hopeite formed (Figure 3.8a and b). The SOD crystals were large single crystals in agreement with
the observations at lower pH. When more phosphoric acid was added (3.2 g, pH 2.69), only hopeite was observed as shown in Figure 2.15c and d. When less phosphoric acid was added and the pH increased to 10 and the product was amorphous.

![Figure 2.15](image)

*Figure 2.15: a-b) SEM images of crystals formed at pH 5.66, achieved by addition of extra phosphoric acid. Crystals have been identified by powder XRD as hopeite and sodalite, and c-d) SEM images of crystals formed at pH 2.69, achieved by addition of extra phosphoric acid. Crystals have been identified by powder XRD as hopeite.*

The range of Zn : P ratios investigated at pH 7 were between 1.5 : 1, 1 : 1 and 1 : 1.5. When there was excess Zn, the gel formed was much thicker than when excess P was present. This gel remained even after 1 month of standing at room temperature, with no product forming. When the excess of P was increased
beyond that in the original synthesis, SOD was still formed as a pure phase. For the 1 : 1 sample, SOD was formed alongside CZP. In this case, the crystals were smaller than those formed at low temperature. However, this was an important result since it showed that the excess of P was required in order to obtain a pure phase SOD.

2.4.6 Cobalt Substitution in SOD-ZnPO

The substitution of Co for Zn in open framework materials has been performed on several systems. For example, the initial reports of the CZP framework involved the isomorphous substitution of Zn for Co. This substitution has also been reported for SOD-ZnPO, where up to 30 % of the Zn was replaced with Co. In this study, seeding was required in order to achieve these levels of substitution. To date, a 100 % substituted SOD has not been synthesised. The purpose of this study was to investigate the importance of the seeding process in the synthesis of Co substituted SOD-ZnPO.

In the initial investigations, seeded experiments were performed with increasing Co concentration, from 10 % zinc substitution up to 50 % substitution. It was found that with seeding, a second phase formed after 30 % substitution of cobalt. This phase was identified as hopeite. When syntheses were performed in the absence of seed crystals, this phase formed at lower loading with only 20 % substitution in the initial synthesis gel required to introduce this phase. Using EDS, it was possible to calculate the total framework substitution of zinc in these syntheses. For the non-seeded syntheses the 10 % Zn substitution in the initial gel led to a 9 % substituted product. For 20 %, the total framework substitution was 13 %, whilst for 30 % gel substitution the framework had 17 % of the Zn substituted for Co. For the latter two samples, the hopeite crystals that were also present were investigated. It was found that in the 20 % gel substituted sample the hopeite crystals had 45 % of Zn substituted for Co, whilst for the 30 % sample 58 % of the Zn was substituted. The Co substituted hopeite morphology was vastly changed, with small crystallites that were ca. 1 μm formed instead of the larger platelets. These are shown in Figure 2.16. The SOD crystals retained their typical
morphology. Therefore, it was observed that the seeding was required in order to get a pure phase SOD product with higher Co substitution than 10 %. If no seed crystals were present, then hopeite would form which had more framework substitution than the SOD. At loading of 40 % and above, this phase was observed regardless of seeding. Seeding has previously been demonstrated to be important in deciding the phase produced in zeolite synthesis. Since seeding was observed to be important in producing single phase SOD rather than a mixed phase, it was also tested on the pH varied syntheses. However, whilst a single phase SOD product could be produced at slightly lower pH (5.7), this synthesis did not produce the large single crystals desired for AFM studies. Instead, there was no observable difference between this product and that obtained at pH 7, although the synthesis was more rapid. At lower pH, a mixed phase was still produced.
Figure 2.16: a) XRD pattern resulting from an un-seeded synthesis in which 30 % of the initial Zn was substituted for Co, b) SEM image showing the morphology of Co substituted hopeite crystals, c) SEM image showing the morphology of Co substituted SOD.

2.4.7 Effect of cations on sodalite growth
In order to balance the negative framework charge of sodalite zincophosphate, sodium cations are incorporated inside the cages. For many zeolites, cation exchange is possible and leads to many of the important properties of zeolites. For many zeolites, the frameworks can be synthesised in the presence of a variety of cations and may include templating organic species. In the case of sodalite, the aluminosilicate type is usually synthesised with Na\(^+\) cations. However, these can be exchanged with a range of other cations including Cu\(^+\), Li\(^+\), K\(^+\) and Ag\(^+\).\(^6\),\(^36\) In this section, the importance of Na\(^+\) in the synthesis of SOD-ZnPO was investigated. This
was performed by attempting SOD synthesis with different cations, and also by altering the amount of Na\textsuperscript{+} used in the synthesis.

The cations selected for testing were Li\textsuperscript{+} and K\textsuperscript{+}. These were selected since lithium had already been proven to form zincophosphate open framework materials,\textsuperscript{37} whilst both lithium and potassium are known to exchange into the aluminosilicate framework. In the synthesis of FAU zincophosphate, the cation used was tetramethyl ammonium, which was located inside the sodalite cage.\textsuperscript{7} This cation was not suitable for these experiments however, since the charge on tetramethyl ammonium (TMA) is 1 +, whilst each sodalite cage required 3 + charge from the extra-framework species in order to balance the framework charge. In FAU, where there are other cation sites apart from those in the sodalite cages, this can be compensated for. However, in SOD, the TMA will occupy the entire cage and therefore leave the framework with an overall negative charge.

For experiments in which K\textsuperscript{+} was used, the product was not SOD. Instead, the product was a potassium zinc phosphate, KZnPO\textsubscript{4}.\textsuperscript{38} These experiments were performed at both 25°C and 50°C with no change to the product. The morphology of the crystals is shown in Figure 2.17. The crystals were hexagonal rods, whilst the crystals have a hexagonal space group. When lithium was used instead of Na\textsuperscript{+}, again the product was not sodalite. In this case, the resulting phase was the Li-ABW framework.\textsuperscript{37}
Figure 2.17: SEM image showing the morphology of potassium phosphate crystals obtained.

The synthesis of SOD was therefore only possible with Na\(^+\) as the cations from the range investigated. In the original synthesis, there was a large excess of Na\(^+\), leading to a 1 mol dm\(^{-3}\) concentration of Na in the mother liquor solution. The Na / P ratio has previously been found to be important in determining the product formed,\(^{39}\) whilst it was also found that Na\(^+\) was particularly important in the synthesis of SOD, with hopeite or ZnPO-FAU forming instead in its absence.\(^{40}\) Therefore, the importance of the excess of Na\(^+\) in the initial synthesis gel was investigated. Firstly, the NaBr was removed leaving only Na contributed from the NaOH in the gel. Then, the Na\(^+\) concentration was reduced further by reducing the amount of H\(_3\)PO\(_4\). In the first case, SOD was still produced. However, when the level was reduced further, hopeite also formed alongside the SOD. This was still an excess of Na\(^+\) with respect to both P and Zn, however showed the importance of the cations in the formation of the SOD phase. This agrees with previous work, which showed the importance of Na\(^+\) in the synthesis of SOD-ZnPO.\(^{41}\) Gier and
Stucky suggested that the reason for the importance of Na\(^+\) could be due to it templating the formation of sodalite cages in solution.\(^7\)

Experiments were also performed where extra Na\(^+\) was added. In this case, SOD was again the sole phase at pH 7. However, when extra Na\(^+\) was added at pH 8.3, the resulting phase was ZnO.\(^42\) The morphology of these crystals is shown in Figure 2.18.

![SEM image showing the morphology of the ZnO Phase.](image)

*Figure 2.18: SEM image showing the morphology of the ZnO Phase.*
2.4.8 Stability of Sodalite Zincophosphate

Metastability is a known property for a lot of open framework materials. Therefore this was investigated for SOD-ZnPO, since long term stability is an important factor in performing in situ Atomic Force Microscopy. This importance was shown by Cubillas et al., who studied the growth of faujasite zincophosphate using in situ Atomic Force Microscopy. In this study, growth was quickly followed by dissolution as a second phase began to grow. Since this new phase formed rapidly, long term AFM experiments were not possible, and control over growth conditions in order to get quantitative measurements were also not possible. In the case of sodalite zincophosphate, the stability of the crystals was investigated in acidic medium by Singh et al. This study found that the SOD would dissolve in pH 3 solutions, forming hopeite. Further, it was suggested that the hopeite could nucleate more easily on the surface of the SOD, with the complex species that were dissolving able to transform into the hopeite. Whilst SOD dissolved in acidic media, the purpose of these investigations was to discover the stability at pH 7.

In order to investigate the long term stability two different approaches were taken. In the first method, solutions were left in their mother liquor over several months, with samples taken at regular intervals. The syntheses were all performed at room temperature to ensure sodalite was present as a single phase, before being placed at four different temperatures. In the second approach, the sodalite crystals were placed into sodium bromide solutions at pH 7, both in the presence and absence of phosphorus. In this way, the solution began undersaturated with respect to the sodalite crystals added. These experiments were performed in solutions with ionic strength > 0.8 M, since these were the conditions present in the sodalite synthesis. Therefore, for AFM experiments these conditions would also be required. The SEM results of the stability experiments are shown in Figure 2.19.
In both experiments, whether from an initially undersaturated or supersaturated solution, the crystals eventually transform into another phase. This occurs at a more rapid rate at higher temperatures, however after 6 months all samples had at least partially converted into NaZnPO$_4$. This phase has previously been identified as a product of the transformation of ZnO in a sodium phosphate solution, and it seems that under these conditions this phase is more stable than the SOD phase. As with the previous report, the crystal morphology of the new phase was barrel-like with a hollow centre. These results showed that the SOD phase is metastable in sodium phosphate solutions, which were used in the *in situ* experiments. However, unlike the FAU experiments where this resulted in dissolution almost immediately, the SOD was stable for a minimum of 2 weeks, even at 70°C. Therefore, these crystals were suitable for *in situ* investigations.

As well as the single phase, the stability of the mixed phases was investigated. In these experiments, the same sodium phosphate solutions were added to crystals that contained mixed phases of SOD and hopeite and also SOD and CZP. Both of these experiments were performed at room temperature. After 3 months, no changes were observed in the SOD / CZP sample. After 6 months, the SOD crystals were transforming into another zinc phosphate phase as with the single phase experiment. This can be seen in Figure 2.20a. For the SOD / hopeite sample, after
1 day sodalite could be observed nucleating on the surface of the hopeite. This showed that the hopeite was dissolving, leading to heterogeneous nucleation of SOD. After 1 week, the SOD coated the surface of the hopeite crystals. This can be seen in Figure 2.20b. Therefore, at low pH SOD will dissolve with hopeite nucleating heterogeneously, however the opposite occurs at pH 7. This means that the sample containing hopeite is unsuitable for AFM studies. This is because the dissolution of the hopeite will change the supersaturation conditions of the fluid cell in which the experiments occur by raising the solution Zn concentration. Even with flow through apparatus, this could lead to erroneous measurements at concentrations that would be otherwise too low for a pure phase sodalite sample to grow. For the CZP containing sample, this is not a problem since the CZP does not dissolve. Measurements can be made in the presence of this phase, since the flowing solution will maintain a minimum supersaturation.

Figure 2.20: a) SEM image showing growth of NaZnPO₄ on top of a SOD crystal (top half) after 6 months in a pH 7 sodium phosphate solution at room temperature, b) SEM image showing heterogeneous nucleation of SOD on hopeite crystals after 1 week in a pH 7 sodium phosphate solution at room temperature.
2.5 Conclusions and Future Work

2.5.1 Conclusions

It can be seen from this work that many phases will form in a small range of experimental conditions, showing the competitive growth of these phases. At lower pH (2-4), the hopeite phase tends to form more favourably, whilst under more mild acidic conditions (pH 5-6) large SOD crystals are also obtained as a mixed phase. At lower temperatures (4 – 10 °C), the CZP phase also forms in competition with SOD; however, larger single SOD crystals are also formed under these conditions, which are particularly suitable for AFM. Although dilution improved the size of the crystals, those produced at low temperatures were still larger and exhibited less intergrowth. Therefore, the crystals from the low temperature synthesis are most suitable for in situ AFM.

The importance of the cations in sodalite synthesis was highlighted. When the level of Na⁺ was reduced, hopeite began to compete as another growing phase. Only Na⁺ containing SOD was formed. The importance of the P in the synthesis was also apparent, with an excess required in order to synthesise SOD as a pure phase.

It was also found that as Co is introduced into the framework, the hopeite phase grows in competition with SOD. This also has a higher substitution rate than SOD. The SOD phase was found to be metastable with respect to another zinc phosphate phase in sodium phosphate solutions; however their short term stability was improved over FAU.
2.5.2 Future Work
To continue these studies, work could be extended to investigations of the other phases involved such as the CZP phase. This better understanding of the zinc phosphate synthesis conditions could allow for greater control over the desired products.

In the syntheses that produced SOD crystals, the samples were not homogeneous, but rather contained a large size distribution as well as different proportions of the facets expressed. Investigations into the reasons for this from an experimental and crystal growth point of view, as well as an attempt to control the size and shape, could be undertaken in order to produce more uniform crystals.
2.6 References

Chapter 3

AFM Observations of the Growth of Sodalite

Zincophosphate
3.1 Aims and Objectives

The aim of this chapter was to investigate the surface features of the three principal facets of SOD-ZnPO using both \textit{ex situ} and \textit{in situ} Atomic Force Microscopy (AFM).

More specifically, the objectives of this chapter were to:

- Understand the principles of AFM, and its application in the study of open framework materials
- Investigate \textit{ex situ} the surface features of SOD-ZnPO and understand the mechanisms by which these are produced
- Study the \textit{in situ} growth of SOD-ZnPO, allowing investigations of the mechanisms of growth
- Determine the types of defect present in the growth of this system
3.2 Introduction

3.2.1 Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a type of scanning probe microscopy (SPM), which is a family of techniques that depends on the interaction of a sharp probe with a surface as it is scanned over it in order to produce a high resolution image. For AFM, this sharp probe is a tip that interacts directly with the surface. These interactions can include both the attractive and repulsive forces that exist between the tip and sample surface. Through the information gathered, a three dimensional topographical image of the surface can be obtained.\(^1\)

The first member in the family of SPM was the scanning tunnelling microscope (STM), which was introduced in 1982.\(^2,3\) In STM, the probe used is a sharp tip, typically a wire made of W, Pt or Ir. This is brought to within several angstroms of the surface, and a bias voltage is applied to the sample. Under these conditions, a tunnelling current is able to pass between the tip and sample, which can be used as a feedback signal. The tip is then rastered across the surface using an x y z scanner using piezoelectric elements. During scanning, the tunnelling current will vary as a function of the distance between tip and sample. By incorporating a feedback loop, the x y z scanner can adjust the tip height (z direction) to keep a constant tunnelling current, with the movement of the scanner giving the topography.\(^4\) Through this technique, it was possible to achieve atomic resolution images for the first time, including images of the Si(111) – (7x7) surface.\(^5\) STM can be used in a variety of environments, including in air and in solution, which allows for in situ investigations to be performed. However, the main drawback of the STM is that it requires that the sample to be used is conductive, limiting the systems that can be studied with this technique.\(^1,4,6\)

The AFM was introduced by Binnig et al in 1986.\(^7\) This technique overcame the disadvantage of STM for imaging conducting surfaces.\(^4\) In AFM, a sharp tip attached to a flexible cantilever is used to scan the surface. As the tip is rastered across the surface, the cantilever bends / deflects as interactions between the tip and surface change. By measuring this bending, it is possible to measure the force
between the tip and the sample surface. The cantilever can be considered as a spring, obeying Hooke’s Law (Equation 3.1),

$$F = - k * x$$

(3.1)

where $F$ is the force (N), $k$ is the spring constant (N m$^{-1}$) and $x$ is the displacement (m). In order to measure the bending of the cantilever, a laser is used. The laser, shining on to the back of the cantilever, is reflected into a four quadrant photodiode detector. Any deflection of the cantilever will result in a movement of the laser spot on the photodiode detector. This is shown in Figure 3.1, which shows the basic operation of an AFM. As with STM, the $x y z$ scanning is performed using piezoelectrics.

![Diagram showing the basic operation of an AFM](image)

*Figure 3.1: Diagram showing the basic operation of an AFM.*

As with STM, AFM allows imaging of surfaces under ambient conditions, and in solution, without surface destruction. This makes *in situ* investigations of crystal growth possible. Further developments have increased the range of conditions accessible with this technique; for example there are now several hydrothermal AFM’s, capable of imaging at temperatures up to 150 °C and pressures of 6 atm.
3.2.1.1 Scanning Modes

There are three main scanning modes of the AFM; contact mode, non-contact mode and intermittent contact (or tapping) mode. In each case, the scanning can be performed in two ways; either at constant height or at constant force. In constant height mode, the height of the cantilever is kept constant with respect to the surface, i.e. the feedback loop is disengaged. As the scanning commences, any surface features encountered will cause a deflection of the cantilever, resulting in a change in applied force. This deflection is taken as the measurement. This mode is rarely used, since the variation in forces means that both the sample and tip are at risk of damage. Instead, the typical scanning mode used is a constant force mode. In this mode, the deflection of the cantilever is recorded by the photodiode detector. Using a feedback loop, the z piezoelectric scanner is then moved in order to return the cantilever to the original contact force. By measuring the movement of the scanner, the height of the surface features can be plotted.

In Figure 3.2 a typical force distance curve for an AFM experiment is shown. This gives the relationship between the distances of the tip from the sample surface. At far distances, there is no interaction between the tip and sample and so no force is recorded. As the tip moves closer to the sample, attractive forces are the major component, and the cantilever will bend as shown by the inset image. It is in this attractive region that non-contact AFM is performed. At one point, these attractive forces will cause the tip to “snap” into contact with the surface, shown by the sudden fall on the curve. After this point, the tip is in repulsive contact and moving the tip further towards the sample will increase this unfavourable interaction. It is in repulsive contact that “contact mode” AFM is performed, as shown in Figure 3.2. The cantilever deflection in this case is also shown inset. Moving in the opposite direction, there is a larger bending due to an attractive interaction measured in the curve. This extra bending is caused by adhesion interactions between the tip and sample as the tip moves out of contact with the surface. The forces typically involved in the attractive region include Van der Waals and capillary forces, whilst in the repulsive region these forces can be related to overlapping of orbitals.
In contact mode, a certain force is applied to the surface by the cantilever, meaning that the tip is in constant repulsive contact with the surface as it rasters over it. This method of imaging has some advantages and disadvantages. By being in repulsive contact, the cantilever will not “snap” into contact as can happen in non-contact AFM due to attractive forces. Further, by being in contact information about the friction of the surface can be obtained (see Chapter 5). This is because the laser deflection measured by the photodiode is composed not only of the vertical deflection of the cantilever, but also the lateral twisting of the cantilever. The disadvantages of contact mode imaging include the possibility of sample damage, and also decreased lateral resolution, depending upon the applied force.\textsuperscript{15,16}

Both non-contact and intermittent contact mode AFM can be described as dynamic modes.\textsuperscript{17} Rather than measuring the static deflection of the tip, in these methods the cantilever is vibrating, and these oscillations are measured. To perform these measurements, a setpoint amplitude is selected and the tip-sample distance adjusted to match this through the feedback system. In non-contact mode, the oscillating cantilever does not make contact with the surface, whilst in intermittent contact mode the tip makes repulsive contact with the surface during

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3.2.png}
\caption{A representative force distance curve between the tip and sample showing the regions in which the different scanning modes take place.\textsuperscript{8}}
\end{figure}
oscillation. The change in amplitude is measured as the tip moves across surface features, and using a feedback mechanism the height of the tip is changed to return this back to the setpoint value. By measuring the movement of the tip, a 3D image can be created. As aforementioned, in non-contact mode the attractive forces, in particular capillary and van der Waals forces, can lead to the tip snapping into contact with the surface. To counteract this, cantilevers with a higher stiffness (spring constant) are used. These dynamic modes of imaging have advantages in that the sample is under less contact, and therefore less likely to be damaged than in contact mode. However, lateral forces are greatly reduced due to the lack of contact, meaning friction measurements are not possible in these modes. \(^{15, 17, 18}\)

### 3.2.1.2 Resolution

The resolution attainable with the AFM is dependent upon the conditions in which the experiments are performed. The vertical resolution of the AFM is usually determined by the piezoelectrics of the instrument (0.1 nm), and is usually much higher than the lateral resolution, which can be determined by the shape of the tip used.\(^ {15}\) For typical experiments, the blunter the tip, the less lateral resolution the AFM will yield. This is shown in Figure 3.3, where the AFM cross-sections for a blunt and sharp tip moving over a surface feature are shown.

![Figure 3.3: The effect of tip sharpness on lateral resolution of the AFM, where the image on the left shows a sharp tip, yielding increased resolution compared to the blunt tip on the right.](image)

\(^{8}\)
Therefore, in order to improve resolution sharper tips can be used. This also aids imaging using non-contact AFM methods, where the use of sharper tips helps to decrease the influence of van der Waals forces.\textsuperscript{19} One way of producing much sharper tips is through the use of carbon nanotubes, leading to increased resolution compared to standard silicon nitride tips.\textsuperscript{20}

Since the introduction of AFM, a challenge in terms of resolution was to produce atomic resolution images like those produced by STM. Several groups reported that they had achieved atomic resolution images in contact mode; however this was not \textit{true} atomic resolution. The reason for this was that relatively large contact forces were being used. This meant that the tip would make several contacts with the surface. The presence of \textit{true} atomic resolution could be determined by the ability to observe defects. This was achieved by using contact forces of less than $10^{-10}$ N. This allowed atomic resolution images of calcite to be produced in contact mode, whilst higher resolutions were achieved using non-contact mode.\textsuperscript{16} By imaging in ultrahigh vacuum (UHV), it was possible to observe Si (111) – (7x7) with atomic resolution, as with STM.\textsuperscript{19}

Since then, developments have led to the ability to image organic molecules in atomic resolution, using non-contact AFM. In order to achieve this, tip modification was required, with a single CO molecule being deliberately picked up. Further, the experiments had to be performed at low temperatures (5 K). In these experiments, images are taken with the tip close enough to the surface that Pauli repulsion between the tip and surface exists; it is measurement of this that gives the atomic contrast observed. The attractive forces involved only contributed a background force.\textsuperscript{21} As well as the atoms, this level of detail has allowed different bond-orders to be distinguished in polycyclic aromatic hydrocarbons and fullerenes. In these images, higher bond order was observed as brighter bonds by the AFM, owing to a stronger Pauli repulsion. This is shown in Figure 3.4, which shows hexabenzocoronene.\textsuperscript{22}
For the experiments reported herein, the contact loads used were a minimum of 10 nN. Therefore the lateral resolution achieved was ca. 20 nm,\textsuperscript{23, 24} whilst the vertical resolution was ca. 0.1 nm.\textsuperscript{25}

\subsection*{3.2.1.3 Scan Rate}

Images collected using AFM are created by raster scanning. This means that an image is built up by scanning sequentially line by line. This leads to a “fast” direction for data collection, which is the horizontal axis on the generated image, and a “slow” direction which is the vertical scan axis made up of the horizontal scans. The rate of collection therefore depends both on the number of lines to be collected and the frequency of line collection, typically referred to as scan rate.\textsuperscript{15} In typical AFM experiments, the scan rate will be up to 10 Hz in the fast direction, whilst scans are usually 512 lines, leading to image acquisition times of ca. 1 minute.\textsuperscript{15, 26} Although these times are appropriate in some cases, for other types of imaging such as visualisation of macromolecular processes it is desirable to increase the acquisition time.\textsuperscript{27}
In general, the acquisition time for AFM is limited by three factors. These are:

1) The measurement bandwidth of the interaction between the tip and sample
2) The rate that the tip can scan the surface in the x and y directions
3) The rate at which the tip is able to follow the contours of the sample

In order to decrease the acquisition time, several approaches have been taken. Initially, in intermittent contact mode AFM, the cantilever was modified in order to increase the rate. This involved using small, low mass “nano-cantilevers” with a high stiffness, that would have a resonant frequency in the GHz region. This would allow images to be taken at 0.5 frames s\(^{-1}\) with feedback (constant force), or 1.5 frames s\(^{-1}\) without feedback (constant height).

More recently, AFM image collection times of 14.3 ms have been achieved, with lateral resolution similar to those achieved in contact mode. This was done by using a micro-resonant scanner to raster the sample relative to the tip. This scanner uses mechanical resonances in order to create the fast scan axis, which is usually a limiting factor in scan rate. This was achieved with a quartz tuning fork. As well as this, the feedback used was mechanical rather than electronic and used an external force applied to the tip that was independent of cantilever deflection to maintain a constant contact with the surface. This was achieved through a capillary water neck between the sample and tip, which gave an attractive force as well as an electrostatic force generated by introducing a voltage between a ground plate below the sample and the conductive coating on the cantilever. Although lateral resolutions similar to contact mode were achieved, the data gained through this technique does not give direct height information. Nevertheless, for scanning fast processes this technique provides video rate scanning.
3.2.2 AFM studies of open framework materials

The first AFM studies of zeolites were performed by Weisenhorn et al., observing the (010) face of clinoptilolite in a variety of solutions. Many early AFM studies tended to be of the cleaved faces of natural zeolites, both in air and under solution. These included studies on scolecite, stilbite, faujasite, mordenite and heulandite. In these experiments, molecular resolution was reported. By observing the surfaces at this resolution, it was possible to compare the pore arrangements with those obtained through crystallography. For example, the 8-ring pores in scolecite could be observed, and bond distances and angles were in agreement within 10% of a structure simulation, whilst the 12-ring pore structure in mordenite was also revealed. These atomic resolution images could also be combined with simulated images in order to determine the extraframework cation positions, for example on the (010) face of heulandite.

Through these investigations, terraces were also observed on the cleaved surfaces. On the (010) face of heulandite, these were 0.9 nm high, representing half the unit cell (Figure 3.5a). This regular sized terracing was explained as there are only four oxygen linkages per unit cell between the heulandite layers at which point cleavage would be easy. These height terraces were also observed emanating from growth spirals. These spirals were the first evidence of this type of growth mechanism through a screw dislocation on zeolites. Spiral growth has since also been observed on other natural zeolites, for example the cleaved (010) surface of stilbite shown in Figure 3.5b.
Figure 3.5: AFM images showing a) 0.9 nm terraces on the (010) face of heulandite,\textsuperscript{45} b) growth spirals on the cleaved surface of stilbite.\textsuperscript{43}

3.2.3 Crystal Growth of open framework materials observed by ex situ AFM

The first investigations of synthetic zeolites were performed by Anderson \textit{et al.} on Zeolite Y (FAU).\textsuperscript{46} This study investigated the outer surface of the zeolite crystal, observing the evidence from the crystal growth process. Through this investigation, terraces were observed on the \{111\} face that were of uniform height equivalent to one faujasite layer. This showed that surface growth was non-continuous.\textsuperscript{47} Unlike the cleaved experiment, these features were a direct result of the growth process, suggesting that zeolites have energetically preferred closed structures.\textsuperscript{41} From this evidence, a terrace-ledge-kink mechanism of growth was proposed.\textsuperscript{46}

Zeolite A was also studied by AFM. Agger \textit{et al.} again observed discrete terraces of uniform height. This time, the height was 1.2 nm.\textsuperscript{48} A terrace-ledge-kink mechanism was proposed. It was revealed that coalescence of the steps created kink sites, which would then preferentially grow compared to other growth sites, causing a curving of this boundary.\textsuperscript{48} Coupled to the AFM results, a simple simulation was used to describe the terrace patterns observed. The AFM and simulation results are shown in Figure 3.6.
Figure 3.6: a) AFM image showing the curved boundary (highlighted) between coalescing terraces and b) simulation reproducing this curved boundary using a TLK approach.\textsuperscript{48}

Whilst discrete terraces were observed, the surface termination was unknown. It was proposed that the termination was likely to be closed cages, since these have the lowest number of surface atoms and are therefore more likely to be long lived species.\textsuperscript{49} Since Zeolite A is made up of three types of composite building unit (α-cage, β-cage and double 4-ring), there were four possible closed cage terminations, shown in Figure 3.7.

Figure 3.7: The four possible 1.2 nm terraces for zeolite A, with terminations at a) double 4 ring, b) diagonal double 4 ring, c) β-cage and d) α-cage.\textsuperscript{50}

Further observations by Sugiyama et al. found three step heights; the 1.2 nm height reported by Agger et al. and also steps of 0.5 and 0.7 nm height. These two
new heights were ascribed to the double four ring (0.5 nm) and diagonal double four ring (0.7 nm). The authors suggested that the 1.2 nm termination was therefore likely to be a combination of these two, leaving the structure shown in Figure 3.7a or 3.7b.\textsuperscript{51, 52} The termination type in Figure 3.7b was also suggested through TEM studies,\textsuperscript{50} although the thickness of the crystals measured may have caused distortion of these images.\textsuperscript{50, 53} Theoretical studies suggested that the upright double 4 rings (Figure 3.6a), diagonal double 4 rings (Figure 3.7b) and β-cages (Figure 3.7c) were the most stable terminations, agreeing with the results of Sugiyama \textit{et al.}\textsuperscript{54} However, during dissolution, Meza \textit{et al.} found that dissolution of a 1.2 nm step occurred in 2 processes; firstly, the dissolution of a 0.9 nm layer, followed by a 0.3 nm layer dissolution.\textsuperscript{53, 55} This suggests a termination such as that in Figure 3.7c, with the 0.9 nm initial dissolution of a β-cage followed by the 0.3 nm removal of a layer of double 4 rings. This type of termination is also supported by the theoretical work, and it could be possible that all three of these occur on the zeolite A surface.\textsuperscript{54}

In the first experiments, the main growth mode was by a birth and spread mechanism. However, spiral growth of zeolites was also observed, despite the complexity of spiral sources.\textsuperscript{56} The first observation of spiral growth on an external surface was on Zeolite A,\textsuperscript{57} There have also been observations of complex dislocation sources, such as on STA-7, where an interlacing spiral mechanism was observed. This type of spiral results from growth anisotropy between the sub-steps emanating from the source, and was a result of the template interaction between two types of sub-step.\textsuperscript{58}

The AFM experiments that were performed up until this time were all \textit{ex situ} observations of the end of batch syntheses. This means that without careful control of the crystal recovery process, these observations were of surfaces that were recently under low supersaturation conditions. In order to observe growth under higher supersaturation conditions Meza \textit{et al.} used a technique in which extractions were taken from a semicontinuous reactor at regular intervals.\textsuperscript{59} This was performed on the previously observed silicalite.\textsuperscript{41, 60} The observation was that
much more surface nucleation was occurring with a high supersaturation, and that only towards the end of the reaction, when supersaturation is low, does the layer spreading mechanism observed for many zeolites dominate. This is shown in Figure 3.8.

![Figure 3.8: Observations of a silicalite surface growing under a) low supersaturation conditions and b) high supersaturation conditions.](image)

3.2.4 In situ Dissolution Investigations

Although ex situ AFM provided a wealth of information about the growth processes, the lack of real time evidence meant that it was not possible to know any changes to the surface during crystal recovery. Further, real time evidence would give a larger amount of information from which a greater understanding of the growth processes could be gleaned. Whilst growth of zeolites in situ was not possible due to the conditions in which growth occurred, dissolution experiments could be performed. Zeolites pose particular problems for in situ AFM, since they typically grow from a gel under hydrothermal conditions. Although dissolution processes are not exactly the opposite of growth processes, these experiments could give some important information about the systems studied.

The first in situ experiments performed on zeolites were the dissolution of zeolite A. This work, as mentioned above, predicted that the most stable units in the
zeolite A structure, and hence resistant to dissolution, were the β-cage and double 4 ring terminated steps. By performing experiments in situ, it was possible to obtain growth rates for the dissolution that was observed. From this, it was shown that mother liquor solutions were able to induce dissolution, with more dilute solutions dissolving the crystals at slower rates.55

These investigations were followed by dissolution studies involving zeolite L. Imaging on this crystal was performed on the (10̅0) face. As with zeolite A, the dissolution of the terrace was not complete in one step, but rather made up of several steps. These could each be attributed to the removal of different structural units, until the terrace was completely removed. The time that was required to perform this dissolution showed which configurations were the most stable. This was evident since the first step of the dissolution, which was on the most stable structure, took 2100 s to complete, whilst some of the species were only present for 30 s. As well as knowledge of the dissolution process, and the relative stability of the different structural units, it was also possible to calculate the activation energy for the process through use of an Arrhenius expression. This gave the activation energy as 21 – 23 kJ mol⁻¹, compared to the theoretical calculation of 35 - 45 kJ mol⁻¹.63

3.2.5 In situ growth investigations
The first AFM experiment monitoring in situ growth of an open framework material was performed by Shoaee et al., monitoring growth of the metal organic framework HKUST-1.64 The growth observed was a seeded growth, brought about by addition of a clear growth solution to the crystals. From these observations, the influence of line defects on the initial substrate surface could be observed because of real-time imaging. These defects prevented growth across them, and therefore led to some step bunching. Ultimately, this resulted in the presence of several growth hillocks surrounding the edge of the dislocation until it was no longer visible. The AFM investigations confirmed a birth and spread growth mechanism, and allowed the observation of new terraces soon after their nucleation. From these, it was possible to see that full terraces did not always nucleate, but rather
smaller sub-units of the terraces. This was observed as a 0.9 nm step, which rapidly grew into the larger, more stable 1.5 nm step. Since the growth rates of the advancing steps could be measured in situ, it was also possible to observe that step growth rates slowed once the vertex of a growing terrace reached the crystal edge. This was attributed to a point effect, whereby there was more mass transport to the vertex than to a step edge, owing to differences in concentration gradient.\textsuperscript{65-67}

The study of metal organic frameworks with AFM was continued with ZIF-8. In these investigations, both spiral and birth and spread type growth were observed. It was also possible to follow the nucleation and development of a single terrace. This allowed an insight into the growth of the terraces, which had a uniform height from ex situ observations. Through real-time imaging, the terraces were found to grow by sequential building of the units through several additions. The final terrace height was 1.2 nm, however this was built through additions resulting in observed heights of 0.4, 0.6, 0.8, 0.9 and 1.1 nm. These heights corresponded to different structural units in the β-cage, showing that the cages were not nucleated complete, but rather that these complete cages were long lived due to their stability.\textsuperscript{68, 69}

The first in situ growth experiments performed on inorganic open framework materials were performed on the zincophosphates. Two frameworks were investigated; the sodalite (SOD) framework, the results of which are detailed herein and the faujasite (FAU) framework.\textsuperscript{70} As with aluminosilicate FAU, the growth on the \{111\} face was made up of layers of single FAU layers of 1.4 nm. Both and birth and spread and spiral growth mechanism were observed in situ, shown in Figure 3.9. Through the use of AFM, it was also possible to image several defects on the crystal surface, and gain an understanding of their origin, as well as investigate the metastability of the FAU crystals when in contact with supersaturated mother liquor.
Figure 3.9: AFM deflection images showing in situ growth of the \{111\} face of FAU-ZnPO by a) spiral growth mechanism and b) birth and spread mechanism. 70
3.3 Experimental

AFM images were collected using a JPK Instruments AG NanoWizard II Atomic Force Microscope operating in contact mode, using silicon nitride cantilevers with a nominal force constant of 0.58 N m\(^{-1}\) (Veeco model NP-10). \textit{Ex situ} images were obtained with scan rate of 1 Hz for scan size < 2 \(\mu\)m, and 2 Hz for scan size > 2 \(\mu\)m. \textit{In situ} images were obtained with scan rate of 4 Hz. \textit{In situ} images were obtained by filtration of 0.5 mL growth solution into a fluid cell, followed by scanning under solution. Unless stated in the text, experiments were performed at room temperature (ca. 23 °C).

The seed crystals used in these experiments were synthesised at 0 °C as shown in Chapter 2. For \textit{ex situ} images, the crystals were attached to a glass slide by heating thermoplastic to 50 °C until it became malleable, then flattening it with a spatula. The crystals were then sprinkled on top and left on the heat for 15 seconds to allow them to embed in the thermoplastic. The slide was then removed from the hot plate and excess crystals were removed using air. For \textit{in situ} experiments, an epoxy resin was used to attach the seed crystals. Once the resin was prepared, it was cured in a 60 °C oven for 4 hours until it began to set. At this time, the seed crystals were applied and the slides returned to the oven overnight to complete the curing process. Once removed, the slides were blown with air to remove any excess crystals that were not embedded.

In order to prepare growth solutions for \textit{in situ} AFM two methods were used. In the first method, SOD-ZnPO was synthesised following the recipe of Gier and Stucky.\textsuperscript{71} A typical synthesis involved dissolution of NaOH (1.68 g, 42 mmol) in deionised H\(_2\)O (21 g) to form solution A. Solution B was created by addition of Zn(NO\(_3\))\(_2\)·6H\(_2\)O (3.57 g, 12 mmol), H\(_3\)PO\(_4\) (1.73 g, 15 mmol) and NaBr (1.03 g, 10 mmol) to deionised H\(_2\)O (15 g). The two clear solutions were then mixed at room temperature, until a homogeneous gel was formed. During the reaction, a clear mother liquor layer would form, from which 0.4 mL was removed, and filtered onto the seed crystals in the AFM fluid cell.
For the second method, the growth solutions were prepared in the laboratory using concentrations similar to those obtained from method 1. These were obtained through ICP-MS measurements on the mother liquor layer obtained. In order to prepare the solutions, a combination of the desired amount of stock solutions of NaBr, Zn(NO$_3$)$_2$.6H$_2$O, H$_3$PO$_4$ and deionised H$_2$O was prepared using micropipettes. The pH was then adjusted to 7 ± 0.05 using HNO$_3$ and NaOH stock solutions, so that the pH was consistent with that of the original synthesis. These solutions were left to equilibrate for a minimum of 48 hours before addition to seed crystals in growth experiments. For experiments involving an excess of phosphorus, the concentration of phosphorus used was 3000 ppm (0.097 mol dm$^{-3}$), whilst sodium concentrations were kept constant across all experiments at 20100 ppm (0.875 mol dm$^{-3}$). For zinc, the concentrations were varied between 1 and 30 ppm (0.015 - 0.459 mmol dm$^{-3}$). Since zinc was the limiting element, this concentration was varied in order to control supersaturation.
3.4 Results and Discussion

3.4.1 Growth observations on the \{100\} face

The SOD-ZnPO crystals were initially observed using \textit{ex situ} AFM. An example of these observations are shown in Figure 3.10. During \textit{ex situ} measurements, two growth mechanisms were observed on the \{100\} face. In Figure 3.10a, the crystal observed has both a “birth and spread” growth centre and a spiral growth centre next to each other. Figure 3.10b and 3.10c show other growth centres observed by \textit{ex situ} AFM. In each of these spiral growth centres can be observed. The growth centres observed by \textit{ex situ} AFM tended to be composed of one main growth centre per crystal, similar to those observed for zeolite A and Y.\textsuperscript{46, 48} Unlike these observations, however, the step spacing observed was not consistent. Instead, step bunches that were > 10 nm in height were observed, shown in Figure 3.10.

![Figure 3.10: Ex-situ vertical deflection AFM images of the \{100\} face of SOD-ZnPO crystals grown at 0 °C, showing a) both a spiral and “birth and spread” growth mechanism, b) a spiral growth centre, and c) a growth centre containing two spiral centres.](image)
3.4.1.1 Step Bunching

Step bunching is a phenomenon that has previously been observed in many different systems. This results from the coalescence of several terraces due to a difference in spreading rates, which creates these bunches.\textsuperscript{72} There are many mechanisms by which step bunching can occur. For example, asymmetry of adatom movement on a surface, possibly caused by the Ehrlich-Schwoebel effect, has been found to cause bunching on Si (111) surfaces.\textsuperscript{73} This effect arises because there is an increased energy barrier to movement down a step, as shown in Figure 3.11. This high activation energy arises because an atom must go through a configuration in which it has fewer substrate neighbours when passing over a terrace edge.\textsuperscript{74} Therefore, it becomes more favourable to add to a step on the same layer (labelled as $\nu^+$ in Figure 3.11), as opposed to addition to a step on the layer below (labelled as $\nu^-$ in Figure 3.11). Since there is asymmetry between the two attachment mechanisms, the crystal will favour addition to an edge site on the same terrace, rather than moving over the energy barrier to add to a lower step, which may lead to step bunching.

In the case of the crystals observed here, they are grown from solution. The role of the Ehrlich-Schwoebel asymmetry effects described above is not well known for this type of growth. This is because in the vapour growth and epitaxial growth for which this effect has typically been described, bulk diffusion and incorporation at steps is not as important as for solutions. This importance of other processes in solution growth means the role of diffusion on a crystal surface is less well understood.\textsuperscript{75} Nevertheless, some studies of Canavalin crystals grown from solution have described observations of growth mounds using this effect,\textsuperscript{76} meaning that although the role of surface diffusion is not fully understood for solution growth, it may still have importance and this effect may still be the cause or a contributing factor towards the presence of step bunches.
Figure 3.11: Diagram showing the Ehrlich-Schwoebel effect. $W_s$ gives the barrier to jump over the step, $D$ is the diffusion constant, $F$ is the deposition flux, $\tau$ is the desorption time, $\nu_-$ is the attachment coefficient moving down a step, and $\nu_+$ is the attachment coefficient for attaching to a step on the same layer.\textsuperscript{74}

Other mechanisms by which step bunching can occur include the effects of impurities,\textsuperscript{77-79} which act to pin back the advancement of steps that are spreading. Since steps on layers above are not affected they will continue growth until bunching occurs. Further, bunching may be induced by a fluctuation of the supersaturation on the surface,\textsuperscript{80} or the presence of foreign or differently oriented particles on the surface, which is similar to the effect of impurities, and means that step growth rate around the particle will be retarded, leading to a curved step form.\textsuperscript{80} This slowing of the growth rate allows other steps to catch up, leading to the bunching effect. Since there are several mechanisms by which this effect could arise, it is not possible to know which of these mechanisms was responsible for the bunching observed, as these images were taken \textit{ex situ} and so the evolution of these bunches could not be followed.

\textbf{3.4.1.2 Birth and spread growth}

In Figure 3.10a, a growth centre formed through birth and spread growth was observed \textit{ex situ}. This type of mechanism was also observed \textit{in situ}, as shown in Figure 3.12. From the \textit{ex situ} images, it seemed that the terraces formed were square with rounded edges. However, from \textit{in situ} observations it can be seen that
the terraces are rectangular, with the preferential growth direction altering between layers. This means that there is anisotropic growth between the [010] and [001] directions on a (100) face, with this anisotropy switching every other layer.

![Figure 3.12: a – d) Deflection images showing birth and spread growth on the {100} facet of SOD-ZnPO.](image)

The reason the terraces in the ex situ image appeared square is because they were made up from several layers stacked on top of each other, leading to an interference pattern where a fast growing terrace on top will be hindered by a slow growing terrace below. Since there was a lot of step bunching in the ex situ images, this was difficult to see, however the same centre was observed in situ, and is presented in Figure 3.13. Here, the rectangular nature of newly nucleated terraces can be seen, with growth of the fast direction hindered by the layer below. In the ex situ image it is possible to see some step splitting, which agrees with this observation.
3.4.1.3 Spiral growth

In Figures 3.10a, 3.10b and 3.10c, ex situ spiral growth centres are shown. From Figure 3.10a in particular, it can be seen that there are two different spirals growing out of the same dislocation. These sub-steps that emanate from the dislocation have a different growth anisotropy compared to each other, which leads to the generation of an interlaced spiral pattern. This interlaced pattern is observed most clearly in Figure 3.14, which is from an in situ growth experiment. This is clearer since there is less bunching on these steps, and therefore the pattern is not lost within the bunches.
Figure 3.14: a) Height image showing interlaced spiral growth on the (100) face of SOD-ZnPO, and b) Cross sectional analysis of the area marked in Figure 5a, showing double and single step heights.

As well as single growth spiral growth centres, there have also been observations of growth mounds containing composite spirals. An example of this is shown in the sequence in Figure 3.15. In this figure, the growth mound to the left can be seen to be made up from two dislocations. This pair of dislocations are of opposite signs, and therefore the steps join up to form closed loops.\(^{81}\) This type of cooperative growth has been observed previously in other systems.\(^{82, 83}\) In this case, an interlaced spiral pattern is still observed.
Figure 3.15: Sequence of AFM images showing spiral growth on the \{100\} face of SOD-ZnPO. The spiral centre on the right is made of one dislocation, whilst the spiral centre on the left contains two dislocations of opposite sign.

In order to explain the origins of the interlaced pattern more clearly, the cartoon in Figure 3.16 is used. Here, the morphologies that would be created by two unhindered sub-steps are shown in Figures 3.16a and 3.16b. However, because each layer is growing on top of a layer with different growth anisotropy, the morphology observed will be the interference pattern between these, as shown in Figure 3.16c. This square pattern, highlighted in grey, will be observed since the fast growing layer is hindered by a slower growing layer below. Therefore it will end up bunching over this slow growing step, creating a double step. In the <110> direction, the growth rates between the sub-steps will be equal, and as such a step
splitting will be observed, and this will lead to the characteristic “zig-zag” pattern highlighted in black in Figure 3.16c. This type of interference pattern is the same as shown for the birth and spread growth centre, and the step splitting can be clearly seen in the in situ images.

Figure 3.16: Cartoon showing the morphology expected for a) anisotropic spiral growth in the y direction, b) anisotropic spiral growth in the x direction, and c) combination of the two leading to an interlaced spiral pattern, with grey shaded area representing the area expressed.

Proof that the interlacing spiral pattern was caused by alternating anisotropic growth of the terraces is shown in Figure 3.17. In Figure 3.17, the sequence shows the growth of two single spiral growth mounds. Due to their positions with respect to each other, two planes are created on which layer spreading can be observed. Here, by tracking single steps, the anisotropy can be observed, which alternates between the layers. The two layers are labelled Ty and Tx in the figure, and by following their progress it becomes clear that they have different growth anisotropy. Firstly, in Figures 3.17a-c, Ty is seen to advance with preference for growth in the y direction. Next, once layer Ty has formed, the next layer Tx can spread out of the other dislocation. This new layer has anisotropic growth, with preference for growing in the x direction. This therefore proves that it is the alternating anisotropic growth leads to the interlacing spiral patterns observed, as well as the observations for the birth and spread mechanism.
In order to investigate the cause of this anisotropy, multiple cross sections were taken in order to find the heights of the terraces observed. From Figures 3.14a and 3.14b, where a representative cross section is shown, it can be seen that the double steps (caused by the interference pattern) have a height of 0.9 nm ($d_{100}$),
whilst the single anisotropic steps emanating from the dislocation have a height of 0.45 nm ($d_{200}$). The anisotropic growth steps growing with a birth and spread mechanism also had a height of 0.45 nm. In previous ex situ observations of SOD-ZnPO by Reddy et al., a minimum step height of 0.9 nm was reported. However, it may be that due to the small size of crystals used they were only able to observe double steps.

Observing the structure of sodalite, it can be seen that $d_{200}$ is the equivalent of half a sodalite cage. Therefore, the identity of the single terraces is likely to be a half sodalite cage. This is because addition of this unit creates a closed structure, which is likely to be more stable and long lived. From Figure 3.18b, it can be seen that this addition is achieved by capping the previous layer in a body centred cubic fashion. The four completed cages on the layer below create a half sodalite cage, which can be completed by the addition of a further half layer. This can also be seen in Figure 3.18a, where the half cage is highlighted in grey.

![Figure 3.18](image)

*Figure 3.18: a) Structural diagram showing 2-D nucleation on the {100} face of SOD-ZnPO leading to the formation of a new terrace, and b) cartoon of the resulting structure in Figure 3.15a, represented as polyhedra.*

With the identity of the terrace known, layer-spreading by addition of further growth units to the terrace could also be investigated. When considering addition to terrace edges, shown in Figure 3.19, it can be seen that the site will share an atom with the new cage to be formed (red atom that is circled), and therefore the “growth unit” represented in the figure contains one atom fewer than in Figure 3.18a. It must be stressed that the “growth units” in the figures do not necessarily
represent the actual growth units for SOD-ZnPO growth. Whilst the actual species that add are unknown, the units shown are used since they represent the atoms required to create another closed cage structure, which is expected to be a longer lived species. Addition to this atom is expected to be the rate limiting step, since this is an addition to the most stable structure. Further additions will then be to open structures with more bonds to attach to, and therefore more facile. This is similar to the reasoning behind the existence of terraces and steps with consistent heights, which are present because they are long lived stable structures.

*Figure 3.19: Structural diagram showing addition to an edge site on the {100} face of SOD-ZnPO leading to the advance of the terrace.*

In Figure 3.20, it can be seen that on a given layer, the atom that is contributed to the new cage is different in the x and y directions. This is highlighted in the top right hand corner of the figure with black circles. The reason for this is because there is a 1:1 ratio of Zn and P in the framework, with strict alternation. Depending on the direction, the shared atom will either be P or Zn. In order to add to the closed structure, addition of Zn in one direction is required whilst P addition is required on the other direction. Therefore, if there is a difference in the rate of condensation of a Zn growth unit onto a P in the framework, compared to the condensation rate of a P growth unit onto a framework Zn, then anisotropic growth would be expected.
Whilst the above explains the origin of the growth anisotropy, it does not explain why this anisotropy switches between layers. The reason for this is related to the symmetry of SOD-ZnPO. There is an n-glide plane perpendicular to the \{100\} face, and the result of this is a rotation of the 4-ring by 90° as well as atoms attached. Therefore, the important shared atoms will also rotate by 90°, alternating the direction of the anisotropic growth. This is shown in Figure 3.20. In this figure, two orientations of the same crystal structure are shown, one showing the (100) and the other the (010) face. The image showing the (100) face shows how the terraces would look on the AFM, whilst the (010) view shows a side view of these terraces, with height shown. In all, there are three monolayers in this figure,
coloured purple, pink and blue. Observing the middle pink terrace, it can be seen that across the 4-rings there are rows of single atoms in each direction, labelled in the diagram. In this case, the Zn rows are moving in the y direction and P in the x direction. The atoms onto which edge site addition will occur are circled, and in this case will be P in the y direction and Zn in the x direction. Observing the terrace above and below, it can be seen that for both of these, the directions have switched. Now, addition in the y direction will occur onto a Zn atom, and addition in the x direction will occur onto a P atom.

Therefore, this shows that the anisotropy observed is caused by the strict alternation of Zn and P exposing the difference in their condensation rates, whilst the alternation of this anisotropy is symmetry induced, caused by the n-glide plane perpendicular to the (100) face.\textsuperscript{85} This explanation ties in with the observations made by AFM, where alternating growth anisotropy is observed for the (100) face.

### 3.4.1.4 Effect of supersaturation on terrace morphology

In the \textit{in situ} images that have been presented so far, it can be seen that the terraces are much less rounded, and show much less bunching than those observed \textit{ex situ}. This could be related to the supersaturation conditions of the solutions from which growth is achieved. Since the synthesis of the seed crystals was left for over 1 month, it is likely that the solution was at equilibrium for a long time. The presence of the CZP phase means that the solution may have even been undersaturated with respect to SOD at the end of the process, in which case the observations may be a combination of features produced by growth and dissolution. In order to investigate the effect, low medium and high supersaturation solutions were used to grow crystals \textit{in situ}. Since the actual supersaturation is unknown (see Chapter 4 for full details) the terms low, medium and high in this case are used to describe the conditions in which obvious changes in morphology are observed rather than quantitative amounts. Although initial solution concentrations were known (\textit{ca.} 10 ppm), the actual concentration is not known as these experiments were performed in a closed cell where the supersaturation would be constantly dropping as zinc is incorporated into growing
crystals. Further, for high concentrations of Zn, nucleation of other phases may also have been occurring, since this occurred upon ageing high Zn concentration solutions. In Figure 3.21, the morphology at “low” and “medium” supersaturation are shown. For the images observed in “low supersaturation conditions, the concentration was achieved by leaving the solution on the crystals over a period of several hours, allowing the fluid cell concentration to drop as Zn was used in growth. Medium supersaturation images were taken immediately after the addition of a mother liquor solution. From the images, it can be seen that at “medium” supersaturation, the terraces are square. When the supersaturation drops, terraces become more rounded. This is because as equilibrium is approached, attachment and detachment will occur at surface sites until the most stable configuration is achieved. The steps also seem to be “ragged.” This may be due to the influence of impurities in the solution, which have caused pinning of steps in other systems at low supersaturations. At low supersaturations, when terrace spreading is slow, it may be that the rate is no longer fast enough to overgrow these impurities leading to this observation.

Figure 3.21: AFM images showing growth on the \{100\} face under a) low b) low and c) medium supersaturation conditions.

Figure 3.22 shows “high” supersaturation images taken after the introduction of Zn to create a cell concentration of 100 ppm, as compared to ca. 10 ppm concentration for “medium” supersaturation. When the crystals are grown at a higher supersaturation, the morphology of the terraces is affected, leading to much more rapid growth. Under these conditions pyramids, or mounds, begin to form in several places on the crystal surface, which spread rapidly. The underlying
crystal surface also undergoes rapid growth emanating from the terrace edges. Eventually, the mounds coalesce on the surface. A similar rapid growth at terrace edges was observed for growth initiation in FAU-ZnPO.\textsuperscript{70}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure322}
\caption{a-c) Sequence of AFM deflection images showing the growth of the \{100\} face of SOD-ZnPO observed after introduction of 2 drops of zinc nitrate solution to a fluid cell containing a mother liquor solution that was unable to induce growth of the seed crystals.}
\end{figure}

A high supersaturation (30 ppm Zn) solution was prepared and left to age for 1 week (see Chapter 4 for equilibration experiments). Before addition to seed crystals, some growth of a zinc phosphate could be observed in the solution. Upon addition to the crystals, the growth rates observed were similar to those observed at medium supersaturation; however the morphology was different. This is shown in Figure 3.23a and b, where a more rounded birth and spread and spiral growth are both shown. In Figure 3.23c it can be seen that several bunched terraces were also produced, with ragged edges. Since the rates were similar to those at medium supersaturation it may be solution concentration of Zn had decreased to these levels as the other zinc phosphate phase grew. The reason for the change in morphology may also be related to this phase. Since the solution will have contained several of these particles it could be that they acted as impurities towards the growth of SOD. More rounded steps have been observed by the presence of impurities for calcite, whilst ragged step bunching has also previously been observed through impurity effects.\textsuperscript{86}
Figure 3.23: Deflection images on the \{100\} face of SOD-ZnPO after the addition of a 30 ppm solution equilibrated for 1 week showing a) spiral growth, b) birth and spread growth and c) step bunching.

3.4.1.5 Ordering Defect on the \{100\} face

Another observation on the \{100\} facet has been of growth being promoted by a defect in the surface. This is shown in Figure 3.24. The linear defect runs along the [110] direction (see white line with arrows). It is difficult to tell if there is any height difference across the defect, since observing the cross section (Figure 3.24c) it can be seen that there is a large amount of noise, and therefore what seems to be a slight decrease in height across the defect could just be noise contribution. Upon inspection of the defect, it can be seen that the growth anisotropy of terraces on the same level switches either side of this feature. This suggests that across the line is a switch in the Zn:P ordering. This is shown in Figure 3.24b. In this structural diagram, the change in Zn:P ordering is highlighted across the white line that passes across the [110] direction, representing the defect. Observing the defect, it can be seen to be a source for multiple spiral centres, showing the important role that defects play in extending growth at low supersaturation on crystals such as these. The origin of this defect may be a low angle dislocation in itself. If this had a height over its total length of half a unit cell, then this could explain the switching in Zn : P ordering. This type of defect would have low height, which under the conditions of this experiment would not be measurable. This may also just be an alternation in Zn : P ordering, however the
presence of several dislocations emanating from the line suggest this may not be the case.

Figure 3.24: a) Height image of the \{100\} facet of SOD-ZnPO, with defect visible moving out of the top left of the growth centre. Arrows show the direction of growth of terrace either side of the defect, b) Structural diagram showing how the defect could be formed. Diagonal white line shows defect position, and c) Cross sectional analysis of the area marked by the white line in a). Two terraces and the defect are crossed by this, the locations of which are marked on the cross section.

3.4.1.6 Mound growth on the \{100\} face
In the examples of birth and spread growth displayed so far, nucleation has been observed to occur randomly over the exposed crystal surface. However, the formation of pyramid type terraces, or mound morphologies have also been observed. This can be observed clearly in Figure 3.25. In this figure, the crystal
initially began growing by a typical birth and spread mechanism. However, after a
certain amount of time, this growth led to the formation of several mounds on the
surface. The reason these mounds occurred was due to preferential nucleation in
the same area, leading to these types of feature, as shown in Figure 3.26.

During the AFM experiment, a 2-D layer spreading growth was first observed, then
changing into a 3-D type growth. This type of growth therefore is similar to a
Stranski-Krastanov type growth. This is one of the three growth modes in
epitaxial growth considering the relationship between the surface free energy of
the substrate, deposit and the interface. The other growth modes are the Volmer-
Weber growth and Frank-van-der-Merwe. Volmer-Weber growth is observed
when the surface free energy of the substrate is lower than that of the interfacial
free energy and deposit free energy, and therefore leads to 3-D island formation
to minimize the area covered by their formation. For Frank-van-der-Merwe
growth, the energy of the substrate is equal to that of the interfacial and deposit
free energy. This only occurs for homoepitaxial growth, and leads to an indefinite
layer by layer growth, such as that shown in Figure 3.12. For Stranski-Krastanov
growth, the surface free energy of the substrate is higher than that of the
interfacial free energy and deposit free energy. Here, layer spreading is initially
observed before the strain becomes too large and 3-D mound formation begins.
Therefore, since homoepitaxial growth is being performed in this experiment, it

Figure 3.25: AFM lateral deflection image showing mounds growing on the \{100\}
face of SOD-ZnPO.
would be expected that a Frank-van-der-Merwe type growth would be observed. However, in this case the Stranski-Krastanov model fits better. This could be caused if defects on the surface mean that deposits cause an increased strain, and therefore lead to a movement to 3-D growth when the strain becomes larger.

![Figure 3.26: Lateral Deflection images showing the \{100\} facet of SOD-ZnPO growing via a birth and spread mechanism with nucleation in the same location leading to mound type growth.](image)

The other cause of this shift from 2-D to 3-D growth could be the Ehrlich-Schwoebel effect. This has been observed in molecular beam epitaxy experiments to increase mound formation by creating anisotropic movement of growth units so that there is a net uphill movement, and therefore nucleation is more likely on the top layer.\(^9\) This mechanism is typically applied under high supersaturation conditions. Whilst this mechanism can describe the reason any mounds forming would go on to create large mounds, it does not necessarily describe the origins of the mounds. This is because growth originally occurs by 2-D layer spreading, and mound formation only occurs later on in the experiment. If there was a defect on the surface in a specific location promoting nucleation, then after repeated nucleation on this point, forming a small mound, this effect would go on to propagate the mound; however it may not necessarily be the reason for the mound appearing. Therefore of the two mechanisms proposed, the surface strain caused by deposits is perhaps the more likely to initiate mound formation.
During the experiments performed, lateral force images were also collected. These measure the twist of a cantilever, giving an insight into the surface friction (see Chapter 5). In Figure 3.26, it can be seen that there are spots (circled) where increased lateral force is observed. Comparing this to the height image, this is only an LFM observation. As a terrace grows over them they also persist. The exact nature of these areas of increased friction is unknown; however it is possible that they are related to surface defects. If this is the case, then that could explain the origin of the mound growth observed, where these defects would act as the location for preferential nucleation.

Another example of mound type growth during in situ experiments is also shown in Figure 3.27. Here, the growth was initiated by foreign particles on the surface during growth. It can be seen how there is preferential nucleation of several layers on top of this particle, with an increased growth rate compared to the rest of the face. After some time, the influence that the particle was exerting over the nucleation rate ceases, and the terraces spread out.
Figure 3.27: Sequence of vertical deflection images showing growth on the \{100\} face of SOD-ZnPO.
3.4.1.7 Low angle defect

Figure 3.28: a) Ex situ image of the \{100\} face of a SOD-ZnPO crystal showing a spiral growth centre, and b) the same spiral centre growing in situ. A low angle defect can be seen moving across the spiral centre.

In Figure 3.28 a type of low angle defect is shown. This extended defect traverses the crystal along the [010] direction, and is highlighted in Figure 3.28a. This type of defect could be a result of a macroscopic defect that the crystal is trying to accommodate. This type of defect has also been observed in the metal organic framework ZIF-8. The defect also seems to be the source of several screw dislocations, as highlighted in Figure 3.28b. In order to measure the angle of the defect, the cross section in Figure 3.29 was used. This allowed the calculation of the angle of the defect, which is 1.1 (±0.1) °.
Figure 3.29: Cross section taken across the defect shown in Figure 3.28 showing the angle of the defect.

3.4.1.8 Surface activation for growth on {100} face

Surface activation seems to play an important role in the growth of sodalite zincophosphate (SOD-ZnPO). The origins of this phenomenon are unclear; however it may be related to either a change in the surface once growth has ceased, or a shielding of the surface owing to deposit of foreign particles post synthesis. The effect that is observed tends to preserve the crystal, preventing growth and dissolution under mild conditions. For example, in the sequence shown in Figure 3.30 a solution that is 5 ppm Zn, 1:1 Zn:P ratio is added to the crystals. As can be observed, over a 20 minute period, no change was observed on the surface. Following this observation, a new solution of higher concentration (8 ppm Zn) was flowed through the solution cell. Once this solution had reached the crystals rapid growth was observed.

Later in the experiment, the original 5 ppm solution that was unsuccessful in initiating growth was flowed back through the fluid cell. Growth continued onwards even after the re-introduction of this solution, until all of the solution was exhausted and water began to flow through the cell. Since the flow rate was high (0.1 mLmin⁻¹), and ca. 10 mL solution was passed through a 0.4 mL cell, only the solution that was being flowed into the cell could have influenced the crystals. This therefore showed that once a crystal is growing, it is possible for a solution to
propagate that growth even if it is not supersaturated enough to initiate growth itself. This suggests that the surface behaves differently before growth is initiated as opposed to during growth, perhaps for the reasons aforementioned.

Figure 3.30: AFM deflection images of a SOD-ZnPO crystal a) 6, b) 18, and c) 30 minutes after the addition of a 5 ppm Zn growth solution.

Figure 3.31: AFM deflection images of a SOD-ZnPO crystal a) 45, b) 48, c) 51, and d) 54 minutes after the re-introduction of a 5 ppm Zn growth solution.

This effect has also been observed for dissolution of SOD-ZnPO with water. In these experiments, the sequence in Figure 3.32 shows the effect of direct addition of water onto the crystals. Here, it can be seen that throughout the series there is no change to the surface. However, once the surface has begun growth, switching the solution from ZnPO$_4$ to water leads to dissolution of the crystal. This can be seen more clearly in Figure 3.33. In this figure, the dissolution of the terrace occurs due to water being flowed into the cell. Since the flow rate is 0.1 mL min$^{-1}$, and the cell holds ca. 0.4 mL of fluid, this would mean that after 4 minutes the cell would be recycled. Therefore, these scans taken 40 minutes after the introduction of the water will be those showing dissolution by water alone, again a scenario only encountered after the surface has been “activated” by the initiation of the growth process.
Figure 3.32: AFM deflection images showing a ZnPO-SOD crystal a) before addition, b) 4 minutes after addition, c) 8 minutes after addition, and d) 31 minutes after the addition of water to the fluid cell.

The dissolution process, shown in Figure 3.33, is mechanically aided by the tip. Initially, the terrace begins to retreat, then an etch pit forms in the place of the dislocation. The tip effect can be seen by zooming out, where the area of tip assisted dissolution is highlighted. Tip enhanced dissolution was also observed for Zeolite L and Zeolite T. However, throughout these experiments the tip did not have an obvious effect on the growth of the terraces.
Figure 3.33: Dissolution of the \{100\} face of SOD-ZnPO caused by flowing water over the crystals.
3.4.2 Observations of the \{110\} face

Initially, the \{110\} face of SOD-ZnPO was observed using \textit{ex situ} AFM. These results showed a birth and spread type growth mechanism. Figures 3.34a-c show three images of the \{110\} face of SOD taken from three separate crystals. In these images, the terrace morphology is rectangular in shape, with slightly rounded edges. This rectangular morphology is caused by anisotropic growth of the terrace, with growth in the \<100\> direction more favourable than growth in the \<110\> direction. Unlike the \{100\} face, this anisotropy remains the same for all layers without alternation. This is expected, since the n-glide plane is not perpendicular to this face and no Zn / P alternation exists.

As well as terraces, there are also etch pits observed on some \{110\} faces, highlighted by the white arrows in Figure 3.34a and Figure 3.34c. These etch pits form when a crystal is dissolving, and this therefore suggests that this face was not experiencing only growth before the crystals were scanned \textit{ex situ}, but rather that at some point dissolution was occurring. Within the crystal sample these images were taken from, there were two phases present; SOD-ZnPO and CZP. Since the two different materials will have different solubilities, it is possible that when the solution was at equilibrium with the SOD-ZnPO it could still have been supersaturated with respect to the CZP phase. If this was the case, then the CZP phase would continue to grow and solution zinc concentration, which was the limiting nutrient, would decrease. This decrease in solution zinc concentration would make the solution undersaturated with respect to sodalite, whilst still supersaturated with respect to CZP. This would lead to sodalite dissolution, which would give the observed etch pits on the \{110\} face.
Inspection of the terrace heights observed on the \{110\} face show an average height of 0.6 nm, which is equivalent to \(d_{110}\). This is shown in the cross section shown in Figure 3.34d. When inspecting the structure of SOD, this terrace height represents a half sodalite cage capping on the \{110\} face, similar to the capping seen on the \{100\} face. Figure 3.35 shows a structural diagram of the \{110\} face, in which there is the generation of a new terrace layer with a height of 0.6 nm by surface addition. In the figure, the half cage that is already present on the surface, and that will be capped by the incoming growth unit(s) is highlighted in grey. Addition of the unit as shown then results in the completion of the sodalite cage,
which creates a new layer 0.6 nm proud of the surface. This new layer is emboldened in the figure (right) to further emphasise the new terrace formed. In the figure, the capping occurs by addition of the unit shown; however this unit is not necessarily the growth unit that actually adds during surface addition.

**Figure 3.35:** Structural diagram showing surface addition on the \{110\} face of SOD-ZnPO.

In order to explain the rectangular morphology observed, a terrace of 0.6 nm units is shown in Figure 3.36. From this image, it can be seen that addition in the two different directions will be different. For attachment of the green sodalite cage in the [1\̅0] direction, less step T atoms are contributed to the new cage that is formed than for addition of the red cage in the [001] direction (5 rather than 6). When the Kossel model was introduced, the number of attachments formed between the growth unit and the crystal was observed to affect the growth rate, with growth of kink sites faster than edge and surface sites because more attachments were formed. In this case, more connections are made in the [001] direction than in the [1\̅0] direction, which will mean a faster growth rate in this direction. This is therefore likely to lead to the anisotropic morphology observed. When cation positions are considered, these also show anisotropy between the two directions. This means that they could also contribute to the anisotropy observed. Since the cations will decorate the surface as it grows, it could be that
they aid the anisotropic growth by interacting with the growth species as they diffuse on the surface, directing them into growth sites. If the surface decoration is different in one direction, as will be the case here, then the strength of this interaction with growth species will change, leading to growth rate differences.

Figure 3.36: a) cation positions on the \{110\} face, showing anisotropy between the two directions, b) a terrace on the \{110\} face, with the two areas for addition highlighted by green and red cages.

Observing Figure 3.37, it seems that nucleation is dominating this surface, suggesting a much more rapid growth rate as compared to during the crystal synthesis, where layer spreading was observed. This means that when the \{110\} face is grown \textit{in situ}, growth is different to \textit{ex situ} observations. This could be due to the different conditions (temperature) in which the crystals were synthesised and in which these experiments were performed; by increasing the temperature, the rate of \{110\} growth seems to be rapidly increased.
Figure 3.37: a-b) AFM images of the \{110\} face of SOD-ZnPO after addition of a growth solution.

Since the growth rate seems to be largely increased on this face, it could be expected that this face would grow out at room temperature, leaving only \{100\} and \{111\} facets present. By monitoring growth in a high supersaturation solution over several hours, it was possible to observe this effect. This is shown in Figure 3.38. In Figure 3.38a, the crystal is shown before the addition of a growth solution. Terraces are visible on the surface, consistent with other ex situ observations. After 4 hours, the crystal was examined again, and the result is shown in Figure 3.38b. Here, the \{110\} face has almost completely grown out, with the \{100\} faces on either side almost meeting. The rapid nucleation observed in Figure 3.37 can also be observed on the small remainder of this facet.
Figure 3.38: a) \{110\} face of SOD-ZnPO observed ex situ and b) the same crystal face observed 4 hours after the introduction of a high supersaturation growth solution.

Following these observations, a low supersaturation solution was added to some sodalite crystals to see if this effect was reproducible without the influence of the AFM conditions; that is the interaction of the tip with the surface and the different boundary layer conditions produced by embedding the crystals. The results of this experiment are shown in Figure 3.39.
Figure 3.39: a + b) SOD-ZnPO crystals 1 week after the addition of a low supersaturation solution, c + d) SOD-ZnPO crystals prior to solution addition.

From Figure 3.39 it can be seen that after one week in contact with a low supersaturation solution the \{110\} face grows out. This agrees with the AFM observations and shows that the high nucleation observed after the introduction is a results of the faster growth of this face as compared to the other faces observed. This result shows the influence of temperature on the relative growth rates of the different faces, with lower temperature leading to expression of the \{110\} face, which grows out at higher temperatures.
3.4.3 Observations of the \{111\} face

The \{111\} face was observed using both *ex situ* and *in situ* AFM. From these images, it was possible to observe two different mechanisms for growth. The first mechanism observed was a birth and spread type growth mechanism. Figure 3.40 shows a sequence of AFM height images of this type of growth. In Figure 3.40e, a cross-sectional analysis is also presented showing the average terrace height measured for this growth mechanism. This height was measured as 0.2 (± 0.1) nm, or $d_{222}$.

![Figure 3.40: a – c) Height images showing isotropic birth and spread growth on the \{111\} facet of SOD-ZnPO, d) Height image showing growth on the \{111\} face from which cross section e) is taken, e) Cross sectional analysis showing single terrace height on the \{111\} face.](image)

The second mechanism for growth observed was a spiral growth mechanism. The sequence in Figure 3.41 shows this type of growth. Again, the terrace height was measured. This time, it was found to be 0.5 (± 0.1) nm, or $d_{111}$. This double terrace height was observed in all spiral growth experiments. In this sequence of images, it
is possible to observe both spiral growth and birth and spread growth occurring at the same time. In the sequence, the formation of several nuclei can be observed. Again, for terraces growing by a birth and spread mechanism the height of the terraces was 0.2 (± 0.1) nm. Another important difference between the growing terraces is the difference in morphology between them. In Figure 3.40, and in Figure 3.41, all of the terraces that are growing by a birth and spread mechanism have round, or isotropic, terrace morphologies. These terraces seem ragged at the edges, with no preferential growth direction observable. Contrasting this, the terraces growing from the spiral growth centre are observed to have a more polygonised morphology, with triangular terraces observed. Although the double steps leading to triangular morphologies are generated at the dislocation, this is not responsible for the difference in morphology. This can be confirmed as the terraces that grow away from the dislocation, and therefore are no longer influenced by it maintain the triangular terrace morphology. Therefore, the difference in morphology is likely to be related to the difference in terrace height.
Figure 3.41: Spiral growth on the \{111\} face of SOD-ZnPO observed a) 216, b) 222, c) 228, d) 234, e) 240 and f) 246 minutes after the introduction of a growth solution. White arrow highlights preferential nucleation at a step edge.

As with the \{100\} and \{110\} faces, it is possible to compare the measured terrace heights with the structure of SOD-ZnPO. This was performed firstly for the 0.2 nm terraces. The result is shown in Figure 3.42, where the terrace height can be correlated with the addition of a layer of 6-ring units onto the \{111\} surface, giving...
a 0.25 nm high terrace. This addition is the smallest terrace possible, and is within the error of the terrace height measurements made on this facet. Whilst a 6-ring is used in the figure, this unit may not necessarily be the growth unit; it could instead be made of smaller or larger units. However, this is the unit required to create a closed structure, which is the most stable and therefore expected to be the longest lived. The addition of the 6-ring unit will occur in capping fashion, completing a sodalite cage. The bonds highlighted in grey in Figure 3.42 show the attachment points of the 6-ring.

![Figure 3.42: Cartoon showing addition to a flat surface (2-D nucleation) on the \( \{111\} \) face of SOD-ZnPO. Cations and Oxygen are omitted for clarity.](image)

In Figure 3.43a a cartoon is shown representing a single layer terrace of these 6-ring units growing on a crystal surface. In this Figure, the sodalite cages are represented as polyhedra. This shows that the 6-ring units that are adding are not directly connected to each other on the surface through framework bonding. Instead, the framework connection is only through the layer below, which represents the existing crystal surface. This was a surprising observation, since the terraces on the surface were observed to grow by a birth and spread mechanism. This means that terrace spreading is observed, which shows that addition of growth units to the edge of an existing terrace is energetically more favourable than addition of these units at a random surface site. Therefore there must be another reason that addition to a terrace is preferred. This is likely to be due to the extra framework species; the water and the Na\(^+\). As mentioned in Chapter 2, the cages of SOD-ZnPO contain water and sodium in tetrahedra, with 75 %
occupancy for sodium. These units have been shown in aluminosilicates to form strong hydrogen bonds with themselves and also the framework, resulting in a pseudo-cubane type extra-framework unit inside the cages. Since these strong extra-framework interactions exist, they will also play an important role in the growth process. In Figure 3.43b and Figure 3.43c, the two possible positions of the cations on the surface are shown. These positions are dependent on the completed sodalite cage below, which will have the cations sited in the centre of the 6-rings. If a cation is located at a particular 6-ring, then an incoming cation will not attach to the same ring due to electrostatic repulsion between the two. When terraces are present, there will be more cations available to interact with incoming growth units, which will make these interactions more favourable and therefore promote layer spreading. This result is of importance, as it shows that the growth processes involved in SOD-ZnPO cannot be considered solely as framework interactions, but rather a combination of the interactions between the framework and the extra-framework species involving several types of bonding.
Figure 3.43: a) representation of a single layer of 6-rings on the \{111\} surface, b and c) possible cation positions on the \{111\} surface.

In Figure 3.44, a terrace layer of 0.5 nm height is represented. This time, the entire layer is attached by through-framework bonding. This type of bonding is stronger than that of extra-framework species. This suggests that terraces of monolayer height grow by a different mechanism to those of double height.
Figure 3.44: Representation of a double layer on the \{111\} face.

Considering the morphological differences observed on this face, the isotropic morphology observed with ragged edges is indicative of slow growth, whilst a more polygonised mechanism seen on the double layers suggests more rapid growth (see Chapter 4). This effect however is not solely due to supersaturation. This is proven by the existence of both rounded monolayers and triangular double layers in the same image in Figure 3.41, which shows the two morphologies present at an identical supersaturation. However, since the two layer types grow by different mechanisms, it may be expected that their growth rates will differ. With the double layers growing by through-framework bonding, it would be expected that these layers would grow more rapidly than those formed by through-extra-framework species bonding. This agrees with the observations made. The triangular shape of the terraces observed can be explained since both the framework and extra-framework species positions are related by the three-fold axis on this face.

Other observations of interest on the \{111\} face relate to the nucleation sites for new terraces. As can be seen by the white arrow in Figure 3.41e, there seems to be preferential nucleation at terrace edges. This step edge nucleation was observed regularly across all experiments, and could be caused either by a different geometry at the step edge leading to preferential nucleation or an increase in concentration of growth units at the edge of terrace edges. If the increase in concentration is the cause, then this could possibly be explained by the Ehrlich-Schwoebel effect.\(^9\) Since movement of adsorbed growth units down
Terraces is hindered, this could lead to a build-up of growth units at terraces edges, giving areas of high supersaturation. This would lead to the enhanced nucleation which is observed.

As well as nucleation at the edges of terraces, nucleation was observed in several cases to preferentially occur at facet edges, as shown in Figure 3.45. In this figure, the supersaturation was higher than in the experiments shown in Figure 3.41, which is characterised by hillocks forming from the edges, driven by this preferential nucleation. In the literature, there are several examples of crystals that grow preferentially at facet edges, including molecular crystals and ionic crystals\(^9\). In these cases, this growth is driven by the Berg effect\(^9\). This effect occurs because the boundary layer (Chapter 1) from which mass transport to the crystal surface occurs does not follow the shape of the polyhedral crystals. This means that at crystal edges and vertices, there will be a smaller boundary layer and hence a higher supply of growth units. This increase will lead to a localised higher supersaturation in these positions, which will result in the preferential growth of these areas. This is also known as polyhedral instability. This explanation seems unlikely for the crystals grown in this study. This is because crystals embedded in the surface will not protrude greatly, and therefore will have a more uniform boundary layer. It would also be expected that if this effect did occur, then synthesised crystals would display this effect\(^7\). Therefore, an explanation for this observed effect could be due to the tip interaction with the surface. The effect described above has only been observed during \textit{in situ} growth experiments, and not in \textit{ex situ} imaging. It could be that the motion of the tip is responsible for creating areas of higher supersaturation at crystal edges and vertices, and this could lead to the preferential nucleation observed.
Figure 3.45: AFM image showing preferential nucleation at a facet edge on the \{111\} face of SOD-ZnPO.
3.5 Conclusions and Future Work

3.5.1 Conclusions

The important results that have been found from this work are the importance of the extra-framework cations in the growth process. This is the first time that their direct influence on a growth mechanism has been observed, and shows that their consideration is vital in future studies on open framework crystal growth.

From the results presented in this chapter, it can be seen that AFM gives a wealth of information about the growth of these crystals. In particular, AFM has allowed the observation of the different condensation rates of Zn and P, showing their importance in the mechanisms of growth. Both layer spreading and birth and spread growth have been observed, as with previous framework materials in the literature. However, the use of in situ AFM has allowed further details to be gleaned such as for growth through a number of defect types. By having control over the conditions of growth, it has also been possible to investigate the effects of solution concentration on the morphology of the surface structures with much greater control than was possible using only ex situ AFM.
3.5.2 Future Work

During observations one crystal sample also had crystals expressing the \{210\} face. This has only been observed on crystals in one sample, which was synthesised at low pH. This observation suggests that at neutral pH, the growth rate of the \{210\} face must be relatively faster in order that it grows out and is not observed. A crystal with \{100\}, \{110\} and \{210\} facets is shown in Figure 4.a, and the AFM observations of the \{210\} face are shown in Figure 4.b and c. As can be seen, no surface features were observed, and \textit{in situ} measurements proved unsuccessful. However, it has been proven that this facet can be produced and future work could focus on producing crystals with a larger \{210\} facet in order to perform AFM measurements and further understand the growth of these crystals.

\textit{Figure 3.46.} : a) Representation of a crystal expressing the \(\{100\}\), \(\{110\}\) and \(\{210\}\) faces, and b)-c) AFM images showing the existence of the \(\{210\}\) face on a SOD-ZnPO crystal.

A comparison between ZnPO sodalite and other members of the sodalite family, including aluminosilicate sodalite would also be an interesting continuation of these studies. Since the results obtained on the \(\{100\}\) face suggest that the interlacing spiral mechanism observed was due to the strict alternation of Zn and P, and their relative condensation rates, other systems with a 1:1 ratio of substituent atoms could investigate if this is a typical result.
3.6 References

8. C. o. P. Cubillas.
32. J. A. Vicary and M. J. Miles, *Nanotechnology*, 2009, **20**.
Chapter 4

Quantitative Measurements of the In Situ Growth of Sodalite Zincophosphate
4.1 Aims and Objectives

The aim of this chapter is to grow SOD-ZnPO in a controlled manner such that quantitative measurements of the growth processes can be obtained, giving an insight into the mechanisms and energetics involved. More specifically the aims are to:

- Gain accurate growth rates by investigating the role of solution flow rate, applied load and other experimental variables
- Investigate the difference in rates between the different growth mechanisms observed in Chapter 3 on both the \{100\} and \{111\} faces
- Obtain the order of reaction for zinc and investigate the effect of varying zinc concentration
- Investigate the effect of temperature on the growth rates
- Observe the effect of varying the Zn : P ratio of the growth solutions used
- Initiate heteroepitaxial growth using Co as a substitute for Zn and measure the effect on the various growth rates
4.2 Introduction

4.2.1 AFM used to quantify the crystal growth of nanoporous materials
In the examples for in situ growth of nanoporous materials given in Chapter 3, all of the observations made were of a qualitative nature. In only one AFM study to date has nanoporous growth / dissolution been quantified. This was the study of Brent et al., who used in situ AFM as well as friction measurements (for more detail see Chapter 5) to study the dissolution of Zeolite L. In that study, it was possible to calculate an activation energy of the dissolution process by using an Arrhenius type expression. However, whilst no quantitative AFM results for the growth of nanoporous materials have been reported, these do exist for several other classes of materials. These investigations have given an insight into the important factors that influence crystal growth. In order to control the growth of SOD-ZnPO, those factors must be considered, some of which are outlined here.

4.2.2 AFM used to quantify crystal growth
In order to understand crystal growth, initial investigations probed the effects of supersaturation, as this is one of the easiest parameters to control in many systems and it had been suspected to affect the crystal growth modes. These studies found that the mechanism of growth was, in fact, dependent on the supersaturation, with a spiral type growth dominating at low supersaturation (See Chapter 1 for general crystal growth introduction). At higher supersaturations on smooth crystal surfaces, such as those involved in molecular beam epitaxy (MBE), it was found that the dominant mechanism was multilayer growth on nucleating islands and spreading of the growth layers. In general, the step velocities were found to be linear with supersaturation. However, at low supersaturation some deviation occurred, either because of trace amounts of impurities or due to the effect of kink density on step advance rates. Figure 4.1 shows the relationship between step velocity and supersaturation on the \{10\bar{1}4\} face of calcite.
Figure 4.1: Relationship between supersaturation ($\sigma$) and step velocity.$^7$

In general, the relationship between step advancement rates can be expressed as follows:

$$v = \omega \beta (C - C_e)$$  \hspace{1cm} (4.1)

Where $v$ is the step speed, $\beta$ is the step kinetic coefficient, $\omega$ is the specific molecular volume, $C$ is the actual concentration of the solution species, $C_e$ is the equilibrium concentration of the solution species. For surface diffusion models, the step kinetic coefficient, $\beta$, represents the kinetics of adsorption, diffusion and attachment of growth units (molecules, atoms) to the steps. This value will be dominated by the process which is rate-limiting in growth.$^4$

By investigating the effect of temperature on growth, the rate of reaction could be related to the activation energy for crystals such as barium sulphate and magnesite.$^{11,13}$ This used an Arrhenius expression as shown in Equation 4.2:

$$k = A e^{\frac{E_a}{RT}}$$  \hspace{1cm} (4.2)
where \( k \) is the rate constant, \( A \) defines a pre-exponential factor, \( E_a \) is the activation energy, \( R \) is the gas constant and \( T \) is the temperature. The rate constant for crystal growth can be obtained by calculating the gradient of a plot of step advancement rate against saturation state. In order to define the saturation state, the growth and dissolution of a simple two component system is considered. Ionic charges are omitted for clarity. For this reaction (Equation 4.3), the law of mass averages is given by Equation 4.4:\textsuperscript{11, 14}

\[
A_\alpha B_\beta (\text{lattice}) = \alpha A\text{(aq.)} + \beta B\text{(aq.)}
\]  
(4.3)

\[
K_{AB} = a_A^\alpha \times a_B^\beta
\]  
(4.4)

Where \( a_i \) represents the activity of the subscript aqueous species and \( K_{AB} \) is the equilibrium constant for the reaction. \( \alpha \) and \( \beta \) are the stoichiometric coefficients of the reaction. The saturation state (\( \Omega \)) then is defined in Equation 4.3:\textsuperscript{11}

\[
\Omega = \frac{a_A^\alpha a_B^\beta}{K_{AB}}
\]  
(4.5)

By calculating the reaction rate constant at several temperatures, a plot of \( \ln (k) \) against \( 1 / T \) can be formed, with the slope giving the activation energy. Therefore, in order to calculate the activation energy, knowledge of the saturation state of the growing solution is required as well as measurements of the growth rates.\textsuperscript{11, 13}

### 4.2.3 Effect of solution stoichiometry on growth

The importance of stoichiometry in the growth and dissolution has been investigated for several systems. In the initial investigations, the effect of the solution stoichiometry on dissolution reactions was quantified, such as for the dissolution of calcium hydroxyapatite.\textsuperscript{15} This study found that the dissolution was more dependent on the calcium concentration than on that of phosphate. In order to investigate the effect of solution stoichiometry on growth kinetics, the supersaturation changes that occur with varying substituent ratios had to be
accounted for. By maintaining a constant supersaturation, the thermodynamic driving force was kept constant and therefore the kinetic effects could be isolated and studied.\textsuperscript{16}

In Chapter 1, the idea of the Kossel crystal was introduced. By using this simple growth theory, it was possible to understand a number of important phenomena.\textsuperscript{17} However, this model is not adequate to study more complex phenomena, particularly when related to the stoichiometry effect, as the real crystal will have more than one distinct chemical component. By introducing more than one type of growth unit, or differences in symmetry, a number of different kink sites will be possible as opposed to the one given by the Kossel model. For example, in the ionic solid sodium chloride there will be two different kink site types depending on whether Na\textsuperscript{+} or Cl\textsuperscript{-} is terminating. These systems where several types of kink site are produced are described as non-Kossel.\textsuperscript{17} When investigating the effect of stoichiometry on growth at constant supersaturation, Chernov \textit{et al.} showed that a stoichiometry of 1 : 1 produced the highest growth rates, by a factor of 6, in both calcium oxalate monohydrate and calcium oxalate dihydrate.\textsuperscript{17} The results were interpreted using non-Kossel growth theory for an AB solid, which considers the attachment and detachment rates of the different growth units at kink sites to be important. If the attachment and detachment frequencies are equal, then a maximum rate will occur at a stoichiometry of 1 : 1.\textsuperscript{18, 19}

Another important result from this work showed that a change in stoichiometry showed a symmetrical relationship with the growth rate, i.e. changing the stoichiometry to 2 : 1 or 1 : 2 had the same effect on the growth rate. This was attributed to the ionic charge of the species involved (+ / - 2) dominating over the other effects involved such as size, shape and spatial symmetry differences.\textsuperscript{17} A symmetrical relationship was also found by Nehrke \textit{et al.} for calcite,\textsuperscript{16} however for the same system Perdikouri \textit{et al.} found that this relationship was non-symmetrical (Figure 4.2).\textsuperscript{19} This difference in observations was attributed to the limited number of concentration ratios explored by Nehrke \textit{et al.}, and it was
suggested that the non-symmetrical relationship in these experiments was the 
result of the differences in desolvation of the Ca\(^{2+}\) and the CO\(_3^{2-}\).\(^{19}\) That the calcite 
growth rate was at a maximum at a 1 : 1 ratio of Ca\(^{2+}\) : CO\(_3^{2-}\) was explained as a 
combination of the unfavourable desolvation of the cation balanced by the 
attraction of the cations by the surface, which was negatively charged at the pH 
the experiment was performed at. From these experiments, it can be seen that 
solution stoichiometry has an important effect on growth, both under varying and 
controlled supersaturation. This can be modelled using a non-Kossel kink model, 
described by a difference in attachment / detachment frequencies.

Figure 4.2: The effect of Ca\(^{2+}\) : CO\(_3^{2-}\) on the growth rate of steps on calcite. S.I. 
represents saturation index.\(^{19}\)
4.2.4 Effect of background electrolytes

The effect of the background electrolytes present on growing solutions has been studied for systems such as barium sulphate and calcite.\textsuperscript{20,21} For barium sulphate, this was investigated by maintaining a constant supersaturation and ionic strength, varying only the ionic salts in the solution. From these results, the type of electrolyte was found to affect the spreading rates and nucleation rates on the surface. This was because the electrolytes affected the hydration of the species in the solution. Since the removal of water from the hydration shells of growth units is an important process in growth (see Chapter 1), this alteration led to an increased variation in growth rates. These effects also led to faster exchange of water around the building units of barium sulphate. This process is related to the kinetic barrier for nucleation, meaning that the presence of electrolytes increased nucleation rates.\textsuperscript{20} It was also found that in general at higher ionic strengths, growth rates increased.\textsuperscript{21} Electrolytes were found to enhance dissolution as well as growth, both for barium sulphate and for calcite.\textsuperscript{22}

4.2.5 Effect of impurities

The role of impurities in crystal growth has been studied extensively.\textsuperscript{23-28} It has been found that impurities generally hinder growth, however, in some cases they can enhance growth rates. The effect of impurities is generally facet specific, and therefore by understanding their role in the growth process impurities can be used as habit modifiers.\textsuperscript{26} There are several mechanisms by which impurities can act to hinder growth. One of these is step pinning by the impurities, which can hinder the terrace advancement.\textsuperscript{26} On calcite, it was found that growth at low supersaturation did not exhibit linear behaviour with respect to supersaturation.\textsuperscript{12} This was attributed to impurities, which led to a decrease in growth rate. Two mechanisms for this inhibition were proposed; that the impurities would act either to block step advancement as mentioned above, or that the impurities would block kink sites directly.\textsuperscript{12} A blocking of step flow was also observed on calcite when poly (vinyl alcohol) (PVA) was added to a supersaturated solution. In this case, the whole surface morphology was changed as the inhibition of step flow led to an initial roughening of the steps, followed by 2-D island formation.\textsuperscript{29}
Meanwhile, the work of Elhadj et al. found that the presence of peptides on a nanomolar concentration enhanced the growth rate of calcite. This was attributed to the decrease in the activation barrier to attachment to kinks, with the biomolecules acting as catalysts. A proposal for how these impurities aided growth suggested that the charge of the biomolecules, which preferentially bind to step edges, may have aided the attachment of incoming growth units.\(^{30}\)

When considering impurities that can substitute into the structure, it was found that addition of Mg\(^{2+}\) to growth solutions of calcite was also found to reduce the growth rates. This was attributed to a thermodynamic effect, whereby lattice strain decreases the enthalpy of calcite precipitation. This study also found that the addition of Mg\(^{2+}\) to the solution changed the solubility.\(^{25, 31}\) In the case of Sr\(^{2+}\) addition to calcite, the results were more complex. At low concentrations of Sr\(^{2+}\), faster growth was promoted whereas at higher concentrations of Sr\(^{2+}\) growth was hindered. This was because at low concentrations the changes in solubility associated with Sr\(^{2+}\) incorporation led to increased growth rates. However, as the concentration increased, the Sr\(^{2+}\) began to reduce growth rates by pinning growing steps.\(^{32}\) This study shows, therefore, that the effects of impurities can be complex. The concentrations of impurities can affect the way they interact with the growing species, and the interactions can be varied depending on the species involved, changing both surface morphologies and growth rates.
4.3 Experimental

4.3.1 Experimental procedures and data acquisition

In situ growth of SOD-ZnPO was observed with a JPK Instruments AG NanoWizard II Atomic Force Microscope operating in contact mode, using silicon nitride cantilevers with a nominal spring constant of 0.58 N m\(^{-1}\) (Veeco model NP-10). A scan rate of 4.5 Hz was used during measurements. For controlled measurements all solutions were prepared in the laboratory from stock solutions of phosphoric acid, zinc nitrate, sodium bromide and cobalt nitrate. For experiments involving an excess of phosphorus, the concentration of phosphorus used was 3000 ppm (0.097 mol dm\(^{-3}\)), whilst sodium concentrations were kept constant across all experiments at 20100 ppm (0.875 mol dm\(^{-3}\)). This was done to replicate the solution concentrations present at the end of SOD-ZnPO as mentioned in Chapter 3.\(^{33}\) The minimum zinc concentration used for measurements was 1 ppm (0.0153 mmol dm\(^{-3}\)), whilst the maximum was 7 ppm (0.107 mmol dm\(^{-3}\)). For solutions where cobalt substituted zinc, the equivalent concentration of zinc was replaced by cobalt, with a constant excess of phosphorus and sodium. The amount of zinc substituted for cobalt in these experiments was 25 %, 50 %, 75 % and 100 %.

For the experiments varying the stoichiometry of zinc and phosphorus, sodium concentrations were again 20100 ppm (0.875 mol dm\(^{-3}\)). The zinc concentration was 1.5 ppm (0.0230 mmol dm\(^{-3}\)), whilst the phosphorus concentration was varied between 0.0230 mmol dm\(^{-3}\) and 0.097 mol dm\(^{-3}\). The Zn : P ratios investigated were 1 : 1, 1 : 2, 1 : 5, 1 : 10 and 1 : 3000.

Since pH was shown to have a large effect on the phases formed, this was maintained at 7 throughout these experiments. Therefore, extra sodium bromide was added in order to maintain similar sodium concentrations to those in the original synthesis.\(^{33}\) However, this meant that an excess of bromide was present in the solutions that was not present in the initial syntheses. The reason that extra sodium bromide was required is that the majority of sodium in the synthesis was provided by sodium hydroxide, which was required in order to neutralise the acidic phosphorus source (phosphoric acid). Although the presence of extra
bromide is likely to have an effect on the growth of SOD-ZnPO due to changes in hydrolysis,\textsuperscript{20-22, 34} this was preferred to the situation in which less sodium was present, since this is directly incorporated into the framework and directly influenced the growth mechanisms.\textsuperscript{33}

The temperature of the system was controlled using the JPK BioCell\textsuperscript{TM} temperature controller, with a separate measurement for the heating element and solution temperature provided. This allowed solution temperature to be controlled accurately, with a precision of 0.1°C.\textsuperscript{35} For \textit{in situ} measurements, solutions were flowed at 0.1 mL min\textsuperscript{-1} using a Harvard apparatus PHD 2000 syringe pump for a minimum of 60 minutes before measurements commenced. Measurements were taken over six temperatures, from 25°C to 50°C.

\subsection*{4.3.2 Cantilever calibration}

At each temperature, measurements were taken using three contact forces; 10 nN, 30 nN and 50 nN. In order to calibrate the AFM contact forces for individual cantilevers, the following procedure was adopted. Firstly, the vertical sensitivity, $S_v$, was measured. This is a measurement of the relationship between the cantilever deflection and the movement of the laser spot on the photodiode detector. This was measured by taking a force distance curve on a SOD-ZnPO surface (See Chapter 3.2.1.1). This curve plotted the deflection of the laser against the vertical displacement of the piezo element, which can be equated to the vertical displacement of the cantilever assuming a non-compliant surface. The vertical sensitivity $S_v$ (\text{nm V}^{-1}) will then be equal to the gradient of the slope, in the repulsive region of the curve (Chapter 3.2.1.1).

After this point the tip was retracted and the vertical spring constant, $K_v$, was measured. This spring constant is a measure of the stiffness of the cantilever when bending along the z direction. The vertical spring constant was measured using the thermal noise method in the AFM software.\textsuperscript{35} This method uses the relationship between cantilever deflection and thermal vibrations from the environment in order to calculate the spring constant. This value is obtained by integration of a
simple harmonic oscillator fit to the resonance peak.\textsuperscript{36} This procedure gave the spring constant in (N m\textsuperscript{-1}) 

By combining the results of these methods, the Force (nN) per deflection (V) was obtained, allowing calibration of the cantilever so that constant comparable forces could be used across experiments independent of the tip used. For the range of cantilevers used, the forces that corresponded to the 1 V deflection value varied between 8 and 12 nN.

4.3.3 Data processing
To accurately determine growth rates from AFM images, two methods were used. The first method involved direct length measurements over the images and could be divided in two sub-methods. In the first one the rates were obtained by measuring the change on the length of entire terraces as a function of time, then halving the result to give the growth rate in a single direction (Figure 4.3a). In the second sub-method, the distance between an anchor point and the moving terrace (Figure 4.3b) was used. The anchor point used was either a particle on the surface or a defect in the crystal that did not move during subsequent scans. This included the centre of dislocations, such as those shown in Figure 4.3b. All measurements to the anchor points were taken perpendicular to the growing terrace, as calculated using the measurement tool provided within the manufacturer’s processing software.\textsuperscript{35}
Once two distance measurements were obtained, the number of lines scanned in between the two measurements was then calculated, and using the scan rate the number of seconds between scans was acquired. This was then used to give the rate in nm s\(^{-1}\). In order to reduce error, each measurement was made over a minimum of three consecutive images, although typically five were used. The measured length of a terrace in each of these images was then plotted against the time taken for the terrace to be re-scanned. The gradient of the subsequent plot corresponded to the growth rate. Any measurements with an \( r^2 \) value less than 0.95 were rejected. A minimum of five measurements were taken for each data point, therefore each point consisted of a minimum of 25 individual measurements. The error bars presented were calculated using the standard deviation of the measurements obtained.

The second method used that developed by Teng to measure calcite step advancement rates.\(^{37}\) In this method, the growth rate was measured using the change in terrace angle between upward and downward scans. This angle changes, since each micrograph takes ca. 2 minutes to produce. In this time, the
surface is continually growing, and therefore the morphology observed will be influenced by scan direction. This can be seen more clearly in Figure 4.4. For this method, the following equations were used to determine the growth rate:

\[ v_s = \frac{R S}{2N} \left( \cot \theta_D - \cot \theta_U \right) \sin \theta_T \]  

(4.6)

\[ \sin \theta_T = \cot^{-1} \left( \frac{\cot \theta_D}{2} + \frac{\cot \theta_U}{2} \right) \]  

(4.7)

where \( v_s \) was terrace spreading velocity (nm s\(^{-1}\)), \( R \) was the scan rate (line s\(^{-1}\)), \( S \) was the scan size (nm), \( N \) was the number of lines in the image. \( \theta_D \) and \( \theta_U \) were the angles between the horizontal axis and the apparent step direction for downward and upward scans. This is highlighted in Figure 4.2. \( \theta_T \) was the angle between the horizontal axis and the real step direction.

![Figure 4.4: Two consecutive AFM lateral deflection images showing how measurements were taken to calculate the growth rate using the step angle method.](image)

In most cases, method 1 was adopted in order to perform measurements. However, at high terrace velocities (> 2 nm s\(^{-1}\)) when it was not possible to track single steps method 2 was adopted. This method was not used under slower
growth conditions since it led to a higher degree of error when the angles measured on the AFM for steps did not deviate far from the real step angle.
4.4 Results and discussion

4.4.1 Solubility Measurements

In Chapter 1, the chemical potential was introduced as the driving force for crystal growth, which is related to the supersaturation of the system. For solution growth, it was stated that this could be approximated to being the concentration of the growth solution divided by the concentration at equilibrium. In order to understand growth experiments in terms of driving force, it was therefore necessary first to calculate the solubility of SOD-ZnPO, since this would give the equilibrium concentration required to calculate supersaturation.

In order to calculate the solubility of SOD-ZnPO, two approaches were taken. Firstly, reactions following the standard recipe of Gier and Sucky were set up and kept at four different temperatures. This reaction was left to proceed, with samples taken at regular intervals to monitor solution concentration and solid phases present. Thus it was possible to determine if equilibrium had been reached. In this experiment, therefore, equilibrium was approached from a supersaturated state. The second method was to add some SOD-ZnPO crystals to a zinc free, pH 7 solution of sodium bromide and phosphoric acid, whose concentrations were similar to those measured at the end of a typical synthesis. By using this approach, the solubility would be calculated from an undersaturated state, and therefore the results of the two approaches could be used to verify that equilibrium had actually been reached. The two experiments were both run for over two months. It was found that equilibrium was not reached before growth of a new phase began in both experiments. This phase was identified in Chapter 2 in the long term stability experiments. It was known that the solutions were not at equilibrium, since ICP measurements from the sample prior to the new phase precipitating gave the concentration of zinc as between 4 and 14 ppm, despite growth being still possible on the AFM at [Zn] = 1 ppm. In these experiments, phosphorus and sodium were both in excess in order to mimic synthesis conditions. Therefore, it was not possible to obtain results for the solubility of SOD-ZnPO due to the instability of SOD-ZnPO in sodium phosphate solutions. The reason AFM results could not be used to derive a value for the solubility (for...
example when a particular solution produced no growth or dissolution) was because other processes could affect the results. For example, in Chapter 3 surface activation was observed to play an important role in growth, and this could have led to inaccurate measurements. Coupled with this, tip effects that were not directly observable could also play a role. However, it was possible to deduce that for all measured temperatures the solubility was likely to be < 1 ppm zinc, since growth was observed at all temperatures at this concentration. Although the solubility could not be directly measured, results from the AFM and solubility experiments confirmed that the crystals are sparingly soluble, which suggests that kink density will be much lower for these crystals. Since the solubility was unknown, growth rates are shown here as a function of known solution zinc concentrations.

4.4.2 Effect of flow rate

During the experiments described in the previous chapter, the results obtained were qualitative only, since the concentrations of the solutions used throughout these experiments were unknown. The reason for this was that during the experiment the solutions were added directly onto the crystals then left static whilst scanning was performed. This meant that as zinc and phosphorus were used in growth, the supersaturation in the cell would be changing. This stagnant solution type experiment would therefore require modification in order to obtain quantitative results. From a qualitative point of view, the change in solution concentration was observed in several experiments, an example of which is shown in Figure 4.5. In this experiment, a mother liquor solution was added to the crystals. This was left for 46 minutes, at which point two consecutive images were taken (Figure 4.5a and 4.5b). The growth of the spiral centres was slow, and it was possible to track single terraces across several images. Compared to this, Figures 4.5c and 4.5d show the experiment 5 minutes after the mother liquor solution was flowed over the crystals to replenish zinc in the cell. Again the two images shown were taken consecutively. In these two images, the edges of the terrace are much straighter; although some ragged edges persisted from the previous growth. The
growth was also more rapid, with it no longer being possible to track a single terrace over several images.

Figure 4.5: a + b) AFM lateral deflection images taken under static flow conditions showing slow growth on the {100} face of SOD-ZnPO, c + d) Images taken under flowing conditions showing rapid growth on the {100} face of SOD-ZnPO.

In order to maintain a constant supersaturation, the growth solutions were flowed over the crystals by means of a syringe pump. By flowing the solutions through the cell, the zinc depleted solution would be removed and replaced by new solution, therefore maintaining a constant supersaturation. In order to effectively quantify the results, the correct flow rate would have to be selected, and this was determined by measuring the growth rates on the {100} face of SOD-ZnPO under a
variety of flow conditions, using a solution with 1.5 ppm zinc concentration (and P
and Na in excess). Solution was flowed over the crystals for 1 hour before
measurements were taken and then the flow rate was changed. The results of this
experiment are given in Table 4.1, and represented in Figure 4.6. Here, the
anisotropic growth is displayed as two measurements; one that is labelled “fast”
and another labelled “slow.” This notation will be used throughout this chapter to
describe the two directions.

<table>
<thead>
<tr>
<th>Flow Rate/mL min⁻¹</th>
<th>Rate fast/nm s⁻¹</th>
<th>Error</th>
<th>Rate slow/nm s⁻¹</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0*</td>
<td>2.2</td>
<td>0.4</td>
<td>0.34</td>
<td>0.02</td>
</tr>
<tr>
<td>0</td>
<td>1.0</td>
<td>0.14</td>
<td>0.19</td>
<td>0.02</td>
</tr>
<tr>
<td>0.025</td>
<td>0.58</td>
<td>0.09</td>
<td>0.07</td>
<td>0.03</td>
</tr>
<tr>
<td>0.05</td>
<td>0.58</td>
<td>0.22</td>
<td>0.09</td>
<td>0.01</td>
</tr>
<tr>
<td>0.1</td>
<td>0.59</td>
<td>0.09</td>
<td>0.09</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 4.1: Growth rates of both the slow and fast directions on the {100} face of
SOD-ZnPO under several flow rates. In all cases the flowing was performed for 1
hour before measurements were taken except for 0*, which was measured
immediately.

In Table 4.1, it can be seen that upon addition of the solution to the crystals,
growth commenced at a relatively fast rate. After one hour in the absence of
flowing, the growth rate began to fall as the solution zinc concentration was
depleted by growth of the sample. Once flowing was initiated, the rate of growth
did not increase, as was perhaps expected from the qualitative observations.
Instead, the growth rate fell again. The rate obtained under flow conditions was
consistent at all flow rates suggesting that this was representative of the true
solution zinc concentration. The higher rates that were observed must have been
due to a contamination, which could have come from previous use of the AFM
slides. Dissolution of these species when the solution was added would increase
the total zinc concentration in the cell, leading to faster growth rates. When the
solution was flowed, the excess zinc from contamination was removed and
therefore the growth rate dropped to the rate dictated by the contamination free solution zinc concentration.

Figure 4.6: Graphs showing the effect of flow rate on terrace spreading rates on the \{100\} face of SOD-ZnPO.

The graphs in Figure 4.6 show that 1 hour after the addition of the growth solution to the crystals in the absence of flowing the rate of terrace spreading has decreased markedly. This is due to the decrease in supersaturation as zinc is incorporated into SOD crystals. Following the initiation of flowing, any excess nutrients remaining in the cell from the contamination were removed, leaving the solution zinc concentration at 1.5 ppm. Since the cell volume was ca. 0.4 mL, at
0.025 mL min\(^{-1}\) flow rate the cell contents would have been completely replaced 3 - 4 times within the hour that the solution was flowed before measurements were taken. These flow rates chosen were lower than those typically quoted in the literature, for example 0.5 mL min\(^{-1}\) used by Teng et al.\(^6,31\) At all three measured flow rates, the results were within experimental error of each other, suggesting that these low flow rates were more than enough to replenish the cell and maintain a constant supersaturation. Had a higher flow rate been required, a positive gradient would have been observed between the three rates displayed in Figure 4.6, as the actual cell zinc concentration would increase across the experiment.

The two most important observations taken forward for quantitative experiments were that solution flowing was required, however not necessarily at a high rate. The rate selected was 0.1 mL min\(^{-1}\) since this was 4 times the experimentally observed required rate. This would replenish the cell every 4 minutes. The second observation was that without flowing, residual contamination could remain present on the slide and produce spurious growth rate measurements. To avoid this, all solutions were flowed for 1 hour in order to ensure excess zinc and phosphorus was removed from the crystal slides before any rate measurements were taken.
4.4.3 Effect of load

As mentioned in the experimental section, each growth rate was measured at 3 loads; 10 nN, 30 nN and 50 nN. The reason for this was to investigate any possible effect of scanning on the growth rates observed. The interaction between tip and sample has previously been observed to have a large effect in the case of dissolution of zeolites. For Zeolite L and for Zeolite T, dissolution was enhanced at higher loads, suggesting a tip assisted dissolution mechanism.\textsuperscript{1, 40} In the case of Zeolite T, it was found that in the absence of a tip interaction there would be no dissolution.\textsuperscript{40} From a qualitative point of view, this tip aided dissolution has also been observed in this SOD-ZnPO system, as shown previously in Chapter 3. Whilst no such obvious examples existed for tip influence on growth, the effect of load was still investigated in order to understand the role played by the tip in growth. When measurements were taken, the results showed that terrace spreading rates were independent of the load applied. This is shown in Figure 4.5, where it can be observed that all data points are within experimental error.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.7.png}
\caption{Graph showing the effect of load on the growth rate of the \{100\} face of SOD-ZnPO at [Zn] = 2 ppm, 30°C.}
\end{figure}
4.4.4 Effect of solution equilibration time

In order to investigate the effect of solution equilibration time on growth rates, an experiment was set up in which the same solution would be used at a variety of time intervals to grow seed SOD-ZnPO crystals. The term equilibration time is used here to refer to the time for which the solutions are aged following zinc addition. This time allows for the different solution species to form, until an equilibrium distribution is formed. The purpose of these investigations was to assess the amount of time for which solutions needed to be equilibrated in order to ensure consistent measurements.

For the equilibration experiments, the rate of growth at 25°C under three loads (10, 30 and 50 nN) was recorded on a {100} face. The solution used was 2 ppm zinc, with excess phosphorus and sodium. Once prepared, the first rate measurement was attempted after 1 hour equilibration, since this was the minimum time after which measurements using the flow through scheme could take place (section 4.4.2). After this time, no growth was observed. This experiment was repeated for other Zn concentrations, and it was found that up to 8 ppm Zn no growth would occur upon immediate addition of growth solution (1 hour equilibration). Since it had previously been observed that growth was possible down to 1 ppm Zn concentration when solutions were left equilibrating for several days (Chapter 3.3), the amount of zinc could not be responsible for this observation. After four hours, growth was observed in the 2 ppm solution, and if left to equilibrate overnight the growth rate increased as shown in Figure 4.8. Since the growth rate increased with equilibration time, it is very likely that this is related to the speciation of the solution. A variety of species exist in solution, and have been observed during the growth of other framework type materials; both aluminophosphate and aluminosilicate. Speciation measurements were therefore attempted, however due to the low concentrations at which precipitation is not observed directly in the laboratory solutions created (< 10 ppm Zn), and the high concentrations of both phosphorus and sodium present, measurements proved difficult. $^{31}$P NMR could not be used, since one peak was observed due to the excess P. Meanwhile, due to the sodium and phosphorus...
present, mass spectrometry could also not be performed. Since it was shown in Chapter 2 that both high concentrations of sodium and phosphorus are necessary in order to form SOD-ZnPO, the results obtained had these quantities been altered would not be comparable to the growth observed when these were present in excess.

Figure 4.8: Graph showing the growth rate of the \{100\} face of SOD-ZnPO in the “fast” direction after the addition of a 2 ppm growth solution at 25°C as a function of the time since the solution was created.

For 2 ppm solutions, the growth rate was not observed to diminish with time (within error) once it reached a maximum shown in the graph; however this was not true for higher concentrations (4 ppm and above). For a 5 ppm solution, a highest growth rate of $2.3 \pm 0.4$ nm s$^{-1}$ was measured 5 hours after solution creation, compared to a rate of $0.58$ nm s$^{-1}$ measured after 4 days of ageing. This was due to the precipitation of another zinc phosphate phase, which could be observed in the solutions as a white powder. The precipitation time for this secondary phase varied depending on a range of factors such as storage temperature (laboratory variation) and the vessel in which the solution was stored. In general the precipitate could be observed in these higher [Zn] solutions after 1 week of equilibration. Since the equilibration at 2 ppm seemed complete after 48 hours, this time was selected as the minimum time that solutions were
left for all measurements reported, whilst a maximum was set at 96 hours to keep experiments consistent.

Although the solution chemistry was not known, this would not affect the results presented in this chapter. This is because the monitoring of growth rates as a function of equilibration time allowed for stable solutions to be obtained. Since the speciation of these solutions has been shown to be important, this highlights that the supersaturation of this system could not be solely described by the approximation that activity can be replaced by concentration, but instead that it is the activity that is important for this system.18

4.4.5 Investigation of the Berg Effect
In Chapter 3, the possibility of the Berg effect being responsible for crystal edge nucleation on the \{111\} face was proposed. In order to test this, terrace advance rate with respect to crystal edge was measured. This found that no Berg type effect was observed. This could be expected, since the crystals were sunk into the resin, and therefore were unlikely to have a high profile to create a concentration gradient difference.42 A representative graph of these measurements is shown in Figure 4.9. This gives the terrace spreading rate measurements as a function of the distance of the terrace from the crystal edge. From this figure, it can be seen that within error there is no Berg effect. In this case, up to 700 nm from the crystal edge was measured. In previous experiments involving glucose isomerase, for which this effect has been reported, the measurements were taken over 200 \(\mu m\).43 However, the total size of the crystal faces measured for SOD-ZnPO were much smaller than this. Since the Berg effect is not present on this face, it could be that instead that the preferential nucleation at the edge of the \{111\} crystal face is either due to the Ehrlich-Schwoebel effect,44, 45 or due to a higher mechanical contact between the tip and the surface at the edge of the facet.
4.4.6 Effect of zinc concentration

The effect of zinc concentration on the growth of SOD-ZnPO was investigated. By increasing the concentration of zinc in the growth solutions (1 to 5 ppm), the supersaturation was also increased. Figure 4.10 shows the effect of changing the zinc concentration on the growth rates of the {100} face of SOD-ZnPO.
From Figure 4.10, it can be seen that between 1 and 3 ppm of zinc, the trend is that increasing the concentration of zinc increases the rate of growth in the fast direction. This is the expected result, due to the increasing supersaturation. However, from 3 to 5 ppm, more zinc in the solution results in a slower growth rate. This can be explained by nucleation of another phase in these solutions. When discussing the effect of equilibration time (section 4.4.4) it was noted that after 1 week some solutions had some crystals growing in them that were visible. As these crystals grew, the solution zinc concentration would fall as more zinc is incorporated into the new phase that is growing. In the AFM experiments nucleation of the secondary phase will lead to a lower "steady-state" zinc concentration inside the fluid cell despite there being more zinc in the inlet solution. If no new phase nucleated, then the solution zinc concentration in the cell will reflect the differences in the inlet concentrations. From these results, it can be assumed that up to 3 ppm \([\text{Zn}]\) nucleation of the new phase has not occurred in the solution. This may be because solution is not supersaturated with respect to this phase at these lower concentrations and therefore nucleation will not occur, or it may be that due to a lower driving force the nucleation has not occurred within the timescale that the solutions were used in (up to 96 hours). With increasing zinc concentrations, nucleation and growth of the new phase in the solutions prepared will be more rapid since there is a higher driving force which will, in turn lead to a smaller \(\text{Zn}\) concentration inside the AFM fluid cell. This would explain the observed trend that shows that increasing inlet zinc concentration above 3 ppm results in a decrease in SOD-growth rate.

For the slow direction, growth in general follows the same trend as for the fast direction, however at 4 ppm the slow direction is still growing faster than at 3 ppm. This could either be due to the slow direction results having a higher error level, owing to the smaller changes in rate observed over these concentrations, or it could be related to the new phase precipitation resulting in change in the solution speciation. Since the 4 and 5 ppm solutions will contain a separate phase in them, as well as having different speciation, it could be that these different
solution species act to promote growth in the slow direction as compared to
growth in the fast direction.

![Growth rate of the {100} face as a function of [Zn]](image)

**Figure 4.11:** Effect of zinc concentration on the growth rates on the {100} face of SOD-ZnPO at 25°C, with only low concentrations displayed.

In Figure 4.11, the growth rates between 1 and 3 ppm are presented. In this concentration range, the new phase that nucleated at higher concentrations is not present. For the reaction being studied, the rate equation will be related to the concentration of zinc as shown in equation 4.8:

\[ r \propto [\text{Zn}]^x \]  

(4.8)

where \( r \) is the rate of reaction, \([\text{Zn}]\) is the concentration of zinc and \( x \) is the order of reaction with relation to zinc.\(^{46}\) By taking the logarithm of this equation (equation 4.9), this allows \( x \) to be calculated as the slope of a plot of log (rate) against log ([Zn]).

\[ \log (r) \propto x \log ([\text{Zn}]) \]  

(4.9)
This calculation is possible because the zinc concentration is the only change made to the solutions, whilst all other species are in excess. The log – log plot for the growth rate with respect to zinc concentration is shown in Figure 4.12.

![Log log plot of growth rate against [Zn]](image)

**Figure 4.12**: log log plot of growth rate versus zinc concentration for growth on the \{100\} face, giving the order of reaction with respect to zinc.

From the plot, it can be found that the order of reaction in the fast direction is 0.88 ± 0.26. Although the gradient does not give an integer, a value of 1 is within the error of this experiment. A value of 1 suggests first order reaction in zinc, whilst a non-integer value suggests that there is a complex mechanism by which growth occurs.\(^{47}\) Since speciation has been shown in this work to play an important role in the growth of SOD-ZnPO, and the importance of extra-framework cations has also been shown, it could be expected that the order of reaction would reveal a complex mechanism.\(^{47}\) It may be the case that this is true, however a first order relationship cannot be ruled out due to the error associated with these measurements. In the case of the slow direction, the data gives a poor fit to the line. Therefore, not much can be concluded from this plot, as the possible fits give too broad a range of gradients. The poor fit of the line is either due to the large error, particularly in the 1 ppm and 2 ppm [Zn] experiments or due to an erroneous measurement at 1.5 ppm.
Figure 4.13: Plot of the calculated aspect ratios (fast / slow) for terraces as a function of zinc concentration.

The final analysis involved exploring the change in anisotropy with zinc concentration. In order to measure this, the aspect ratio of the terraces was measured. This is defined in Equation 4.10:

$$\text{Aspect ratio} = \frac{r_{\text{fast}}}{r_{\text{slow}}}$$  \hfill (4.10)

Where $r_{\text{fast}}$ is the growth rate in the fast direction and $r_{\text{slow}}$ is the growth rate in the slow direction, both in nm s$^{-1}$. From the results presented in Figure 4.13, it can be seen that within experimental error the aspect ratio remains constant between 1 - 3 ppm [Zn]. The aspect ratio does change for 4 and 5 ppm solutions. For 4 ppm solutions, the aspect ratio decreases compared to those measured at 1 – 3 ppm, whilst at 5 ppm the aspect ratio increases. This measurement could therefore be due to experimental error, since any effect that the new phase would have on the aspect ratio should occur in the same manner for both 4 and 5 ppm solutions. It was suggested when discussing Figure 5.10 that the slow rate continuing to increase in rate at 4 ppm was either due to impurity effects or error in measurements. These results, with an opposite effect on aspect ratio observed for 4 and 5 ppm solutions suggest that the latter is the reason for this observation.
4.4.7 Effect of Temperature

In Chapter 3 growth on both the \{100\} and \{111\} faces was investigated in order to discern the mechanisms of growth. On the \{100\} face, anisotropic growth was observed. Meanwhile, through investigations on the \{111\} face, it was established that two mechanisms exist; one involving through-framework bonding and one involving through-extra-framework species bonding. Since two mechanisms were observed on this face, the rates of growth between monolayers (through-extra-framework) and bilayers (through-framework) were investigated. In Figure 4.14, the growth rates as a function of temperature on the \{111\} face are shown at $[Zn] = 2$ ppm. When the temperature of the system is increasing two effects are occurring; firstly, an increase in temperature will increase the solubility of SOD-ZnPO. This will act to reduce the growth rate, since the supersaturation will decrease with increasing SOD-ZnPO solubility (at constant solution concentrations). The second effect is that the growth rate will be increased due to the increase in energy in the system.

![Figure 4.14: A graph showing the growth rates of the monolayers and bilayers on the \{111\} face of SOD-ZnPO between 25 and 50°C. $[Zn] = 2$ ppm](image)

From Figure 4.14, there is a measurable difference in the growth rates between monolayers and bilayers. This was expected due to the difference in mechanisms,
and could be observed qualitatively in Chapter 3 as the difference in the degree that the steps were polygonised. The growth rates for the more polygonised, triangular terraces were higher than those for the less polygonised isotropic monolayers. This was expected, since the more polygonised steps were advanced by creation of stronger through-framework bonds, whilst the isotropic monolayers advanced by the creation of weaker through-extra-framework bonds. By performing growth experiments at several temperatures, the activation energy for the observed growth can typically be calculated. However, in order to perform these calculations, the supersaturation of the solutions used is also required,\textsuperscript{11, 13} in order to relate the growth rate to the rate constant. Since this could not be calculated, the activation energy could not be calculated. Nevertheless, some important observations could still be made from the results shown in Figure 4.14.

From the gradient of the two lines, it can be seen that the difference between the growth rates for the two mechanisms increases with temperature. This means that the increase in growth rate with temperature is more prominent on the steps that have through-framework bonding than for those that connect through extra-framework bonds. Since the two steps grow by different mechanisms, the energetics of the processes will be different and the difference in the extent of the effect of temperature on growth could be expected.
The rates of growth on the \{100\} face were also measured, as shown in Figure 4.15. It can be seen in this Figure that an increase in the temperature causes an increase in the growth rates of the terraces. For both the \{100\} face and \{111\} face the fastest growing mechanism is also the one that is most affected by temperature. In Figure 4.15, as with the observations on the \{111\} face, the gradients of the two slopes are different. The \{100\} fast direction has the steepest slope, which means that the difference in growth rate between the two directions is increasing with the temperature effect. Unlike for the \{111\} face, both growth directions on the \{100\} grow with the same mechanism. The only difference in growth rates is related to the condensation rates of zinc and phosphorus (Chapter 3). Therefore, it can be hypothesised that the temperature will not affect the two condensation rates equally. In this case, the difference in gradient would be expected.
4.4.8 Effect of Zn:P ratio

Since the stoichiometry of growth solutions has been shown to be an important factor in the growth rates for several crystal systems, the effect on SOD-ZnPO crystal growth was investigated. For SOD-ZnPO, the charge on the growth units is not the same ([PO$_4$]$^-$ [ZnO$_4$]$_2^-$), unlike for the systems reviewed in the introduction. As well as this, the solutions used have a high ionic strength (I > 0.8 M) and the cations have been shown to be important in the growth processes. Therefore, the system studied here is more complex, in principle, than others that have been investigated.$^{16, 17}$ Experiments were performed by altering the Zn : P ratio from 1 : 3000 to 1 : 1. The growth of SOD-ZnPO in excess zinc was also attempted; however the rates of this interaction could not be measured since growth under these conditions led to a changed surface morphology, shown in Figure 4.16. This morphology formed between solution addition and AFM scanning, and led to no discernible terraces from which measurements could be made. These features were monitored over 30 minutes with no obvious change observed. Therefore, at all times Zn was the limiting nutrient.

![Figure 4.16: Surface morphology observed after addition of a growth solution containing excess Zn. In this experiment Zn : P was 2 : 1.](image)

The surface features observed in Figure 4.16 seem to be similar to those observed in experiments performed on dolomite by Kaczmarek and Sibley.$^{48}$ It was
suggested by the authors that the lack of discernible terraces may be due to the steps being too close together (less than 4 nm apart). When this is the case, the tip is unable to distinguish between them and the resulting image shows a smooth edge, created by the tip shape. Another explanation they offered was that the surface was coated in amorphous material, which would quickly react to form the dolomite. It is unclear why the morphology observed in the case of SOD-ZnPO occurs, however this change in the growth mechanism was observed on several different crystals in the presence of excess zinc. Nevertheless, for experiments where zinc was the limiting nutrient it was possible to obtain growth rates on the \{100\} face, as shown in Figure 4.17.

![Figure 4.17: The effect of varying solution stoichiometry on the growth rates on the \{100\} face of SOD-ZnPO.](image)

From the results presented in Figure 4.17, it can be seen that a similar observation to those in section 4.2.3 can be made; that is that as the stoichiometry approaches 1 : 1 the growth rate increases. There are two reasons that this could be the case. The first could be due to changes in the supersaturation of the solution with changing stoichiometry. This could not be ruled out since the supersaturation was not constant in these experiments. The second reason could be due to the
changes in the kink attachment / detachment rates, as described by Zhang and Nancollas (see section 4.2.3), that was observed under constant supersaturation.  

Since the growth experiments in excess zinc could not be performed, it was not possible to identify whether the 1 : 1 ratio would give the maximum growth rate for this system. As mentioned by Perdikouri et al., it could be expected that if the rates of incorporation of the different species are different, then the maximum could occur at a point away from a 1 : 1 ratio. Since it has been shown from the anisotropic growth observed that zinc and phosphorus have different incorporation rates (Chapter 3), this means that the 1 : 1 ratio may not have produced the fastest growth. This also meant that the symmetry of the stoichiometric effect could not be probed, however it is expected that this result would prove anti-symmetric since there is a difference in charge between phosphorus and zinc units, and their incorporation rates are different as evidenced by the anisotropic growth observed. These experiments show that the stoichiometry of the solution is important in defining the growth rate of a SOD-ZnPO. Although the effects observed cannot be conclusively attributed to kink attachment / detachment rates, a rate change with stoichiometry has been shown to be observable at high ionic strength (I > 0.8 M), despite there being complex interactions occurring such as framework bonding and non-framework cation and water incorporation.

As well as investigating the change in growth rate as a function of stoichiometry, the experiments performed here also allowed further investigations into the mechanism of growth on this facet. In the previous chapter, the growth of the \{100\} face of SOD-ZnPO was observed to occur by an anisotropic growth mechanism. There were two possibilities suggested for why this might be the case. The first involved the excess phosphorus present in the growth solutions as a possible cause, whilst the second was related to a difference in the condensation rates between phosphorus and zinc leading to anisotropic growth. By proving that growth using a 1 : 1 stoichiometric solution was possible, and that under these conditions anisotropic growth was still observed, it was determined that the
difference in the condensation rates between zinc and phosphorus was the cause of the anisotropic growth. In order to further study this, the change in rates of the two growth directions with respect to each other were investigated over the same range of Zn : P ratios as above. Since the initial growth solutions used contained a large excess of phosphorus, the amount diffusing onto the crystal surface would be far higher than that of zinc. Therefore, by altering the ratio of Zn : P, it was hypothesised that this change in the amount of phosphorus available to the surface would limit growth in the direction in which phosphorus addition was the rate limiting step. This was investigated by measuring the aspect ratio of the “fast” rate versus “slow” rate of growth on the \{100\} face of SOD-ZnPO at different stoichiometries. The variation in aspect ratio is shown in Figure 4.18a. In Figure 4.18b and c, corresponding AFM lateral deflection images are shown of the lowest and highest aspect ratio respectively for comparison.
It can be seen that as the amount of solution phosphorus is reduced, the aspect ratio decreases. This means that the difference in rates between the fast direction and slow direction is much less pronounced. There are two possibilities that could lead to this decrease in aspect ratio; firstly, a more rapid increase in the rate of growth of the slow direction as compared to the fast direction would result in a lower aspect ratio. Secondly, a lower aspect ratio could be achieved by the rate of growth in the fast direction being slowed with respect to the slow direction. In either scenario the direction in which phosphorus addition is rate limiting would be the fast direction. This is because in the first example, an increase in the

Figure 4.18: a) Graph showing the change in aspect ratio (fast rate / slow rate) with changing Zn : P, b) LFM image of growth from a 1 : 1 Zn : P solution leading to low aspect ratio terraces, c) LFM image of growth from a 1 : 3000 Zn : P solution leading high aspect ratio terraces.
relative growth rate of the slow direction when there is less phosphorus suggests that more zinc is accessing the sites in which growth is fastest for this species. This would mean that zinc is rate limiting addition for the slow direction, making phosphorus rate limiting in the fast direction. Meanwhile, if the second mechanism is correct; that is that decreasing the excess of phosphorus leads to a relative reduction in the growth rate of the fast direction compared to the slow direction, this would also make phosphorus addition rate-limiting in the fast direction. This is because a reduction in phosphorus would mean less is available to the growth sites. This will lower the rate of the direction at which phosphorus addition is rate-limiting more severely, which in this case is the fast direction. Since the growth rates observed are not constant, as shown above, it is not possible to know which of these is more likely, and a mixture of both may also be the case. Nevertheless, by quantitatively measuring the change in aspect ratio it has been possible to show that the addition of zinc is slower than that of phosphorus, leading to the growth anisotropy on the {100} face. The reason for this difference may be due to desolvation effects, since the desolvation of cations has been assumed to be limiting for surface-reaction controlled crystal growth.  

4.4.9 Heteroepitaxial growth using Cobalt

The growth of SOD-ZnPO substituted with a varying degree of Co has been reported previously in the literature. Le et al. substituted up to 30 % of framework Zn for Co when measuring the thermodynamics of zinc phosphates. In Chapter 2, the substitution of Co was also performed, showing the importance of seeding in achieving higher substitutions of Co. The incorporation of cobalt as a substitute of zinc was also investigated using in situ AFM in order to observe the effect on the growth mechanism of these materials.
Figure 4.19: AFM vertical deflection image showing etch pit formation by dissolution of SOD-ZnPO after the addition of a CoPO solution.

For initial experiments, the addition of a CoPO growth solution in the absence of zinc was attempted. Although no pure CoPO-SOD frameworks have been reported in the literature, it was hoped that cobalt phosphate layers could be heteroepitaxially grown over the seed crystal zinc phosphate layers. However, upon addition of the solution dissolution was observed. This was apparent due to the formation of etch pits on the surface of the sodalite, as shown in Figure 4.19. Since direct overgrowth of cobalt was not possible, the next attempts at growth involved a mixture of Co and Zn in the growth solutions. Since the proposed reason for the anisotropic growth observed is that there is a difference in Zn and P condensation rates, the rates of growth and the aspect ratio (fast rate / slow rate) were measured, in order to ascertain the influence of Co substitution. This is shown in Figure 4.20.
Figure 4.20: a) Graph showing the effect of varying the amount of Zn substituted by Co on the terrace spreading rates on the \{100\} face of SOD-ZnPO, b) graph showing the change in aspect ratio (fast rate / slow rate) as a function of Co substitution, c) LFM image taken during growth with a 75 % Co substituted solution, d) LFM image taken during growth with a 0 % substituted solution.
From Figure 4.20a, it can be observed that as the amount of Co substituted into the solution for Zn is increased, the rate of growth in the fast direction is slowed, whilst the rate of growth in the slow direction is increased. This leads to a decrease in aspect ratio, as shown in Figure 4.20b. In Figure 4.20c, an LFM image is shown during growth with a 75 % substituted solution. This was the solution that gave the lowest aspect ratio measurement. However, because the surface contained large features and many defects that influenced the growth, it was not possible to locate a single terrace growing that would allow a direct observation of this aspect ratio change. Growth with a higher aspect ratio is presented in Figure 4.20d for comparison.

The change in aspect ratio shows that with increasing Co concentrations the terraces move towards a square morphology. This is never fully achieved, with anisotropic growth always observed throughout these experiments. A change in aspect ratio was expected, since the presence of Co substituting the Zn will change the condensation rates for this addition process. Since the growth direction that is limited by zinc condensation was shown in section 4.4.8 to be the slow direction, the increase in this rate associated with Co addition suggests that Co condensation occurs more rapidly than Zn condensation. Finally in order to fully prove that the cobalt was adding directly into the framework, rather than acting as an impurity only in the solution, an experiment was set up in which a 50 % Zn, 50 % Co solution with a total Zn / Co concentration of 0.0230 mmol dm$^{-3}$ (equivalent to 1.5 ppm Zn) was flowed over some SOD-ZnPO crystals over a 2 month period. The crystals were then retrieved and examined using Energy-dispersive x-ray spectroscopy (EDS). From these results, it was found that the sample had a Zn : Co ratio of 10 : 1, showing that cobalt was incorporated into the framework during these experiments.

Whilst the change in aspect ratio could be expected, the decrease in growth rate in the fast direction was a surprising result. Unlike during the Zn : P ratio experiments, the stoichiometry of P : Zn / Co remained constant throughout this experiment. Therefore the stoichiometric effects described above were not
expected to influence the results observed. Since the condensation rates for incorporation of Zn / Co were increased, it would be expected that in the fast direction, which is limited by P condensation, they would have stayed constant. However, a clear reduction in growth rate was observed. An explanation for this could involve the speciation of the solution. As shown in the equilibration experiments, the speciation of the solutions seems to play an important role in the growth of SOD-ZnPO. Although the concentrations were kept constant throughout this experiment, the difference in speciation will affect the activities of the different ions. This change in activity may have caused the observed change in rates. Another explanation could relate to the interaction of the Co$^{2+}$ with the two different site types acting as an impurity. It has already been shown for calcite that Mg$^{2+}$ and Sr$^{2+}$ affect different sites to a different degree, and this could also be the case with Co$^{2+}$. 25, 32, 51
4.5 Conclusions and Future Work

4.5.1 Conclusions

From this work, it can be seen that quantitative analysis of the growth rates can give important information towards the understanding of the growth of these materials. Throughout this chapter, it has been shown that the growth processes involved are complex, and that in order to control growth for quantitative measurements several factors need to be considered including solution ageing times and solution flow rates. However, through control of the experimental conditions, the nature of growth is more understood. By combining the experimental results of the chapter, it is possible to show that the growth of SOD-ZnPO is highly dependent on both the speciation and the stoichiometry of the solutions used. This shows that it is the activity of solutions that is important in determining supersaturation and that an approximation using equilibrium concentrations would not be accurate. The importance of speciation was shown, since ageing solutions meant that growth could be achieved at 1 ppm Zn, rather than the 7 ppm Zn required for growth without ageing. This ageing, however, led to the nucleation of a zinc phosphate phase in the clear solutions, meaning that control over the zinc concentrations could only be achieved up to 3 ppm.

Through growth rate measurements, it was possible to identify Zn as the element that condenses slowest, and hence determines the layer spreading rate on the \{100\} face of ZnPO-SOD. By substituting Co for Zn, the rate of growth in this “slow” direction increased. This could have been a result of the Co acting as an impurity, or due to changes in speciation. That Co growth alone was not achieved may be related to the speciation effects, which also led to diminished growth in the fast directions. It was also possible to identify a difference in growth rates between layers on the \{111\} face, allowing confirmation of the growth mechanism suggested in Chapter 3.

Coupled to the mechanistic details obtained, it was possible to quantify some key processes. By calculating the order of reaction for Zn, the role played by this species could be postulated. This type of information will be important when
combining experimental data with modelling, since this will allow more accurate relationships to be built between programme and laboratory evidence.

4.5.2 Future Work

All of the experiments in this chapter were performed at pH 7. In Chapter 2, pH was found to have a large effect on the different phases that form, as well as the rates of crystal formation. Therefore, to extend this study, the growth rates and morphologies of the facets could be observed over a pH range. This could include investigations into the transformation between the ZnPO-SOD and hopeite phases at lower pH (ca. 3).

In Chapter 3, it was observed that the \{110\} face grew rapidly at room temperature. However, from \textit{ex situ} images terraces were observed on this face. Therefore, observations of the \{110\} face could be attempted by initiating controlled growth at low temperatures, such as those in which the initial seed crystals were grown (4°C).

Throughout this work, the speciation of the solutions used for growth experiments has been revealed to play an important role in the growth processes observed by AFM. It was not possible to measure the speciation in this system where the solubility was so low with respect to zinc, whilst containing high concentrations of phosphorus and sodium. Therefore, in order to further this work a new system, perhaps a zeolite, in which the solution chemistry can be correlated to AFM results could be investigated. Zeolite growth has been proven possible from clear solutions at low temperatures, so should be possible to measure by AFM. The main challenge, however, is finding a suitable material to hold the crystals that will not be damaged by the high pH solutions required.
4.6 References


Chapter 5

Nanotribological study of the growth of Sodalite Zincophosphate
5.1 Aims and Objectives

The aim of this chapter was to investigate the nanotribology of the surface of SOD-ZnPO using lateral force microscopy measurements (LFM). More specifically the aims were to:

- Observe and quantify the terrace friction on the \{100\} face of SOD-ZnPO
- Understand the enhanced friction that is observed at step edges
- Quantify the friction in terms of energy and relate this to the growth processes
5.2 Introduction

5.2.1 Lateral Force Microscopy (LFM)

In this Chapter the friction on the \{100\} face of SOD-ZnPO surface will be investigated. For these experiments, Lateral Force Microscopy (LFM) is used measuring lateral deflection with AFM. In normal AFM operation, the vertical (normal) deflection of the cantilever is measured. During scanning, as well as deflecting vertically due to forces acting normal to the sample surface, the tip will also twist in response to lateral forces that the tip encounters whilst scanning the surface. These friction forces act against the movement of the tip against the sample surface.\(^1\) As the tip is rastered across a surface, the twisting of the cantilever is measured as a lateral movement of the laser spot in the photodiode detector. In Figure 5.1a the twisting of a cantilever is shown that leads to this lateral deflection. Depending on the friction of the surface being probed, this can cause more or less twisting of the cantilever. Figure 5.1b shows a schematic of a four quadrant photodiode detector that is used for AFM experiments. The components of the detector can be separated in order to measure both lateral and vertical deflections simultaneously. The vertical (normal) deflection is calculated as \((Va + Vb) - (Vc + Vd)\) in the photodiode detector (see Figure 5.1b), whilst the lateral deflection is measured as \((Va + Vc) - (Vb + Vd)\).

![Figure 5.1](image_url)

**Figure 5.1:** a) twisting of the cantilever related to the lateral force;\(^2\) b) Figure showing the four quadrant photodiode detector, with equations showing the measurement of normal and lateral deflection.
As the tip is rastered across a crystal surface, it will encounter different features. Changes in friction may not be related to topography. Instead, if an area of higher friction is traversed this will cause more bending of the cantilever which will be recorded by the LFM. Measurements taken are composed of both forward and backward scans. These will have opposite signs, since the cantilever twist that is measured will be in opposite directions. By combining the trace and retrace measurements, a friction loop is formed. A characteristic friction loop is shown in Figure 5.2. Following the trace (solid line) in Figure 5.2a, the friction loop initially has a steep slope. This is because the tip will not be twisted when scanning is commenced. Once the tip is twisted, it will slide over the sample. At the start of a retrace scan (right to left, dashed line), the slope is related to the cantilever twisting in the opposite direction.
Figure 5.2: Images showing two friction loops resulting from the twisting of a cantilever as it moves forward and backwards over a sample surface. In a) a friction loop is shown as the cantilever encounters an area of low friction (A) and high friction (B) with no topographic change. $V_1$ and $V_3$ represent the twist imparted on the low friction section for trace and retrace scans respectively, whilst $V_2$ and $V_4$ represent the twisting that occurs in the high friction section for trace and retrace respectively. In b) the friction loop for moving over a topographic feature is shown. 

In Figure 5.2a the friction loop represents movement of the tip over two surface areas of different friction. A is a lower friction area than B. Since in the trace and
retrace scans the cantilever twists in opposite directions, the high friction area results in a higher signal in the trace direction, but a lower signal in the retrace direction. Therefore, in order to obtain a measurement of friction, (trace – retrace / 2) is taken. This will give the average of $V_2$ and $V_4$ in Figure 5.2a for the high friction area. In Figure 5.2b, the friction loop as a topographic feature is traversed is displayed. This time, the twisting involved in moving uphill over the feature is different to the friction involved in moving downhill over the feature. The friction measured as (trace – retrace / 2) will involve an averaging of the uphill and downhill movement, as the trace movement is in the opposite direction to the retrace direction. This means that differences in slope will cancel out. However, when there is a sharp topographic feature, such as a step edge, the uphill contribution may be larger than downhill, in which case a contribution will remain in the friction measurement. This is described in more detail in section 5.2.2.3.

5.2.1.1 Sources of Error for LFM measurements

Within lateral force microscopy experiments, there are several potential sources of error. For example, the laser position on the back of the cantilever will have an effect on measurements. Ideally, the laser is positioned directly above the tip. If this is not the case, however, then the twisting of the cantilever will lead to a measured deflection in the photodiode that contains error. This is because the angle of twisting is measured at the point which the laser beam is reflected off the back of the cantilever. In order to account for this, the laser position is not altered throughout experiments, so that measurements within a single experiment are comparable.

Another source of error is related to the angle at which scanning is performed can have an effect. This is because there will be cross-talk between the twisting of the cantilever and with the buckling spring constant of the cantilever.

The tip shape will also have a significant effect on friction, affecting measurements. This is because friction depends upon the contact area between the tip and sample. This relationship is shown in more detail through the
continuum mechanics models in Section 5.2.2.1. Therefore, the same tip was used in experiments where comparisons were made. The tip may experience wear throughout an experiment, as reported by Cubillas et al., however in their experiments even though the contact area may have changed this did not have a significant effect on the friction measurements, suggesting that other influences had a greater impact on measurements.¹

5.2.2 Friction measurements on crystal terraces
In general, the friction of a terrace can be considered to depend upon two terms. One of these is related to the roughness of the terrace, and scales with the applied load. The other is related to adhesion, and is related to the tip contact area.⁷ It has been shown that the type of friction that is observed on a crystal terrace is related to the force that is applied normal to the terrace. For low normal force (0-0.5 nN applied load), it was found that friction was independent of normal load, and instead was dominated by attractive forces between the tip and sample. These were caused by van der Waals and capillary forces.⁸ At higher applied loads, frictional force will increase with normal force. This is because the applied normal force inhibits the sliding motion of the tip as it moves across the terrace.⁸ Depending on the terrace conditions, a tripping force may be introduced, leading to waviness in the lateral force loop.⁹ This is known as a stick-slip friction, an example of which is shown in Figure 5.3. For this type of growth, movement across the terrace is not uniform, but rather the tip will “stick” until a potential barrier is overcome, allowing the tip to slide across the terrace (slip region).
5.2.2.1 Modelling the tip sample interaction

In order to model the tip sample interaction, several models have been proposed based on continuum mechanics. The simplest of these models is the Hertz model. This model does not account for adhesion between the two solids in contact, and can be defined as:

\[ A = \left( \frac{3RL}{4K} \right)^{1/3} \]  
(5.1)

Where \( A \) is the contact area between a sphere and a plane, \( R \) is the tip radius, \( L \) is the load and \( K \) is the reduced elastic modulus of the two materials in contact. \( K \) can be defined as the following:

\[ K = \frac{4}{3} \left( \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \right)^{-1} \]  
(5.2)

Where \( \nu_1 \) and \( \nu_2 \) are the Poisson ratio and \( E_1 \) and \( E_2 \) are the Young’s moduli of the sphere and plane materials. Since experiments have shown adhesion components...
between the tip and surface, which can be observed by means of a force distance curve, a more advanced model was proposed by Johnson, Kendall and Roberts, known as the JKR model. This model describes two spheres in contact and includes a term for adhesion between the two interacting surfaces. By assuming that one sphere has an infinite radius this model can be extended to a plane-sphere contact. The JKR model is defined as:

\[
A^{3/2} = \frac{\pi^{3/2}R}{K} \left[ L + 3\pi R \gamma + \sqrt{6\pi R \gamma L + (3\pi R \gamma)^2} \right]
\]  

(5.3)

Where \(A\) is the contact area between a sphere and a plane, \(R\) is the tip radius, \(K\) is the reduced elastic modulus of the two materials in contact, \(L\) is the load and \(\gamma\) is the interface surface energy or Dupré energy of adhesion. This is the work per unit area required in order to separate the surfaces from contact to infinity. The friction force is related to the contact area, \(A\), as follows:

\[
F = \tau_0 A
\]  

(5.4)

Where \(F\) is the friction force, and \(\tau_0\) represents the shear strength of the contact. This allows friction force to be related to the shear strength of contact. Since adhesion forces are ignored in the Hertz model, this tends to underestimate the contact area. Therefore, typical shear strengths calculated by the JKR model will be smaller than those calculated using the Hertz model.

5.2.2.2 Effect of temperature and scan rate on friction

The friction that is measured will be influenced by a number of factors. The effect of temperature has been studied for terraces using the stick-slip growth model. This found that as temperature increases, the required load to overcome the energy barrier for sliding decreased, and therefore friction decreased. However, more recent work has shown that the temperature dependence of the slip length is also of importance. By decreasing the slip length, the overall friction will increase. The overall temperature dependence will therefore be a combination...
of the two. At low temperatures (< Room Temperature) the slip length effect dominates, whilst at higher temperatures, the effect on sliding energy is more important.\textsuperscript{18} Therefore, in the range of temperatures used within these experiments, the friction on a terrace would be expected to decrease with an increasing temperature.

The effect of scan rate on friction at the atomic scale is not clear. In some cases, no dependence on the scan rate has been observed as long as the sliding velocity (scan rate) was below the slip velocity, which is around 60 \( \mu \)m s\textsuperscript{-1}.\textsuperscript{19, 20} Meanwhile, other studies have found a logarithmic dependence of the friction on scan rate. These suggested that the cause was a temperature effect on the stick-slip mechanism, rather than a mechanical effect.\textsuperscript{8, 21, 22} Within the experiments reported here, the scan size was kept within a range of 10-13 \( \mu \)m, so as to avoid any thermal effects that may otherwise arise. This range was also below the slip velocity, meaning that temperature effects may not be present at the studied tip velocities.

\textbf{5.2.2.3 Friction anisotropy on crystal terraces}

By using LFM alongside AFM measurements, details of the chemical species on a surface can be uncovered. With LFM, it was possible to observe differences between chemical compounds on a surface even with no change in topography for Langmuir-Blodgett (LB) films.\textsuperscript{3} In these experiments, friction for the inorganic silicon substrate was found to be 10 times that of the organic species, whilst fluorocarbon scanning resulted in four times the friction compared to the scanning of hydrocarbons.\textsuperscript{3} Further observations on thiolipid LB films were able to show anisotropic friction that was purely mechanical in nature. This friction difference was observed even though there was no chemical contrast within the sample, and was attributed to differences in molecular packing and tilt.\textsuperscript{23}

For CaSO\textsubscript{4}, SrSO\textsubscript{4} and BaSO\textsubscript{4}, anisotropic friction has been observed on the (100) face. This friction difference was between different monolayers, and was caused by the change in orientation of the sulphate between the layers.\textsuperscript{7} This therefore
showed that molecular orientation can have an effect on the friction observed. This relationship between molecular orientation and friction was also observed on the triglycine sulphate (010) terrace, which displayed anisotropic friction that followed the asymmetric arrangement of molecules on different terraces. As well as the ex situ experiments described, in situ measurements have also observed anisotropic friction. When investigating the friction of heteroepitaxial growth of otavite (CdCO₃) on a calcite (CaCO₃) terrace, Cubillas and Higgins found that the relationship between the friction of Cd rich films and calcite layers was dependent on the applied normal force (load). At low loads, the calcite layers showed higher friction. However, as load was increased the friction became the same, before the Cd rich layers became higher friction. This result was explained by friction at low loads being controlled by adhesion energy, whilst at higher loads the shear strain became more important. This effect was influenced by the strain of Cd overgrowth and at higher loads this became the more important interaction. Therefore, friction measurements on terraces can be important in mapping both chemical and mechanical differences of a surface both in and out of growth. These mechanical differences can exist due to the orientations of different terminating groups.

5.2.2.4 Friction at step edges
Although the majority of studies have focused on the friction of a crystal terrace, some studies have investigated the effect of surface topography, such as surface steps on the friction. In general, the friction observed at step edges is larger than that on the terrace. However, the factors that contribute to this friction vary within the literature. At low contact load, where the normal force was 0.5 nN or less, the step edge friction on a silicon calibration grating with 170 nm step height was observed to be equal in both the uphill and downhill movements of the tip. The friction observed was due to attractive forces such as van der Waal’s or capillary forces, and the increase in magnitude at step edges was related to a Hamaker summation of these forces.
Under higher contact loads, two different observations were made. Sundararajan and Bhushan found that when imaging a silicon grid pit or gold ruler at 25 nN load, the friction of uphill movements largely increased at step edges whilst friction downhill was slightly reduced. This meant that when the overall friction was calculated (trace - retrace / 2) there was an increased friction contribution at the step edge. This topography-induced contribution to the friction was explained using a modified version of the ratchet mechanism of friction, which states that the friction force is proportional to the degree of the slope of the surface being scanned. This is typically used for small slope angles. The ratchet mechanism of friction can be expressed by the following for uphill (5.5) and downhill (5.6) movements:

\[
F_u = W (\mu_0 + \tan \Theta) / (1 - \mu_0 \tan \Theta) \tag{5.5}
\]

\[
F_d = W (\mu_0 + \tan \Theta) / (1 + \mu_0 \tan \Theta) \tag{5.6}
\]

Where \(F_d\) and \(F_u\) represent the friction force of downhill and uphill movements respectively, \(\Theta\) is the angle of the surface being scanned with respect to the plane, \(W\) is the normal load applied and \(\mu_0\) is the coefficient of friction of the tip-sample interaction. These parameters are shown in Figure 5.4. This means that a tip moving up a surface slope will experience more friction than when moving down the same slope.
This ratchet effect alone could not explain the increase in friction moving up a step edge. In order to explain this extra friction, a “collision” factor was added that related an increase in torsion to the impact of the tip at the step edge. Since there is no step collision moving downhill, the collision force was only observed for uphill movement, whilst the ratchet effect was observed in both directions. This led to the much larger uphill friction observed, which meant that on conversion to friction a peak still remained for the step edge movement. Meanwhile, Sung et al. described the extra friction at the step edge as being due to the change in slope experienced by the tip, with larger changes in slope causing greater changes in friction.

The other observations at higher contact forces were that the friction in both the uphill and downhill directions was observed to increase. The data of terrace friction and step edge friction was modelled using both the Hertz and JKR models. This gave a higher shear stress on step edges as compared to on the terraces. From this, it was possible to calculate the energy barriers for movement over step edges. By plotting the friction effect moving uphill independently from friction effect of moving downhill, it was found that downhill movement was independent of load, whilst uphill movement scaled with load. The extra downhill
Step friction was explained in terms of an Ehrlich-Schwoebel barrier existing at a step edge. This is an energy barrier that is related to reduced atomic coordination as the tip moves over the step edge. The friction was still described by the stick-slip mechanism, but with this energy barrier being larger than those on the terrace, as shown in Figure 5.5. The uphill movement was also described by increased barriers to stick-slip motion. Further work by Steiner et al. has since shown that this barrier is related to the tip shape, with atomically sharp tips able to avoid this barrier. The reason put forward for this was that the barrier is related to the mechanics of the AFM. As a blunt tip moves over a step edge, the normal force will begin to reduce whilst some of the tip is in contact with the step edge. This change in force results in the AFM moving the tip down, which created a large repulsive effect for the section of tip in contact with the step edge. This results in the increased friction.

![Figure 5.5: Energy barrier for stick-slip movement used to describe the increased friction at a step edge.](image)
5.3 Experimental

5.3.1 Calibration of the AFM for friction measurements

The signal that is recorded during an experiment is the lateral voltage, $V_L$ (V). In these experiments, it is the friction (N) that is important in the analysis of measurements. The lateral voltage can be related to the lateral force (friction) using the following:

\[ F_L = \frac{3}{2} K_L \left( \frac{h}{L} \right) S_L V_L \]  

(5.7)

Where $F_L$ is the lateral force (N), $K_L$ is the lateral spring constant (N m$^{-1}$), $h$ and $l$ represent the height and length of the cantilever used (m) and $S_L$ is the lateral sensitivity (m V$^{-1}$). The value for $V_L$, which is the difference between the trace and retrace lateral deflection, was obtained using the method shown in section 5.3.3. The values for $h$ and $L$ were measured from scanning electron micrographs of the cantilever used. These are shown in Figure 5.6.

![Cantilever measurements taken for calibration of the lateral deflection.](image)

*Figure 5.6: Cantilever measurements taken for calibration of the lateral deflection.*

The calculation of the lateral spring constant ($K_L$) can be performed by taking into account the geometry of the cantilever used. Within these experiments, triangular cantilevers were used. For these cantilevers, the following expression can be used to determine $K_L$:

\[ K_L = \left[ \frac{Et^3}{(3(1+\nu)h^2)} \right] \times \left[ (\tan\theta)^{-1} \log \left( \frac{w}{d \sin \theta} \right) + \left( \frac{L}{w} \right) \cos \theta - \left( \frac{3 \sin 2\theta}{8} \right) \right]^{-1} \]  

(5.8)
Where $E$ is the Young’s Modulus for silicon nitride and $\nu$ is the Poisson’s ratio for silicon nitride (0.24).\textsuperscript{35} $L$, $t$, $h$, $\Theta$, $w$ and $d$ are all cantilever dimensions, which are marked in Figure 5.6. In order to calculate $K_L$, the thickness of the cantilever is required, alongside the Young’s modulus for silicon nitride. This term ($Et^3$) involves a measurement that is difficult to make accurately, and cantilever properties. However, $Et^3$ is also involved in the geometric calculation of the vertical spring constant ($K_V$) as shown in the following:\textsuperscript{36}

$$K_V = \left(\frac{Et^3w'}{2L't^2}\right) \cos \theta \left[ 1 + \left(\frac{4w't^3}{b^3}\right) \times (3 \cos \Theta - 2) \right]^{-1}$$ (5.9)

Where $w'$, $b$ and $L'$ are cantilever dimensions, marked in Figure 5.6. This equation can be used to obtain $Et^3$ since the value of $K_V$ can be measured directly using the AFM software. This is done using the resonance frequency of the cantilever.\textsuperscript{37}

Finally, the lateral sensitivity, $S_L$, was required in order to convert the lateral voltage into force. The sensitivity is a measure of the response of the photodiode to cantilever deflection or torsion. The vertical sensitivity ($S_V$) can be obtained by taking the slope of a force distance curve (as in Chapter 4), since the deflection is equal to the movement of the piezo. This value is not the same as the lateral sensitivity. The reason for this is that the laser used may have an irregular cross-section.\textsuperscript{38} This means that there may be cross-talk between the lateral and vertical deflections of the cantilever. This can occur for several other reasons including misalignment of the laser and rotation of the photodiode detector. However, this must be accounted for because the response to normal forces is larger than lateral forces, and normal forces are also typically larger than lateral forces.\textsuperscript{5}

In order to calculate the relationship between lateral and vertical sensitivity, the method of Liu et al. was used.\textsuperscript{39, 40} This method was to directly measure the relationship between movement of the photodiode pairs in the lateral and vertical directions and measured voltage. In order to do this, knowledge of the pitch of the
positioning screws operating the photodiode detector was required. This was 0.25 mm per turn.\textsuperscript{41} The screw was turned in 1 / 12 portions, and the deflection recorded. This was done for both the lateral and vertical directions, and the results are presented in Figure 5.7. From the slopes, $S_1$ was calculated to be $1.5 \times S_v$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.7.png}
\caption{Graphs showing the response (V) to movement of the photodiode detector in a) the lateral and b) the vertical directions.}
\end{figure}
5.3.2 Calculation of Error

In this chapter, the error will be presented in two ways. The first method is related to the precision of the data recorded during experiments with the AFM. This is obtained by calculating the standard deviation of the measurements taken at each experimental condition. The error bars on plots in this chapter reflect this quantity. For each data point, a minimum of five measurements were taken and averaged. The calibration of the AFM for friction methods incurs a large error (see below), therefore for each experiment compared the same tip was used, with the laser position unaltered manually. A measurement at 25 °C, 50 nN load was taken at the start and finish of a single experiment involving growth from a 1.5 ppm Zn solution to investigate the effect of tip wear and laser drift on the error (see section 5.2.1.1). Both results were within experimental error of each other meaning that this effect was not large enough to greatly influence the measurements made. This is shown in Figure 5.8.

![Figure 5.8](image)

**Figure 5.8:** Measurement of friction obtained from the step edge of a growing SOD-ZnPO crystal in a 1.5 ppm solution, taken at 25 °C with an applied normal force of 50 nN a) at the beginning of the experiment (after ca. 1 hour), b) at the end of the experiment (after ca. 8 hours).
The second error calculation is related to the cantilever calibration process that is required in order to convert the lateral deflection (V) into friction (nN). This process requires a large number of measurements when using the geometric method in equations 5.8 and 5.9 in order to calculate both the vertical and lateral spring constants ($K_V$ and $K_L$). For the overall error of the experimental calibration process, the individual errors for each measurement are required. These are as follows: $12 \Delta K_N = \pm 0.01 \text{ N m}^{-1}$, $\Delta V_L = \pm 0.007 \text{ V}$, SEM measurement errors = 0.1 $\mu$m and cantilever angle measurements = $\pm 0.2^\circ$. The associated error involved in the calculation of $K_L$ was obtained using a propagation of errors method. This gave a calculated lateral spring constant and associated error of $215 \pm 38 \text{ N m}^{-1}$.

### 5.3.3 Data Processing

Lateral force data was batch processed using a custom Matlab® code (written by Dr Pablo Cubillas). Terrace friction was calculated by taking the difference between the value of the trace and retrace scans, then dividing by 2. This is shown by the short red line in Figure 5.9. During measurements, scanner / drift effects mean that data does not always match-up in the forward and backward directions.\(^1\) This was verified by observing that specific features in the image did not match up in trace and retrace scan through height measurements. In order to account for this drift, the batch processing code contained a subroutine that would perform a correction to align the data. This was achieved by squaring the value at all the data points. The code then moved the retrace image by 1 pixel at a time, calculating the sum of the trace and retrace at each point. When the maximum value was found, which corresponded to the alignment of the data, the pixel movement required to find this point was applied to the retrace image. Data measurement on terraces was performed over a user selected area, giving an average lateral deflection (V) and the standard deviation for these measurements. Each data point presented for terrace measurements were therefore obtained in a single image.

For the step edge friction, data was obtained by measuring the lateral deflection cross-sections across the edge. Each data point presented is an average of several
cross-sections obtained across both different terraces in the same image and across different images. Two methods were employed in order to quantify the data. In the first, the friction was measured as the difference between the “peaks” in both the trace and retrace direction that were a result of traversing the step edge. This is represented by the long red line in Figure 5.9, and gave the total friction at the step edge. Since it was the increased friction that was involved in traversing the step edge that was of interest in these experiments, the second method involved subtracting the friction on the terraces (short arrow) from the step edge friction (long arrow) to leave only this increased friction.

Figure 5.9: a) Trace lateral deflection image and b) retrace lateral deflection image from which the measurement in c) was taken. In c the dashed red line represents the baseline. The long red line is 2 x the step edge friction, and the short red line is 2 x the terrace friction.
5.3.4 Experimental procedure

Measurements were performed with a JPK Instruments AG NanoWizard II Atomic Force Microscope operating in contact mode, using silicon nitride cantilevers with a nominal force constant of 0.58 N m\(^{-1}\) (Veeco model NP-10). A scan rate of 5 Hz was used during measurements, with image width varying between 1 – 1.3 \(\mu\)m to maintain a small range of tip velocity (10 - 13 \(\mu\)m s\(^{-1}\)). In all measurements, the scan angle was kept at 0 ° in order to avoid a contribution from cantilever buckling (see section 5.2.1.1). Solutions were flowed over the crystals at 0.1 mL min\(^{-1}\), with the cell volume 0.4 mL. For step edge measurements, contact forces of 10, 12, 14, 16, 18, 20, 30 and 50 nN were used. For terrace friction measurements, contact forces of 10, 30 and 50 nN were used. The temperature of the system was controlled using the JPK BioCell™ temperature controller, with a separate measurement for the heating element and solution temperature provided. This allowed solution temperature to be controlled accurately, with a resolution of 0.1 ° C. For step friction measurements four temperatures were used; 25 ° C, 35 ° C, 45 ° C and 55 ° C. For all other measurements, the temperature was set to 25 ° C. All measurements were taken on the \{100\} face of SOD-ZnPO.

The solutions used to perform the growth measured were prepared in the laboratory from stock solutions of phosphoric acid, zinc nitrate and sodium bromide. The concentration of phosphorus used was 3000 ppm (0.097 mol dm\(^{-3}\)), whilst sodium concentrations were kept at 20100 ppm (0.875 mol dm\(^{-3}\)). The minimum zinc concentration used for measurements was 1 ppm (0.0153 mmol dm\(^{-3}\)), whilst the maximum was 2.5 ppm (0.0428 mmol dm\(^{-3}\)).
5.4 Results and discussion

5.4.1 Terrace Friction
When observing the lateral deflection images of the terraces on the \{100\} face of SOD-ZnPO, a friction difference can be observed between different layers. This effect is observed most clearly in the birth-and-spread growth image displayed in Figure 5.10. Since the figure shows a trace image, the darker areas represent areas where there is less twisting of the cantilever, i.e. lower friction and the lighter areas represent areas of higher friction.

![Lateral deflection images showing anisotropic growth on the \{100\} face of SOD-ZnPO growing by a birth and spread mechanism.](image)

Upon closer inspection, it can be seen that this change in friction alternates with every layer similar to the anisotropic growth that has already been observed on the \{100\} surface in Chapter 3. This friction difference could therefore be related to whether the tip was scanning across the “fast” or “slow” direction on the terrace. In order to prove that the direction the tip moved across the terrace (either across the “fast” or “slow” direction) was responsible for the friction change observed, an experiment was performed on a single crystal that was rotated within in a single experiment, shown in Figure 5.11. This rotation was of 76° and meant that the direction of scanning on an individual terrace was reversed, i.e. on terraces where the tip previously followed the “slow” direction the tip now...
followed the “fast” direction and *vice versa*. This resulted in a reversal of the friction observed, with the terraces that were previously displaying high friction now displaying low friction. This meant that the area of high friction was consistently when scanning predominantly across the slow direction, whilst the area of low friction was consistently when scanning predominantly across the fast direction. This means that there is a difference in friction between scanning in the [100] and [010] directions on a (001) surface. As with the growth anisotropy, this friction anisotropy also alternates every layer suggesting that it is related to the ordering of the zinc and phosphorus. If this is the case, it would be expected that at 45 °, this friction difference would disappear. However, due to the necessity of scanning at a 0° angle, these observations are challenging, as they rely on a crystal being oriented at exactly 45 ° before being sealed in the cell. Therefore, this could not be confirmed within these experiments.
As mentioned in section 5.2.2.3, anisotropy has been observed in other systems, where it has been related to the orientation of certain structural groups to the scan direction.\textsuperscript{7, 24, 42} Since the ordering of the cations on the \{100\} face of SOD-ZnPO is the same between alternating layers, this is not the cause of this effect, but rather it results from the difference caused by the zinc / phosphorus ordering. A structural diagram is shown in Figure 5.12, in which the ordering of the zinc and phosphorus is highlighted. This shows that the different atoms line up in rows
across the 4-rings, as highlighted by the white writing. From Chapter 4, it was determined that the slow direction was limited by the addition of zinc. This addition would be to an attached phosphorus (omitting consideration of bridging oxygens and surface terminations), which is represented by the blue atoms in Figure 5.12a. Meanwhile, the addition of phosphorus would require attachment to zinc, represented by the red atoms in Figure 5.12b. This means that for the pink middle terrace, zinc limited growth would occur in the y direction, whilst phosphorus limited growth would occur in the x direction. For the purple and blue layers this is reversed, with zinc limited growth in the x direction and phosphorus limited growth in the y direction. This shows that the areas of high friction are observed when the tip is scanned parallel to the zinc rows, and perpendicular to the phosphorus rows.

![Figure 5.12](image)

*Figure 5.12: Structural diagrams showing three terraces (purple, pink and blue) growing on the {100} face of SOD-ZnPO observed from a) the (100) direction, and b) the (010) direction.*

The reason that this anisotropic friction is not observed *ex situ* may be due to the error related to these measurements. Figure 5.13 shows the difference between a
scan on a crystal surface *ex situ* and *in situ*. This shows that *ex situ* scanning has a lot more error involved, which could be a result of surface contamination on the crystals that are being observed. In typical friction experiments, freshly cleaved surfaces are used,\textsuperscript{15, 29, 30, 32} which can reduce these effects. However, the crystals observed *ex situ* in this study could have impurities on the surface present from the growth and recovery processes used for the seed crystals. During growth experiments *in situ*, a clean surface is being scanned, which allows the measurements to be made.
Figure 5.13: a) lateral deflection response to a scans taken in situ and ex situ on the same crystal, b) AFM lateral deflection image for the ex situ scan (white line), c) AFM lateral deflection image showing the area from which the in situ scan was taken (white line).

In order to quantify the friction difference observed, measurements were taken over a series of loads. Some representative results are shown in Figure 5.14a, b and c, which shows friction on the terrace for both the higher friction terrace (scanning across zinc rows) and the lower friction terrace (scanning across phosphorus rows). Each data point represents an area selection from a single image (3 per load are shown out of 50 measured). In Figure 5.14d, the three loads
are combined onto the same graph in order to show the effect of load on friction on the terrace.

Figure 5.14: Average lateral force measurements taken from several different scans for both the high and low friction terraces, measured at a) 10 nN, b) 30 nN and c) 50 nN. The results are combined in d) to show the effect of load on friction.
In Figures 5.14a, b and c, in all cases there is a difference in friction between the two terrace directions. This friction is consistently higher scanning across the zinc. In work on CdCO$_3$ growing on CaCO$_3$, a dependence on load for which area showed higher friction was observed.\textsuperscript{1} This was related to the dominance of adhesion type interactions at low load (below 40 nN), as compared to shear interactions at higher loads (above 40 nN). In these SOD-ZnPO experiments, the loads selected covered a similar range to this. The surface that is being scanned during these experiments will be terminated by either terminal hydroxide or ordered water molecules, and it could be that the ordering of these molecules is the cause of the friction differences observed at low loads. Since at higher loads the tip will be in direct contact with the surface, it is unlikely that the hydration of the surface terminal groups alone can explain the friction effect observed.\textsuperscript{1} Instead, this may be related to the difference in the tip interaction with terminal groups attached to zinc and phosphorus. The exact nature of this difference in interactions is difficult to predict without a good knowledge of the surface structure. However, it is likely that the anisotropic friction is related to the zinc and phosphorus ordering as the friction anisotropy follows the anisotropic terrace growth shown in Chapter 3. In Figure 5.15a and b, the (010) and (001) faces are shown respectively. This allows the observation of the positions of zinc and phosphorus on the (100) face, reinforcing the difference between scan directions on a single layer. The zinc and phosphorus T atoms are circled in the figure. No surface terminations are shown (e.g. hydroxide groups). In Figure 5.15c, a view of the (100) face is shown, as it would be observed by AFM. From this image, it can be seen that there is a difference between the [010] and [001] directions when considering the zinc and phosphorus atoms. Therefore it seems more than probable that the amount of tip twisting will be related by the relationship between the scan direction and the alignment of the surface atoms and their terminal groups.
Referring back to Figure 5.14, it can be seen that overall, the friction difference observed between terraces is quite small when compared to the effect of load on friction. This means that the overall friction measurements contain a large amount of variation. The error in measurements at a single load could be related to drift of the laser and other experimental errors, and could lead to friction measurement variation of up to 20%. However, the important point from these results is that at all loads the friction difference can be observed and measured. This difference is present at both high loads and low loads, and always gives a higher friction scanning across zinc rows rather than the phosphorus rows. At high loads, it could be that in direct contact with the surface the friction difference is a result of the difference in scanning zinc and phosphorus and their terminal groups. The tip will interact differently with different atoms, and the surface terminal groups may be arranged differently, which could lead to the increased friction. At low loads, the tip is instead likely to be in contact with the terminal groups and hydration layers. The friction difference here is expected to be due to ordering of water and other terminal groups.
5.4.2 Step Edge Friction

The second effect observed is the increase of LFM signal at step edges under growth conditions. The terrace “lighting up” shows that extra twisting of the cantilever occurs as the tip moves over a step edge. The figure shows that this increase is observed both moving up and down the terrace. This shows that the lateral force increase is not simply a topographic effect. Comparing the LFM measurements image before growth, this effect is quite pronounced. This is shown in Figures 5.13b and 5.13c. By using equation 5.7, it was possible to convert the measured lateral deflection (V) into friction (nN). In order to investigate the origins of this effect, the friction was plotted against varying load (applied force normal to the surface). This plot takes the friction (trace - retrace / 2) at the step edge, which is plotted as red squares. The friction on the surface step (trace - retrace / 2) is also plotted. This measurement was taken during a growth experiment, with [Zn] of 1.5 ppm and temperature of 25 °C.

![Graph showing the difference in friction as a function of load for both the surface and at the step edge, taken on the {100} face of a growing SOD-ZnPO crystal at 25 °C with [Zn] 1.5 ppm.](image)

*Figure 5.16: Graph showing the difference in friction as a function of load for both the surface and at the step edge, taken on the {100} face of a growing SOD-ZnPO crystal at 25 °C with [Zn] 1.5 ppm.*
There is a positive relationship between the load applied and the measured friction. At all loads measured, the step edge friction was higher than that of the surface. From previous work performed by scanning crystals ex situ in ultra-high vacuum (UHV), this type of relationship has also been observed.\(^\text{30}\) In both cases, as well as a general increase in friction with load, the difference between the friction on terraces and at step edges also increases. The data previously obtained by Meyer et al. was fitted to both the Hertz and JKR model. For this fit, the load effect on friction began to decrease at higher loads. Within this experiment, this is not observed, with the dependence of friction on load seemingly linear. This may be because the experiment in which the load effect began to decrease was performed over a much larger range than in this experiment, with measurements up to 140 nN applied load. Had higher loads also been investigated here, it may well follow the same trend as in the experiment of Meyer et al.\(^\text{30}\) However, due to the requirement to perform all related experiments with the same tip for comparison it was not feasible on an experimental timescale to investigate a much wider range of applied loads.

By comparing the contributions of the uphill and downhill scans at the step edge, it was possible to suggest the processes that account for the frictions observed. In order to investigate the difference in uphill and downhill scans, the difference between step edge and terrace friction (frictional increase) for one scan direction (trace only) was used for both uphill and downhill measurements. This method is used instead of taking difference between trace and retrace since this difference includes a contribution from both uphill and downhill tip movement. This is shown in Figure 5.17.
Figure 5.17: Plot of the difference between surface and step edge friction for measurements taken when the tip moves up the step and when the tip moves down the step.

The plot in Figure 5.17 shows that with increasing load, it is the movement up the step edge that is contributing to the overall increase in friction, whilst the downhill friction does not change with load. This observation agrees with previous *ex situ* experiments.\textsuperscript{29, 31, 32} Originally, it was proposed that the step barrier for moving down the step was related to the Ehrlich-Schwoebel barrier.\textsuperscript{43, 44} However, a further study found that this effect did not exist using small contact loads and atomically sharp tips.\textsuperscript{32} This suggested that the barrier for downhill movement was only applicable for blunt tips and is related to the movement of the AFM whilst part of the tip is still in contact with the step edge.\textsuperscript{32} Within the experiments described here, the tip radius will be ca. 20 nm.\textsuperscript{12}

It was also observed in the literature that the uphill friction is always larger than the downhill friction due to a higher energy barrier that is overcome in order to move up a step.\textsuperscript{31} From the results presented here, this is the case at all applied loads except for 10 nN. At this load, the error in the two measurements (uphill and downhill) means that a definite difference in friction cannot be observed. This is because the friction difference is smaller at lower loads.
5.4.3 Investigation of the step energy related to in situ growth

In a previous study of the dissolution of zeolite L\textsuperscript{13} it was observed that, when operating the AFM to monitor lateral deflection, there was a substantial twisting of the cantilever specifically at the point of the surface that was dissolving. This showed that extra energy was being imparted to the tip as a direct result of the dissolution process that was occurring. This same observation was made during dissolution experiments involving Zeolite T\textsuperscript{45}.

In growth experiments performed on SOD-ZnPO, the extra friction at step edges is not localised as in the dissolution experiments, but instead all of the edge experiences increased friction (e.g. Figure 5.11c). Similar observations of NaCl and MoS\textsubscript{2} crystals \textit{ex situ} have shown this type of non-localised increased friction at step edges in the absence of growth.\textsuperscript{30-32} Therefore, the increased step edge friction observed for SOD-ZnPO may not necessarily be related to the growth process. Instead, it could be that the measurements taken \textit{in situ} show friction differences that should be present in \textit{ex situ} measurements, but are not observed due to the surfaces being unclean. Therefore, the aim of this section is to investigate the increased energies at step edges under a variety of growth conditions in order to establish the influence, if any, of the growth process on the energy imparted to the tip at the step edges.

For AFM measurements, it was assumed that the AFM cantilever acts as a perfect spring. Therefore, the deflection of the cantilever can be described by Hooke’s law (Equation 5.10). The energy of the processes involved, which include the mechanical movement on the step and the extra energy imparted to the tip by the sample compression, can be related to the elastic potential energy in equation 5.11. By combining equations 5.10 and 5.11, an expression for the total energy can be obtained, shown in Equation 5.12:\textsuperscript{13}

\[
F_L = -K_L z
\]

(5.10)
\[ V = \frac{1}{2} K_L z^2 \quad (5.11) \]

\[ V = \frac{F_L^2}{2K_L} \quad (5.12) \]

Where \( F_L \) is the lateral force (N), \( K_L \) is the lateral spring constant (N m\(^{-1}\)), \( z \) is the displacement of the cantilever (m) and \( V \) is the potential energy (J). This method was used to convert the friction that was measured into energy. The extra energy involved in traversing the step, used in this analysis, was then calculated by subtracting the calculated surface energy from the calculated total step energy. This was converted to kJ mol\(^{-1}\) through multiplication by the Avagadро constant, \( N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \).

In order to investigate the effect with respect to growth conditions, the effect of both supersaturation and temperature were investigated. For supersaturation measurements, the amount of zinc was altered with 1, 1.5 and 2.5 ppm solution zinc concentrations used. In Figure 5.18, the results of experiments performed at three concentrations are presented. The results indicate that the change in energy released at the step with increased load is a linear relationship.

**Figure 5.18:** graph showing the extra energy for traversing a step edge as a function of load for three different solutions, with [Zn] of 1, 1.5 and 2.5 ppm.
The results also show that there is an effect of supersaturation on step energy. There are two reasons why this effect may occur. Firstly, this could be due to a decrease in friction on the terraces with increasing supersaturation, which would result in a larger difference between surface and step edge friction. Secondly, this could be due to an enhanced energy imparted to the tip at the step edge. By measuring the surface friction at varying supersaturation, it was found that there was no change in surface friction, and therefore the second effect was responsible for these observations. This is shown in Figure 5.19. This means that the extra energy imparted to the tip at step edges originates at least in part as a result of the growth processes occurring. From the friction experiment in 5.4.2, the increase in energy with increasing load can be attributed to changes in the energy of uphill movement only since the downhill movement was load independent.

![Friction observed at 50 nN applied load, 25 °C for terraces and step edges at various solution Zn concentrations](image)

**Figure 5.19:** Graph showing the difference in friction between the step edge and the terrace for three different [Zn], which were 1, 1.5 and 2.5 ppm. The temperature was 25 °C and the applied normal load was 50 nN.

In Figure 5.18, the energy difference between the three solution zinc concentrations increases with increasing load. However, this increase maintains a constant ratio of the step edge energies between the three solutions. This means that the change in step edge energy with supersaturation can be related by the
gradient of the energy vs load graphs for each solution. The intercept of these graphs, meanwhile, is expected to be a positive integer. This is because of adhesive forces that are present even in the absence of an applied normal load. The results presented do not follow this trend, which may be related to the error in measurements rather than a real effect. Since the supersaturation effect on step energy is related to the gradient, this means that it is during uphill movement that the extra energy related to the growth process is imparted to the tip.

The reason that an increase in the concentration of zinc increases the step edge energy could be related to the growth process. Therefore, the growth rate was plotted against the step edge energy in order to investigate this effect. This is shown in Figure 5.20, with the data at three different applied loads plotted. This shows that at all loads there is a linear relationship between growth rate and step energy.

![Figure 5.20: Graph showing the relationship between step edge energy and the terrace spreading rate.](image)

As well as supersaturation, the effect of temperature was also investigated for a solution zinc concentration of 1.5 ppm. This relationship is shown in Figure 5.21a. These results show that with an increasing temperature there is an increase in the difference between the terrace energy and the energy released at the step. Again,
this may not necessarily be due to an increase in the energy imparted to the tip at the step edge with increasing temperature, but may instead be related to a decrease in friction on the terrace. Within the temperature range investigated here, a decrease in terrace friction with increasing temperature is expected as explained in section 5.2.2.2. If a decrease in friction on the surface was to occur, this would mean an increase in the difference between the terrace and edge friction, leading to the observed energy difference. In order to investigate this, the surface friction at varying temperature was measured, shown in Figure 5.21b. As with the concentration experiments there was no decrease in terrace friction with increasing temperature. This means that as with the concentration experiments, the increase in energy imparted to the tip at increasing temperatures is related to the increase in twisting of the cantilever as it moves up a step.
Another point from Figure 5.21a is that the intercept of the step energy against load plot is expected to be a positive integer. This is because of adhesive forces that are present even in the absence of an applied normal load.\textsuperscript{46} The results presented do not follow this trend. However, due to the large error in the measurements at higher loads, this may be due to a non-linear relationship between the load and step energy.
In Figure 5.22, the relationship between the step energy and the terrace growth rate is plotted. This shows the data collected when varying both temperature (red squares) and zinc concentration (blue diamonds), and is therefore independent of the cause of the growth rate changes. In this figure, an increase of step energy with growth rate is shown. From Chapter 4, it was seen that by increasing both the temperature and the concentration of zinc the growth rate of SOD-ZnPO increased. Therefore, the extra friction effects observed at the step edge may be related directly to an increase in the growth rate. Since there is large error in some of the temperature effect measurements, it is not possible to know whether the relationship is linear or not. It may instead be the case that the temperature effect does not have the same gradient as the concentration effect measurements, but rather exhibits higher step energy at the same growth rate. Nevertheless, an increase in the rate of growth has been shown to increase the energy imparted to a tip as it moves over a step edge, resulting in an increased friction. The difference in energy imparted to the tip at different temperatures and zinc concentrations is related to the slope of the applied load against step energy plots. This means that it is during the uphill step movement that this extra energy related to the growth
process is imparted to the tip. This is because the downhill movement was shown to be load independent, therefore not influencing the gradient change with changing conditions.

The reason for the increased energy may be related to the growing terrace moving into the tip. With a full scan rate of 5 Hz (trace and retrace) and scan size of 1 μm (2 μm for trace and retrace combined), the tip velocity will be 10 μm s\(^{-1}\), or 10000 nm s\(^{-1}\). Meanwhile, the maximum terrace spreading rate measured in these experiments was 0.83 nm s\(^{-1}\). This is equivalent to 1 sodalite cage per second, whilst each line scan takes 0.1 s. This means that it will require 5 line scans in order for the terrace to advance by an average of 1 sodalite cage. Each scan is of 1000 nm, whilst the growing edge will be at most 1 nm per scan, therefore tip contact time with actual growing terrace will be \(\frac{1}{1000} \times 0.1\) s. This suggests that incorporation into the step will not be a rapid enough process to directly cause a large consistent friction increase such as that observed, but rather the tip will be colliding with an effectively static step edge. Therefore, the increased friction is likely related to a different effect that an increased growth rate will have on the step edge area.

When the growth rate increases, several changes at step edges will occur. Firstly, there will be more growth species that are diffusing in and out of the kink sites as the crystal grows. At a higher growth rate, the nucleation of new kink sites is also more rapid.\(^{48}\) The number of kink sites at a crystal step edge has previously been suggested to affect shear strength. It was predicted by Meyer \textit{et al.} that the shear strength would be considerably higher in the presence of a higher kink density.\(^{30}\) Therefore, the increase in nucleated kink sites induced by an increased growth rate could be the reason for the increased energy imparted to the tip.

Another explanation could be that the growing crystal will be composed of more incomplete cages with more under-coordinated bonds as the growth process occurs, which could cause an increased friction. Moh \textit{et al.} found that for the ZIF-8 metal organic framework (MOF) with sodalite topology the terraces were not
nucleated as complete cages, but rather that the cage was built up over several layers.\textsuperscript{49} If the ZnPO-SOD cage grows in the same way, rather than nucleating as a complete cage, then this building of cages will occur at step edges as well as during nucleation of a new terrace. At higher growth rates, the number of incomplete cages will increase. Since the tip radius is \textit{ca.} 20 nm, each scan will involve on average more interactions between under-coordinated species that are part of incomplete cages at step edges, which could increase the friction between the tip and sample.

Finally, the enthalpy of reaction may contribute, with a localised heating at the growing step edges. This could impart energy to the tip which could cause a local extra friction to be observed.

From the suggestions above, there are several mechanisms by which the step edge friction may be enhanced. This may be a result of one of, or a combination of the above reasons. Nevertheless, this work has been able to show that there is an enhanced friction at step edges that is directly related to the growth processes. For an increasing concentration of zinc, and an increasing temperature there is an increase in step energy.
5.5 Conclusions and Future Work

5.5.1 Conclusions
Anisotropic friction has been observed on the \{100\} face of SOD-ZnPO. By rotating the crystals, this effect could be proved to be related to the ordering of Zn and P on the surface. This shows that LFM could be a useful technique for probing the subtleties in surface structure. Further investigations on the effect of load have shown that this anisotropic friction persists at both high and low loads, and that the direction of high and low friction is consistent. This means that the reason for the difference in friction cannot be solely influenced by the hydration layer, but must occur at the crystal surface since this is what is scanned at high loads. From this, it was suggested that the different interactions between the tip and the zinc and phosphorus may play a role in the friction, with the subsequent hydration effects meaning that the effect is persistent even at low loads.

Step edge friction was also quantified. The results showed that, as with dissolution experiments performed previously,\(^{13}\) the magnitude of the friction effect for growing steps depended on the growth rate. By observing the dependence of both uphill and downhill movement on load, it was possible to attribute the differences in the energy imparted by growth to the uphill movement of the tip over the step. At both higher supersaturation and temperature an increase in step energy was observed. By ruling out changes in terrace friction, it was found that these energy differences occur at the step edge and are likely to be related to the chemistry that is occurring at the step edges.
5.5.2 Future Work

It was suggested in section 5.4.1 that the anisotropic friction may be present ex situ, but obscured by the error involved in the measurements taken. This could be related to impurities on the surface. This could be proven by performing measurements following the procedure used by others in order to minimise the error. This could include annealing the surface or investigating crystals in vacuum. This would allow the effect on ex situ measurement error to be understood for both surface and step edge friction.

Anisotropic friction has been observed and related to the surface structure of SOD-ZnPO. This investigation could be extended by investigating the {100} face of other sodalite structures to observe if this effect is observable with different framework atoms, and if so whether the effect is more pronounced. This may allow a clearer understanding of the process. In order to understand the origin of the process, molecular modelling could be used to investigate the surface structure of SOD-ZnPO.

In order to investigate the step edge friction further, a fully quantified dissolution experiment could be performed. This would allow direct comparison between the friction effects observed during growth and dissolution, possibly revealing further details about the mechanism by which extra energy is imparted to the AFM tip.
5.6 References

4. C. O. P. Cubillas.
41. JPK Instruments, 2011.
Chapter 6

Conclusions and Future Work
6.1 Conclusions

The main aim of this work was to use AFM to observe *in situ* growth on an inorganic open-framework material for the first time. The material selected was sodalite zincophosphate for several reasons. Firstly, the simplicity of the structure and the lack of organic structure directing agent required meant that it was a good model system to study. This was further enhanced due to the ordering of the metal atoms within the framework. The reason that the zincophosphate was selected was due to the low temperatures and pressures at which typical syntheses were conducted. This meant that these crystals were particularly amenable to *in situ* AFM investigations.

The investigations on the {100} face showed anisotropic growth of the terraces, which was related to the differences in condensation rates of phosphorus and zinc. This difference could be observed because of the strict alternation of phosphorus and zinc in the framework. This result is likely to be important for other ordered open-framework materials, including aluminosilicate zeolite phases. This work also identified for the first time a number of growth defects in the sodalite system.

The investigations on the {111} face showed two different mechanisms. For the birth and spread mechanism, monolayer spreading was influenced by through-extra-framework bonding related to the cations and hydrogen-bonded water. For double layers generated by spiral growth, the layers spread through strong framework interconnectivity. The layers spreading by through-framework bonding did grow faster than those spreading by weaker through-extra-framework bonds; however the existence of the monolayers influenced by extra-framework species shows their importance in the growth process. This means that the process cannot be considered simply as strong framework bonding, but rather the extra-framework species must be considered in any models since they are able to directly influence the mechanisms observed. If the extra-framework species did not have any influence on the growth mechanism, then layer spreading would not
have been observed for the monolayers. This means that these results are direct evidence of the influence of extra-framework species on the growth mechanism. This type of picture of crystal growth is likely to be universal for open-framework materials, whether inorganic, inorganic/organic, or purely organic.

Whilst the initial growth of sodalite zincophosphate was relatively facile, more issues were encountered when attempting to gain control over growth for quantitative measurements. By investigating a wide range of synthesis conditions for sodalite zincophosphate, parameters for in situ quantitative measurements could be more carefully selected. For example, the importance of having an excess of phosphorus in achieving a pure phase sodalite led to an excess in laboratory prepared growth solutions. Meanwhile, the pH was maintained at 7 across all experiments due to the large influence this had on both reaction rate and product. However, even with these considerations, there were some difficulties that were mainly related to the low solubility of sodalite zincophosphate. It was still possible to exert some control, and some important information could be obtained through this data. From the ageing experiments, it was shown that speciation is likely to be important in the growth process. Due to the low solubility of sodalite zincophosphate, as well as the high ionic strength and excess phosphorus, a full understanding of the growth solution was not obtained. Other important results included an understanding of the role that solution stoichiometry plays growth, with less excess phosphorus leading to an increase in growth rate. It was also possible to show that phosphorus addition was rate limiting in the “fast” direction on the {100} face, and to investigate the substitution of zinc for cobalt.

Considering the LFM experiments, the anisotropic friction observed on the {100} face follows the anisotropic growth observed in the AFM measurements. This suggests that the cause of this anisotropy is related to the symmetry of the layer, related to the zinc and phosphorus positions. It seems likely that scanning areas containing more zinc or phosphorus will lead to different measured friction, although this is complicated since the tip contact area will contain several of each atom type. Therefore, in order to gain a full understanding on the origins of this
anisotropy, a detailed understanding of the crystal surface during growth would be required. From the range of contact loads studied, it can be seen that the effect observed is not only present for the hydration layer, but also at higher loads when contact with the surface is more likely.

The main result from the LFM work is that the step edge friction is related to the growth rate of the terrace. There were several suggestions for how these were related, however with the AFM utilised in these experiments having a lateral resolution of ca. 20 nm, a more detailed explanation could not be obtained. Had a higher resolution been available, then the kink density could have been found. Since one explanation related the increased friction with increasing shear strength owing to a higher kink density, this higher resolution could allow this to be investigated. It would also be of interest to investigate whether this effect is universal for other systems. In other systems where step edges are made up of simpler units, this could allow further elucidation of the mechanism by which extra friction is observed during growth.

Whilst several interesting phenomena have been measured using LFM, the methods of quantification mean that high errors are associated with individual measurements. This means that comparing quantities across different experiments is difficult, for example comparing the size of anisotropic friction in several systems. This drawback is an issue, however it is much simpler to observe general trends such as those described herein, meaning that this technique can give some important information to add to the understanding of the growth processes and crystal properties.
6.2 Future Work

This work has led to the first in situ AFM studies on inorganic open-framework materials. To date, the zincophosphates are the only inorganic open-framework materials to have been successfully grown in situ. This is related to the low temperatures and neutral pH at which they grow making them particularly amenable for AFM. However, from this work, it has also been shown that an understanding of the solution chemistry has proven difficult. Therefore, to extend these studies, in situ growth could be attempted on different inorganic systems such as aluminophosphate or aluminosilicate (zeolite) materials. Since these crystals do not grow under conditions as mild as the zincophosphates, this will lead to technical challenges in terms of AFM operation. However, the existence of several hydrothermal microscopes suggests that the high temperatures and pressures associated with growth of aluminophosphate and aluminosilicate materials are issues that could be resolved. Since the solution chemistries of these systems are better understood, this would give more perspective to the results gained from microscopy, and allow more detailed conclusions to be obtained from both qualitative and quantitative measurements.

For the LFM work, again investigations of other systems would be useful. In this case, the systems that would aid understanding of the observed phenomena would not be open-framework materials, but rather less structurally complex materials, perhaps those that grow by single atomic layers. This would mean that step edges would be simpler to consider, which would aid elucidation of the reason for an increasing friction with growth rate.