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Titanium Isotope Cosmochemistry

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Abstract:

The University of Manchester

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Degree of Doctor of Philosophy

'Titanium Isotope Cosmochemistry'

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High precision measurements of Ti isotopes within terrestrial and extra-terrestrial materials were made in order to investigate the processes at work within the early solar system. Variations of Ti isotopes also enabled the investigation of the specific stellar sources that created the material that formed the solar system. Titanium was chosen as it is a refractory element, relatively resistant to secondary processes and found abundantly in all solar system materials.

Measurements were performed using a Thermo Fischer Neptune MC-ICPMS at the Open University, Milton Keynes. Various samples of carbonaceous chondrites, ordinary chondrites, enstatite chondrites, achondrites, lunar, terrestrial and early solar system components were analysed. Mass independent measurements of various solar system materials revealed a correlation between $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{46/47}$ Ti_{49/47} defining a best line with a slope of 5.34 \pm 0.34. The correlation indicates that solar system materials contain nucleosynthetic components that match a SNII stellar source. Utilising aliquots previously analysed for Zr isotopes for Ti isotope analyses revealed a correlation between $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{96/90}$ Zr_{94/90} for the carbonaceous chondrites that is controlled by the CAI content of the particular carbonaceous chondrite group. Step wise dissolution of ordinary chondrites and carbonaceous chondrites revealed multiple nucleosynthetic Ti components contributing to the solar system.

Stepwise leachate dissolutions were conducted on the carbonaceous chondrites Allende, Murchison and Orgueil to compliment the study of the same samples for Zr by Schönbächler et al. (2005). In addition, sample aliquots of QUE 97008 and Murchison from the work of Qin et al. (2011) were also investigated for Ti. The two investigations allow the comparison of Ti in different phases to be compared with other isotope systems such as Zr (Schönbächler et al. 2005) and Cr, Sr, Ba, Sm, Nd and Hf (Qin et al. 2011).

Mass dependent fractionation and absolute nucleosynthetic anomalies of Ti within solar system materials was determined by utilising the double spike procedure. Mass dependent analysis enabled the Stable isotope composition of terrestrial materials to be investigated, revealing mass dependent fractionation between terrestrial basalts and andesite's. Utilising the double spike procedure also enabled the calculation of absolute nucleosynthetic anomalies for Ti within solar system materials. The absolute nucleosynthetic anomalies data revealed that CAI's contain two different compositions with one representing an exotic stellar source and the other representing the mainstream solar system composition.

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Dedication:

I would like to dedicate this work to my wife Ffion Bryn Jones for all her support and help over the course of the PhD. Her love, encouragement and friendship has enabled me to for fill my ambition of achieving my doctorate. A special feeling of gratitude must also be made to my parents for all their love and support over the years.

I also dedicate this dissertation to all the staff and students within the School of Earth, Atmospheric and Environmental Sciences who have been so helpful and constructive over my academic career. A special mention must also go to the staff and PhD students of the Open University who made me so welcome during all my visits to their campus.

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When I heard the learn'd astronomer,

When I heard the learn'd astronomer,

When the proofs, the figures, were ranged in columns before me,

When I was shown the charts and diagrams, to add, divide, and measure them,

When I sitting heard the astronomer where he lectured with much applause in the lecture-room,

How soon unaccountable I became tired and sick,

Till rising and gliding out I wander'd off by myself,

In the mystical moist night-air, and from time to time,

Look'd up in perfect silence at the stars.

Walt Whitman, 1892

'The Author'

The author graduated from the University of Manchester in 2008 with a Bachelor's degree with honours in Geology with Planetary Science. In the summer of 2008 the author began work as a geophysical engineer utilising seismic techniques within the private sector. In December of the same year the author changed roles to become a geotechnical engineer for a local authority within the Snowdonia National Park. In September 2010 the author re-joined the School of Earth, Atmospheric and Environmental Sciences within the University of Manchester to begin a Ph.D. studentship under the supervision of Prof Maria Schönbächler. In April 2014 the author began work as a geotechnical engineer again.

1. Chapter 1

1.1. Introduction

In the mid-18th century the great philosopher Immanuel Kant proposed that the solar system formed from the accretion of material from a chaotic distribution, which subsequently developed into a flattened disk and formed the Sun at its centre with the planets forming by secondary condensation in the disk (Kant, 1755). Later in 1796 Pierre-Simon Laplace published the seminal work 'the system of the world' in which for the first time the apparent variations in the orbits of planets were described to be self-correcting and that the solar system had arisen from a primitive rotating cloud (Laplace, 1796). Both pieces of work were revolutionary and mark the beginning of mankind's attempt to describe the formation of the solar system through natural processes neglecting the need for input from a divine source.

The greatest advancements in understanding the formation of the solar system and even universe didn't come from the observations of the macroscopic world but from investigating the atomic. In 1913, Frederick Soddy inferred the existence of radioactive isotopes from the study of decay chains, showing that elements could be chemically identical but have different masses (Soddy, 1913). Independently in 1913, J.J Thomson discovered that stable isotopes existed from his work on canal rays utilising neon at the University of Manchester (Thomson, 1913). Thomson's work was subsequently confirmed and advanced by his research assistant F. W Aston who went on to identify a further 212 naturally occurring isotopes. Today there are over 288 natural stable isotopes known to exist in the universe with a further 3000 unstable nuclei. Two independent studies by Burbidge et al. (1957) and Cameron (1957) established which nucleosynthetic processes formed the elements and nuclei found in the solar system. They showed that the solar system was made of material from several different nucleosynthetic sources. Clayton (1968) showed that different nucleosynthetic sources would generate a distinct isotopic fingerprint within the material formed enabling the identification of the stellar source.

The aim of this study is to analyse the isotope composition of titanium (Ti) within various solar system materials to a high precision in order to determine its nucleosynthetic sources and infer possible formation processes during the early solar system. This study will investigate the mass independent and mass dependent fractionation effects found within solar system material for Ti isotopes. In order to evaluate the isotopic ratios held within solar system

material I will first give an overview of the production processes of the elements; followed by the formation processes involved in the birth of the solar system. The overview will then detail the material to be investigated in this study followed by previous research carried out on isotopic ratios within solar system material for Ti and other elements.

1.2. Nucleosynthesis

Nucleosynthesis is the nuclear process responsible for the formation and evolution of baryonic matter in the universe. The process can be described by a nucleus being impacted by a particle to form a new nucleus and a new particle. This process can be given the notation X (a, b) Y where nucleus X is impacted by particle a, to form nucleus Y and particle b. In all such nuclear reactions, the total energy, momentum and angular momentum are conserved. Nucleosynthesis is an evolutionary process by which heavier elements are formed by the combination of lighter elements (Clayton, 2003). In order to give an overview of how nucleosynthesis has led to the formation of our solar system it is necessary to begin with the formation of the primordial elements hydrogen and helium.

The birth of the universe started with a big bang, which was determined from the observations of Cepheid variable stars in other galaxies by Edwin Hubble. He demonstrated that the more distant galaxies were moving with greater velocity than those in closer proximity, which suggested that the universe is expanding (Hubble, 1929). By utilising the current expansion rate of the universe we can extrapolate back to the time of the formation of the universe. This idea was reinforced by the discovery of the cosmic microwave background radiation (CMB) by Penzias and Wilson in 1965, which showed that the whole of space is filled with thermal radiation left over from the Big Bang (Penzias and Wilson, 1965). Current measurements of the CMB by the Wilkinson Microwave Anisotropy Probe (WMAP) determined the current density, composition and expansion rate of the universe in order to give an estimated age of 14.1 ± 1.0 billion years for the universe (Tegmark et al., 2004).

Immediately after the big bang (nanoseconds) the universe began expanding in a gas of fundamental particles consisting of quarks and antiquarks, leptons and antileptons, neutrinos and antineutrinos (Langanke and Wiescher, 2001). As expansion increased the temperature decreased to below 10¹⁴ K allowing the annihilation of quarks and antiquarks. Due to quarks slightly outnumbering antiquarks, the remaining quarks that weren't annihilated were able to form protons and neutrons. As the universe expanded further and the temperature continued to

fall below 10^{10} K the density of the universe became too low for neutrinos to continue interacting with matter (Phillips, 2013). At 100 s old the universe expanded and cooled sufficiently to enable neutrons to combine with protons to form light nuclei with an H composition of ~75% and He composition of ~25% (Clayton, 2003). This proportion was determined by the ratio of neutrons to protons that existed when neutrons and protons ceased to be continually transformed into one and another by the reactions:

$$v_e + n \leftrightarrow e^- + p$$
 and $\overline{v_e} + p \leftrightarrow e^+ + n$ (1.1)

Where v_e the neutrino interacts with *n*, the neutron, which forms an electron e^- plus a proton *p*. In the reverse reaction the antineutrino $\overline{v_e}$ interacts with the proton *p*, to form a positron e^+ and a neutron *n*. Eventually after 300,000 years the temperature dropped below 4000 K enabling stable atoms to form. Matter and radiation were now able to separate, making the universe transparent to electromagnetic radiation (Gamow, 1948). It is this radiation that has now cooled to a temperature of around 3 K that was first detected by Penzias and Wilson in 1965 (Penzias and Wilson, 1965).

1.2.1. Stellar formation

As discussed above in section 1.2 the remnants of the big bang left a universe consisting of around 75% of H and around 25% of He and a small amount of ⁷Li in an expanding space (Clayton, 2003; Phillips, 2013). The next evolutionary step occurred due to gravity acting as an attractive force causing contraction of this material (Phillips, 2013). The contraction and compression of the left over matter, led most importantly to the formation of galaxies and stars. The first stars started with essentially only H and He (Umeada and Nomoto, 2003). The contraction of material prior to star formation creates a pressure difference that opposes gravity. From equation 1.2 it can be deduced that the pressure increases towards the centre of the star to oppose gravity.

$$-\frac{d^2r}{dt^2} = g(r) + \frac{1}{\rho(r)}\frac{dP}{dr}$$
(1.2)

Where, $-\frac{d^2r}{dt^2}$ is the pressure gradient, g is gravity and ρ is the pressure. When the pressure gradient $\frac{d^2r}{dt^2} = 0$ for an element of matter at any point r from the centre of a spherical system will be in hydrostatic equilibrium when :

$$\frac{dP}{dr} = -\frac{Gm(r)\rho(r)}{r^2}$$
(1.3)

Where the pressure gradient, $\frac{dP}{dr}$ is equal to the gravitational constant, G multiplied by the mass *m* of the particle over the distance r^2 . By multiplying equation (1.3) by the volume of a sphere and integrating over all distances, we find that the average pressure $\langle P \rangle$ needed to support a system with gravitational energy E_{GR} and volume V is given by:

$$\langle P \rangle = -\frac{1}{3} \frac{E_{GR}}{V} \tag{1.4}$$

Equation 1.4 is called the viral theorem, which gives the average pressure needed to support a self-gravitating system. The approximate minimum condition for condensation is given by equation 1.5, where a star mass M containing N particles with average mass \overline{m} at a uniform temperature T will reach critical density at higher masses:

$$\rho_j = \frac{3}{4\pi M^2} \left[\frac{3kT}{2G\bar{m}} \right] \tag{1.5}$$

This equation is termed the Jeans mass and density and the critical density required is low and achieved more easily if the mass of the cloud is large. From consideration of the equation the condensation of a large gas cloud will most likely take place in several stages as the density rises, smaller parts of the cloud will contract independently (Phillips, 2013).

1.2.2. Stellar evolution

The life of a star is dependent upon its starting mass, and to a lesser extent its metallicity (Phillips, 2013). Astronomical observations allow us to study the formation, evolution and death of stars. Stellar evolution is summarized by the Hertzsprung-Russell diagram (Fig. 1.1), which shows the relationship between a stars luminosity and effective temperature. The HR diagram illustrates the wide diversity of stellar objects observed in the universe and also provides an evolutionary track for a star of a certain mass (Chiosi et al., 1992).





Stars with masses of less than 0.08 solar masses (M_{solar}) evolve into brown dwarfs where gravity is countered by the pressure of degenerate electrons. Proto-stars with masses >0.08 M_{solar} have core temperatures and pressures high enough for thermonuclear reactions to begin and hence further nucleosynthetic evolution (Phillips, 2013). These new stars enter the main sequence, where they will spend the majority of their lifetime (Fig. 1.1). A star's main sequence stage is driven by the competing forces of gravitational collapse and radiation pressure. Inward collapse of the star is countered by the radiation and gas pressure produced by thermonuclear reactions, such that the two opposing forces reach a hydrostatic equilibrium (Phillips, 2013).

The evolution of the star from its initial composition will generally follow a sequence of thermonuclear stages. Each stage, counter acts the gravitational contraction by releasing energy by the creation of a more tightly bound nuclei. Figure 1.2 illustrates the binding energy per nucleon for atomic nuclei with a broad maximum around ⁵⁶Fe, where the nuclei are most tightly bound.



Figure 1.2. Binding energy per nucleon for atomic nuclei demonstrating the broad maximum at ⁵⁶Fe <u>http://www.met.reading.ac.uk/pplato2/h-flap/phys9_1.html</u>.

The progression of nucleosynthesis up to Fe is dependent on the possible thermonuclear reaction rates available. In order for a nuclear reaction to occur the nuclei require a thermal energy component from the environment given by the maxwellian energy distribution and also penetrate the coulomb barrier of the nuclei resisting fusion (Phillips, 2013). Figure 1.3 illustrates the area at which point fusion is likely to occur termed the Gamow peak. Figure 1.3 also indicates that fusion dominantly takes place in a narrow energy range around E_0 (greatest probability of fusion).



Figure 1.3. Illustrates the energy window (probability) for the fusion of nuclei at a given energy. Adapted from Phillips, (2013)

One would expect nucleosynthesis to cease at the creation of nuclei near iron as they cannot release energy during nuclear processing. However, from the observations of the photosphere of the Sun we see that the Sun is composed of heavy nuclei beyond the iron peak indicating that secondary nuclear processes occur (Asplund et al., 2009; Burbidge et al., 1957; Cameron, 1957) (Fig. 1.4).





1.2.3. Nucleosynthesis in massive stars

In the following sections a brief review of stellar evolution and nucleosynthetic processes which produce the isotopic signatures found in solar system materials is given:

As discussed above the evolution of stars follow a path of contraction to increasing temperature and central density. As the Star loses energy through radiation and the formation of neutrinos it contracts. To counteract the contraction nuclear fusion firstly processes H into He, followed by He into C and O (Phillips, 2013). The following stages move through carbon, neon, oxygen and silicon burning until a core of Fe is produced and no further energy can be released. Most stages proceed convectively, as the energy produced cannot be transported by radiation alone and convective cycling dominates. The consequence of convection as the dominant heat transport method creates a process by which effective mixing takes place creating a chemically homogeneous shell (Phillips, 2013).

Fuel	Product	Secondary product	Т (10 ⁹ К)	Duration (yr)	Main Reaction
н	He	¹⁴ N	0.037	8.1x10 ⁶	4H→ ⁴ He (CNO cycle)
Не	O, C	¹⁸ O, ²² Ne	0.19	1.2×10^{6}	$3^4 \text{He} \rightarrow {}^{12}\text{C}$
С	Ne, Mg	Na	0.87	9.8x10 ²	$^{12}C + ^{12}C \rightarrow$
Ne	O, Mg	Al, P	1.6	0.6	$^{20}\text{Ne}\rightarrow^{16}\text{O+}^{4}\text{He}$
0	Si, S	Cl, Ar, K, Ca	2	1.3	¹⁶ 0+ ¹⁶ 0→
Si	Fe	Ti, V, Cr, Mn, Co, Ni	3.3	0.031	28 Si \rightarrow ²⁴ Mg + ⁴ He

Table 1.1 Burning stages, main and secondary products, typical burning temperatures and timescales for a 20 M_{solar} star.

(Truran Jr and Heger, 2003)

1.2.3.1. Hydrogen burning

The primary stage of any nuclear fusion process in stars is hydrogen burning, which processes hydrogen into helium by the proton-proton (pp) chain or carbon nitrogen oxygen (CNO) cycle (Burbidge et al., 1957; Phillips, 2013). The pp chain occurs in low mass stars or those of low metallicity (Phillips, 2013). The CNO cycle occurs in high mass stars or low mass stars with a greater metallicity which utilises the initial composition of carbon, nitrogen and oxygen as a catalyst for the addition of 4 ¹H into ⁴He (Table. 1).

1.2.3.2. Helium burning

Helium burning is an important process as it produces three important chemical elements, oxygen and carbon and neon. The carbon is produced mainly as ¹²C via the triple alpha process by the reaction ⁴He (α, γ) ⁸Be*(α, γ) ¹²C*(, 2 γ) ¹²C (Burbidge et al., 1957) (Table. 2). As helium becomes depleted and the concentration of carbon in the core becomes high enough helium will fuse with carbon to form oxygen via the ¹²C (α, γ) ¹⁶O. The production of oxygen is followed by the production of neon by the fusion of helium with oxygen via ¹⁶O(α, γ) ²⁰Ne. As helium becomes depleted in the central region of the star the temperature is high enough for the ²²Ne(α, n) ²⁵Mg reaction to occur, which is an important reaction that provides a source of neutrons for the s-process to occur and create elements up to atomic mass 90 (Phillips, 2013).

1.2.3.3. Carbon burning

Once the helium burning at the centre of the star ceases, the core composed mostly of carbon and oxygen contracts increasing the temperature to around 8.7×10^8 K. At this temperature carbon burning produces ²⁰Ne, ²³Na and ²³Mg via the reactions: ¹²C (¹²C, α) ²⁰Ne, ¹²C (¹²C, p) ²³Na, ¹²C (¹²C, n) ²³Mg respectively (Phillips, 2013). The s-process is able to

continue beyond the helium burning phase into the carbon burning phase as neutrons are released by the ${}^{12}C$ (${}^{12}C$, n) ${}^{23}Mg$ reaction.

1.2.3.4. Neon and oxygen burning

Neon burning begins when the temperature rises beyond 10^9 K creating an environment of high energy thermal photons that are capable of breaking up ²⁰Ne by a photodisintegration reaction of ²⁰Ne (γ , α) ¹⁶O. The alpha particles released through this reaction fuse with the undissociated ²⁰Ne to form ²⁴Mg via ²⁰Ne (α , γ) ²⁴Mg (Phillips, 2013).

As neon burning comes to an end the star's core will consist mainly of ¹⁶O and ²⁴Mg. Yet again the core of the star will contract and the temperature will rise, at the critical temperature of $2x10^9$ K the oxygen burning phase will begin processing two ¹⁶O into ²⁸Si and an α particle (Phillips, 2013).

1.2.3.5. Silicon burning

Silicon burning in the core will begin when the temperature reaches $3x10^9$ K, at which point the photodisintegration of ²⁸Si occurs. The destruction of ²⁸Si releases α , n and p enabling the creation of heavier nuclei of higher stability. During silicon burning photodisintegration competes against capture reactions where the capture of nuclei occurs quicker than the initial photodisintegration allowing the build-up of heavy nuclei.

In conclusion massive stars generate most of the elements during mainstream nucleosynthesis from oxygen through to iron from the initial hydrogen and helium which they are formed (Table. 1). Massive stars also create heavy elements between mass number 80-90 by the s-process. They are also sites that produce neutron rich isotopes such as barium, thorium and uranium by the r-process.

1.2.4. AGB, Supernova Ia and II core collapse

1.2.4.1. Asymptotic Giant Branch (AGB)

Around 97% of all stars that have main sequence lifetimes of less than 10 Gyr become AGB stars and experience thermal pulses due to helium flashes (Wallerstein et al., 1997). Burning in the AGB phase alternates between He and H shells, which are separated by a Heintershell, and surround an inert C-O rich core (Lugaro et al., 2004). The H-burning shell produces He that is deposited into the inactive He-intershell. This causes the temperature and density of the He-shell to increase, forcing rapid He-burning to occur for a short period. The He-intershell becomes convective and moves the products of nucleosynthesis to the interface between the H and He-shells. When the He-shell is ignited the rising temperatures cause the overlying shells to expand. Expansion of the H-shell causes it to cool and H-burning stops (Phillips, 2013). Decreasing temperatures also stop He-shell burning. The lack of energy production causes collapse until new H shell burning regions. This process may be repeated many times (10-100 cycles) and the star is now referred to as a thermally pulsing (TP) AGB star.

During the TP-AGB phase stars suffer further mass loss through stellar winds, providing suitable conditions for the formation of dust containing isotopic and elemental signatures that reflect the composition of the star at this point (Ferrarotti and Gail, 2006). Thermally Pulsing-AGB stars produce much of the ¹²C and most of the s-process isotopes in the Universe. The s-process is defined as; seed nuclei capturing a neutron to produce new nuclei. The neutron flux is so low that stable nuclei can exist for 10^4 - 10^5 years before capture of a further neutron. If however the nuclei are unstable, there may be sufficient time between neutron capture for β -decay to new nuclei. Subsequent neutron captures and β decays produce increasingly heavy isotopes until the heaviest stable isotope produced by the s-process is reached, ²⁰⁹Bi (Meyer and Zinner, 2006). The *s*-process happens in environments with neutron densities of typically 10^{6} - 10^{11} cm⁻³ (Lugaro et al., 2003). If the neutron capture time and β decay half-life are approximately the same then branching may occur (Abia et al., 2001). The s-process will follow both paths from this point, resulting in distinctive s-process isotopic signatures. For example, s-process production of ⁸⁶Kr is influenced by the branching point found at ⁸⁵Kr (Abia et al., 2001). As there are 10⁴ years between neutron captures in the sprocess, the environment in which it occurs must be stable for at least $\sim 10^6$ years. Also, as free neutrons are unstable particles that decay after ~15minutes, for the s-process to continue they must be continuously produced. The s-process is predicted to predominantly occur in or near the He-burning shells of TP-AGB stars (Burbidge et al., 1957). At this site the reaction ²²Ne $(\alpha, n)^{25}$ Mg occurs that releases abundant amounts of neutrons to fuel the creation of ⁴⁶Ti, ⁴⁷Ti, ⁴⁸Ti ⁴⁹Ti and even ⁵⁰Ti (Gallino et al., 1998).

1.2.4.2. Supernova Ia

Stars whose mass is $< 8 \text{ M}_{\circ}$ are not large enough to produce the temperatures and densities required for further element synthesis beyond oxygen (Meyer and Zinner, 2006). They eject so much material during the planetary nebula phase that their lives end as electron degenerate C-O white dwarfs (Hillebrandt and Niemeyer, 2000). In a binary system the C-O white dwarf may accrete enough mass to initiate explosive C burning at or near its core which

creates a thermonuclear disruption when it is at or near the Chandrasekhar mass limit (Livio, 2000). These violent events are termed Type Ia supernovae. Disintegration reactions break some of the nuclei down to fundamental alpha, proton and neutron particles. The temperature and pressures involved in Si burning allow equilibrium conditions to develop where nuclear reactions occur quickly between all nuclear species and light particles (Meyer and Zinner, 2006). Quasi statistical equilibrium (QSE) develops when all nuclear species heavier than C are in equilibrium under exchange of light particles (Meyer and Zinner, 2006). In such equilibria neutron rich iron group elements such as ⁵⁰Ti, ⁵⁴Cr, ⁵⁸Fe and ⁶⁴Ni isotopes increase in abundance (Meyer and Zinner, 2006). As an iron core has now developed in the star, further synthesis of elements does not occur by hydrostatic equilibrium. Shock heating of the Si-rich layer drives explosive Si burning. In the innermost regions where extreme densities exist, the heating is sufficient for the matter to achieve Nuclear Statistical Equilibrium (NSE). The expansion and cooling is sufficiently rapid to leave a large abundance of free alpha particles. This expansion is thus known as the alpha rich freeze out from NSE, some reassembly of the free alpha does occur in the late stages of the freeze-out, which creates abundant ⁴⁴Ti (Meyer and Zinner, 2006). In the outer layers of the Si shell, the matter is less heated from the passing of the shock. At this site nuclear burning does not achieve full NSE and only achieves QSE, and is the principal site for production of the short lived radioisotope ⁵³Mn (Meyer et al., 1996). In the oxygen rich layers explosive burning occurs at even lower temperatures than explosive Si burning. These regions can develop significant production of isotopes such as ⁴⁴Ti and ⁴⁸Ti (Meyer and Zinner, 2006).

1.2.4.3. Supernova Type II

Massive stars ($M_0>8$) can end their lives by a second type of explosion, the gravitational in which part of the star falls down and transfers energy to the remaining layers. Filippenko (1997) classifies the supernovae as Type II, Ib, Ic based on their light curves. Since no fuel is available for the Fe core to burn, a combination of disintegrations and electron capture initiates the sudden collapse of the core. The inner part of the core collapses subsonically, and as it reaches nuclear matter density, the pressure rises dramatically due to nucleon-nucleon interactions and causes the collapse to halt and the core to "bounce" (Meyer and Zinner, 2006). The outer part of the collapsing core, on the other hand, falls in supersonically; thus it does not receive the signal from the inner core to cease collapsing and it crashes onto the inner core. This impact generates a shock, which moves through the star expelling all the matter into the

Inter Stellar Medium (ISM). The remnant star is an extremely dense proto-neutron star at temperatures of 10×10^9 K.

Type II supernovae produce nuclei from oxygen to calcium and iron peak nuclei. Models investigating charged particle nucleosynthesis in massive stars have shown that oxygen through to titanium are overproduced relative to iron, producing between 30%-50% of these elements in the galaxy ((Nomoto et al., 1997; Thielemann et al., 1996; Woosley and Weaver, 1995).

1.3. Solar system formation

The solar system formed from a solar nebula over 4.568 Ga ago (Bouvier and Wadhwa, 2010). As discussed in section 1.2.1 stars form from the gravitational collapse of a molecular cloud core. From the collapse of the molecular cloud all the material will not collapse to form the star allowing the mixing of gas and dust in a disk around the protostar (Boss, 2007). In order to constrain the processes which occur during collapse and mixing we can use astronomical observations of young stellar objects to infer formation and structure mechanisms (Boss, 2007).

Visible wavelength astronomical observations of interstellar clouds are retarded by interactions of light with gas and dust. To investigate these environments IR wavelengths are utilised, as they do not interact with the gas and dust making the environment visible to us (Boss, 2007). The IR observations reveal molecular clouds that are composed mainly of molecular hydrogen, helium and carbon monoxide (Boss, 2007). Precollapse cloud cores composed of molecular gas have temperature ranges between 7-15 K and gas densities around 10^3 - 10^5 mol cm⁻³ (Boss, 2007). The density profile of the pre collapse molecular cloud resembles a gaussian distribution, with flat densities profiles near the centre declining to low densities towards the outer edges of the cloud (Boss, 2007).

Dense molecular clouds initially resist collapse due to gravity by a combination of effects of turbulent motions, magnetic fields, gas pressures and centrifugal forces (Boss, 2007). The turbulent motions perish over timescales comparable to the free fall time of the cloud leaving magnetic fields as the main obstacle to the collapse of the cloud (Boss, 2007). The magnetic field strength of molecular clouds can range between 10 and 1000 μ G (Crutcher, 1999). The magnetic field within the molecular cloud is attached to the charged particles. However the motion of neutral gas molecules past charged particles within the molecular cloud

creates a process by which the magnetic fields diminish allowing a rapid contraction of the cloud (Boss, 2007). This effect is termed ambipolar diffusion and inferred to be the primary process by which regions of low mass stars form (Shu et al., 1987).

1.4. Classification of Meteorites

Meteorites are remnants of planetesimals, planets and other bodies within the solar system that have fallen to Earth. Meteorites preserve information of the material and processes that created them. Below is a brief outline of the characteristics of different meteorite groups used within this study.

Meteorites are named based on the location in which they are found on Earth such as the Murchison meteorite which fell in Murchison, Australia. An important consideration in classifying meteorites is whether they are finds or falls. Falls will have a recorded entry event associated with their fall and consequently would generally have had less time or a well-defined time span to interact with the terrestrial environment compared to a meteorite, whose fall date is unknown.

Meteorites display a wide range of characteristics and can be separated into divisions of; chondrites, primitive achondrites and achondrites based on the degree of planetary differentiation experienced (Fig. 1.5). The chondrites are the least differentiated of all meteorites and are thought to be examples of the initial material that formed the solar system (Weisberg et al., 2005). The achondrites are examples of highly differentiated planetary and asteroidal material (Weisberg et al., 2005). The achondrites comprise an array of different types of meteorites from metal poor stony meteorites, stony irons and irons. The primitive achondrites are meteorites which display characteristics of differentiation but still retain a chemical similarity to their chondritic predecessors.

Meteorites are also subdivided into groups, where a group is defined as having a minimum of five unpaired chondrites of similar petrology, whole rock chemistry and O isotopic characteristics (Weisberg et al., 2005). Groups of meteorites within the carbonaceous chondrites are given C as the first initial and the second initial denotes the type specimen for that group, such as CI describing the Ivuna like group (Fig. 1.5). Two or more groups which display similar characteristics and properties may also be denoted as a clan such as the CM-CO clan.



Figure 1.5. Diagram demonstrating the systematics of meteorite classification scheme showing the major class and groups. Adapted from (Weisberg et al., 2005)

1.4.1. Chondritic Meteorites

Chondritic meteorites formed as conglomerates of components from the solar nebula with each component recording their own diverse nebular histories. Examples of components within chondritic meteorites are Calcium Aluminium rich Inclusions (CAIs) and chondrules which occur in varying amounts with different chondritic meteorites. Therefore the chondrites represent the result of a sequence of complex events that occurred at the birth of the solar system (Weisberg et al., 2005). In addition to early solar system components chondrites also host interstellar grains formed by stellar outflows and supernova which hence predate the formation of the solar system (Ott, 2001).

However, most chondrites undergo varying degrees of secondary processing either after formation of individual components or after parent body formation, which complicates the interpretation of initial formation (Weisberg et al., 2005). The classification of secondary and tertiary properties found within chondrites is based on the work of Van Schmus and Wood. (1967) and is displayed in Table 1.2. Chondrites are allocated a number according to petrologic type with 3.0 representing the most pristine unaltered samples. Numbers from 3.1 to 6 indicate an increasing degree of recrystallization due to thermal metamorphism; which is most commonly associated to have taken place on larger parent bodies such as asteroids, within a few tens of millions of years after accretion (McSween et al., 1988). It is manifested by increasing degrees of chemical and textural equilibration of primary components. The highest degree of metamorphism recorded by rocks that can still be properly called chondrites is at temperatures below the appearance of partial melts defined by the Fe-Ni-S metal sulphide system so that peak temperature is below 950 °C. Overpressures were low and of little significance as most parent bodies are less than 100 km in diameter. Numbers 2.1 to 1 represent increasing degree of hydrous alteration which results in the production of hydrous phases from essentially anhydrous primary precursor assemblages, as well as oxidation effects (Zolensky and McSween Jr, 1988). Aqueous alteration most likely occurred on parent bodies after accretion, when fluids were mobilized in low temp heating events. The source of the water is most likely ice that accreted in the original parent bodies (Zolensky and McSween Jr, 1988). Aqueous alteration has also been suggested to have occurred as a nebular process beyond the SNOW line through the interaction of low temperature nebular gases with solid phases prior to accretion (Bischoff, 1998). The main heat source for both thermal metamorphism and aqueous alteration is commonly attributed to the short-lived radioisotope ²⁶Al (Bischoff, 1998).

Another important secondary process affecting chondrites is shock metamorphism. Chondrites are given values from S1 (unshocked) to S6 (very strongly shocked) to indicate the shock pressures experienced (Weisberg et al., 2005). Shock metamorphism is the effect of impact processing recorded in unbrecciated as well as brecciated chondrite which manifests itself as the shock metamorphism of the constituent minerals and occurrence of impact melts (Stöffler et al., 1991). Shock pressures up to about 90 GPa are recorded in chondrites (S6) (Stöffler et al., 1991). Many chondrites have suffered impact processing (Bunch and Rajan, 1988). Many chondrites are breccias, attesting to the common impact processing that took place in the protoplanetary disk during solar system formation.
Table 1.2. The variability of secondary alteration for different carbonaceous chondrite classes. From (Weisberg et al., 2005).

	Increase in degree of aqueous alteration		Pristine]	Increase in degree of thermal metamorphism		
	1	2	3	4	5	6	
CI							
СМ							
CR							
СН							
СВ							
CV							
CO							
СК							
Н							
L							
LL							
EH							
EL							
R							
K							

As discussed earlier in section 1.4 the chondrites consist of several primitive components, that formed independently in the proto planetary disk (Hezel et al., 2008). One of the most important earliest solar system components are the Calcium-Aluminium rich inclusions (CAIs), which are submilimeter to centimetre sized refractory rich inclusions (Hezel et al., 2008; Weisberg et al., 2005). The CAIs are thought to have formed by high temperature

processes of condensation and/or evaporation in the proto planetary disk (Ebel, 2006). Chondrites also contain chondrules, which are spherical components generally composed of mafic minerals which are less refractory than the CAIs (Scott et al., 2005; Shu, 2001). Encompassing the chondrules and inclusions in chondrites is the fine-grained matrix (Weisberg et al., 2005).Within the matrix chondrites contain small (µm scale) presolar grains of diamond, silicon carbide and graphite, which pre date the birth of the solar system and display extreme isotopic compositions consistent with various stellar nucleosynthesis processes (Amari et al., 2000a; Clayton and Nittler, 2004; Huss, 2003; Jose and Hernanz, 2007; Ott, 2001; Zinner, 1998; Zinner et al., 2005a; Zinner et al., 2005b). Figure 1.6 displays the average petrological characteristics of the major chondrite groups along with the names of samples of those chondrites analysed for Ti isotope within this body of work.



Figure 1.6. The content of important components within chondrites. CAI – AOA (vol%) are the modal abundances of Ca, Al-rich Inclusions (CAIs) and Amoeboid Olivine Aggregate (AOA) refractory inclusions. Figure is adapted from Hezel et al. (2008) and Weisberg et al. (2005)

1.4.2. Carbonaceous chondrites

The following section provides a detailed description of the major meteorite groups which have been utilised within this study. The study will mainly focus on the analysis of Ti isotopes within whole rock samples of solar system materials, therefore necessitating the understanding of the components within the meteorites utilised in the study.

The carbonaceous chondrites contain pristine examples of early solar system components such as CAIs (Hezel et al., 2008) (Fig. 1.6). They also display a range of chondrule abundances (CH>CR>CV>CM>CI) (Hezel et al., 2008) (Fig.1.6). This section aims to give a general overview of the characteristics of the different carbonaceous chondrite groups and also a brief overview of the samples utilised in this study.

1.4.2.1. CI (Ivuna type)

In spite of being altered, brecciated and lacking in early solar system components such as CAIs, chondrules and metal (Fig. 1.6), the CI chondrites are often regarded as the most primitive solar system material as their bulk chemical composition is close to that of the solar photosphere. The CI chondrite group mostly consists of matrix material (Hezel et al., 2008). They have undergone aqueous alteration and are designated petrologic type 1 due to the heavily hydrated minerals phases (Bischoff, 1998). Typical CI chondrites consist of fine grained, phyllosilicate rich matrix with minor magnetite, sulphides, sulfates and carbonates (Endress and Bischoff, 1996; Endress et al., 1996). Despite being hydrothermally altered, brecciated and having their primary mineral assemblages erased it is peculiar that the CI chondrites still display primitive chemical compositions.

1.4.2.2. CM (Mighei like)

The CM group of chondrites are the most common group of carbonaceous chondrites found on Earth (Weisberg et al., 2005). CM like materials have also been found within other chondrite groups and achondrites as clasts (Zolensky et al., 1996), indicating that the CM meteorites were widely dispersed in the early solar system. The CM group on average consist of 5 vol % of CAIs and around 20 vol% of chondrules (Fig. 1.6). Most CM meteorites are found to be of petrological type 2 (Table. 1.2), however the degree of aqueous alteration varies significantly (Mcsween Jr, 1979).

1.4.2.3. CO (Ornans like)

The CO group of chondrites contain around 34 vol % matrix (Fig. 1.6), and range between petrolgical type 3.0 to 3.7 (Scott and Jones, 1990). Rubin (1998) showed that when comparing the pristine 3.0 examples with the metamorphosed CO chondrites, the secondary minerals produced via metamorphism such as ilmenite and sodalite were absent.

1.4.2.4. CV (Vigarano like)

The CV chondrite group contain a high abundance of large chondrules (~1 mm) and CAIs at around 45 and 10 vol %, respectively (Fig. 1.6). Petrologically the CV chondrites are classed as mostly type 3; however the CV group do display a diverse range of oxidation states. The subgroups are divided based on the petrological characteristics between CV_{red} , $CV_{ox A}$ and $CV_{ox B}$ from the work of Weisberg et al. (1997). The matrix/chondrule ratios increase in the order CV_{red} (0.5-0.6)- $CV_{ox A}$ (0.6-0.7- $CV_{ox B}$ (0.7-1.2), with a correlated decrease in order for the metal/magnetite ratios (Weisberg et al., 2005). Recent analysis has shown significant mineralogical differences between the CV subgroups imparted onto them via alteration process ((Krot et al., 1998a; Pravdivtseva et al., 2003).

1.4.2.5. CK (Karoonda like)

The CK group of chondrites are highly oxidised, which is demonstrated by several characteristics: the high fayalite content of their olivine (Fa₂₉₋₃₃), near complete absence of Fe,Ni metal, high Ni content in sulphides and abundant magnetite with exsolution lamellae of ilmenite and spinel (Weisberg et al., 2005). Most CK chondrites are of high petrologic type (4-6). The lowest petrological type (<4) display similar petrographic and chemical characteristics to the CV3 oxidised chondrites (Greenwood et al., 2010) which has led observers to support the clan relationship between these two groups.

1.4.2.6. CR (Renazzo like)

The majority of CR chondrites are petrological type 2 and are characterized by large (mm sized) Fe, Ni-metal rich, porphyritic chondrules (Weisberg et al., 1993; Weisberg et al., 1995). The abundance of CAIs is relatively low around 0.5 vol % (Fig. 1.6). The mineralogy, petrology, and chemistry of the CR chondrites are described in detail in several papers ((Bischoff, 1998; Bischoff et al., 1993; Kallemeyn et al., 1994; Krot et al., 2002; Wasson and Kallemeyn, 1988; Weisberg et al., 1993; Weisberg et al., 1995).

1.4.2.7. CH (ALH 85085 like)

The unusual composition of CH chondrites with chondrule abundances of around 70 vol % (Fig. 1.6), high abundances of metal (~20 vol %) and small amounts of matrix (~5vol %) has led to the interpretation that the CH group are meteorites that formed from the collision of asteroids and do not represent materials formed in the solar nebula (Wasson and Kallemeyn, 1990).

1.4.2.8. CB (Bencubbin like)

The CB group chondrites display characteristics which stand out from the other carbonaceous chondrite groups (Weisberg et al., 2001); these include a very high metal abundance of between 60-80 vol % (Fig. 1.6), almost no discernible CAIs or matrix (Fig. 1.6) and a large depletion in moderately volatile lithophile elements. The meteorites of the CB group have been interpreted to be highly primitive nebular materials containing metal that condensed directly from the solar nebula ((Krot et al., 2005; Krot and Bizzarro, 2009; Newsom and Drake, 1979; Weisberg et al., 2001).

1.4.3. Ordinary chondrites

The ordinary chondrites are the most common type of meteorite found on Earth, constituting over 85% of meteorite collections (Weisberg et al., 2005). The groups within the ordinary chondrites are named H, L and LL which are defined by the abundance of Fe, and characterised by the ratio of metallic Fe to oxidised Fe (Fe⁰/FeO). They are characterized by a high abundance of chondrules which range from 60-80 vol % (Fig. 1.6) and are made up of various textures and mineral compositions (Weisberg et al., 2005). The O isotopic compositions of ordinary chondrites plot above the terrestrial fractionation line, which contrast sharply with carbonaceous chondrites (Fig. 1.7) (Clayton, 1993; Weisberg et al., 2005). Ordinary chondrites span a large petrologic range from 3-6. Of the samples that are most pristine, some display evidence of aqueous alteration ((Sears et al., 1982; Sears et al., 1980).



Figure 1.7.Three isotope plot of O isotopic compositions of different meteorite classes. Data compiled from Clayton et al, (1976), Clayton, (1993) and Clayton and Mayeda (1996, 1999)

1.4.4. Enstatite chondrites

The mineralogy and mineral chemistry of enstatite chondrites indicate that they formed under highly reducing nebular conditions (Keil, 1968). The enstatite chondrites plot on the terrestrial fractionation line close to the composition of the Earth and the Moon (Fig. 1.7) (Clayton, 1993). The enstatite chondrites are separated into EH (High Fe) and EL (Low Fe) groups where the EH chondrites are more reduced than the EL chondrites (Keil, 1968). The EH chondrites range in petrologic type from 3-5 while the EL range from 3-6 (Weisberg et al., 2005).

1.4.5. R (Rumuruti like) chondrites

Initial characterization of the first R chondrite find suggested a closer relationship to ordinary chondrites than carbonaceous (Binns and Pooley, 1979). The O isotope characteristics are similar to the ordinary chondrite class; however the three isotope O isotope composition plots above the ordinary chondrites, leading to the R chondrites being a separate meteorite class (Fig 1.7). The R chondrites are olivine rich rocks (65-78 vol %,(Bischoff et al., 2011)). R-chondrites contain around 40 vol % of chondrules, which is significantly lower than in ordinary chondrites (Fig 1.6). The refractory lithophile element abundances of R chondrites are closer

to the ordinary chondrites but display O isotope compositions similar to the carbonaceous chondrites (Fig 1.7) (Weisberg et al., 2005).

1.4.6. Ungrouped chondrites

The final undifferentiated chondrite group is the K (Kakangari) chondrites, which do not display the same properties as the carbonaceous, ordinary and enstatite classes (Weisberg et al., 1996).

1.4.7. Primitive achondrites

The primitive achondrites represent partial melts or melt residues from local heating events on planetary bodies during early stages of differentiation or possibly local impact events (Weisberg et al., 2005).

1.4.7.1. Ureilites

The principal group of ureilites are understood to be coarse grained highly equilibrated, ultramafic achondrites (Weisberg et al., 2005). However, their O isotope composition does not follow a mass dependent fractionation trend typical of achondrite bodies; instead they plot along the carbonaceous chondrite line, which has led to the inferred relationship with CV chondrites (Fig 1.7)(Clayton and Mayeda, 1988). The principal constituents of ureilites are olivine and low-Ca pyroxene with interstitial carbon in the form of graphite and microdiamonds along with metal, sulphides and minor silicates (Weisberg et al., 2005). Goodrich et al. (2013) investigated chromium valences in olivine in order to determine the oxidation conditions under which ureilites formed. He showed that the chromium valences observed were due to parent body magmatism conditions and not inherent from the nebular precursor assemblages.

1.4.8. Achondrites

The achondrites are differentiated meteorites which include meteorites from asteroids and planetary bodies such as the Mars and the Moon. The achondrites contain metal poor stony meteorites, stony irons and irons (Weisberg et al., 2005). Among the achondrites are the howardites, eucrites and diogenites (HED) which are polymict breccias, basalts and orthopyroxene cumulates respectively (Weisberg et al., 2005). The howardites, eucrites and diogintis are thought to be impact ejecta off the asteroid Vesta (Binzel and Xu, 1993). The HED meteorites display similar whole rock O isotopic compositions (Fig. 1.7) (Clayton et al., 1991). Mesosiderites are also breccias with an approximately equal proportion of silicates and Fe, Ni-metal plus troilite making up its composition. Achondrites composed of olivine and metal are termed pallasites which are subdivided into four different kinds depending on metal composition and O-isotopic composition. The iron meteorites are famed for displaying Widmanstätten structures. The iron meteorites comprise of 13 different groups with 10 of the groups displaying unique geochemical trends due to fractional crystallisation.

1.5. Isotopic anomalies

Previous sections discussed that the solar system was created from a variety of stellar sources (Burbidge et al., 1957) and its material had experienced a variety of chemical and physical processes during its formation. In order to gain an understanding of the sources and processes which created our solar system, analytical techniques are utilised to study the isotopic ratios within solar system materials. Nucleosynthetic compounds (Stellar source) as well as thermodynamic and kinetic fractionation processes (solar system formation processes) can induce changes in the isotopic ratios of two isotopes of the same element. The subtle variations observed in the isotopic ratios can be mass dependent in which the isotopic abundances deviate with regard to the difference between the masses of the two isotopes or secondly; mass independently where the variations do not scale in proportion with the mass difference between the two isotopes. The next section aims to provide an overview of previous studies conducted on Ti in order to understand mass dependent and mass independent fractionation processes within solar system materials and components.

1.5.1. Ti isotopes

Titanium has five stable isotopes (relative abundance) ⁴⁶Ti (8.25%), ⁴⁷Ti (7.44%), ⁴⁸Ti (73.72%), ⁴⁹Ti (5.41%) and ⁵⁰Ti (5.18%). The earliest studies conducted into Ti isotope compositions of solar system materials relative to terrestrial standards utilised thermal ionization mass spectrometry (TIMS). Heydegger et al. (1979) measured utilising Ti⁺ beams and inferred an excess in ⁵⁰Ti in Allende CAIs from a statistical analysis of several inclusions. Precision and reproducibility were improved in later studies, which used TiO⁺ beams with corrections for oxygen isotope contributions (Niederer et al., 1980a). Ca-Al-rich inclusions (CAIs) from the Allende and Leoville meteorite were found to exhibit extensive variations for Ti isotope abundances, when normalising to ⁴⁶Ti/⁴⁸Ti (Niederer et al., 1980a), while bulk meteorites, terrestrial and lunar samples yielded identical results within analytical uncertainties. Niederer et al. (1980a) inferred from the distinct correlation between the neutron rich isotopes of Ca and Ti and the absence of substantial effects at ⁴⁶Ca in the FUN samples

EK-1-4-1 and C-1, that the effects reflect quasi-statistical equilibrium (QSE) and nuclear statistical equilibrium (NSE) nucleosynthesis in the outer layers of a supernova core. Niemeyer and Lugmair (1981) analysed several fine and coarse grained normal Allende inclusions which showed resolvable excesses in ${}^{50/46}$ Ti_{48/46} ranging from +7 ε to +28 ε , where ${}^{50/46}$ Ti is the isotope ratio being calculated and Ti_{48/46} is the isotope ratio being utilised to correct for instrumental mass fractionation and ε is the deviation from the terrestrial standard in parts per ten thousand. Niemeyer and Lugmair (1981) inferred that the observed excesses in ^{50/46}Ti_{48/46} were due to relative enrichment of isotopes synthesized during hydrostatic burning in or near the core of a massive star. In 1984, Niemeyer and Lugmair (1984a) set out to establish if the isotopic anomalies reported for Allende inclusions could be found in other meteorite classes as well. Measurements of chondrules from ordinary chondrites revealed no enrichment in ^{50/46}Ti_{48/46} while samples from C1 and C2 meteorites showed smaller excesses in ^{50/46}Ti_{48/46} compared to Allende inclusions. Niemeyer and Lugmair (1984a) inferred that at least 4 isotopic components of Ti are required to account for the isotopic variations within Allende inclusions. Niemeyer and Lugmair (1984b) again inferred neutron rich hydrostatic burning within a massive star as the source of the ${}^{50/46}$ Ti_{48/46} anomalies, while an *s*-process mechanism was proposed as a viable source for the anomalies on the neutron poor Ti isotopes (⁴⁶Ti, ⁴⁷Ti, ⁴⁸Ti and ⁴⁹Ti). The authors also argue that the Ti isotope anomalies are linked to the diversity of nucleosynthetic sources found in the ISM rather than a late stage supernova injection model. Niederer et al. (1985) published work on the absolute isotopic abundance of Ti, where the normalization for fractionation using ${}^{46}\text{Ti}/{}^{48}\text{Ti}$ (reporting data as ${}^{x/46}\text{Ti}_{46/48}$) was investigated as well as utilising a double-spike tracer consisting of ⁴⁶Ti and ⁵⁰Ti. The absolute Ti compositions of FUN CAIs (Fig. 1.8) show significant mass dependent isotope fractionation effects corresponding to an enhancement in the heavier isotopes relative to the lighter isotopes as compared to Ti in a TiO₂ standard and in chondrites (Fig. 1.9) (Niederer et al., 1985).



Figure 1.8. Absolute nucleosynthetic Ti isotope compositions for FUN inclusions. From Niederer et al. (1985)



Figure 1.9. Absolute nucleosynthetic Ti isotope compositions for whole rock meteorites. From Niederer et al. (1985)

Ireland et al. (1985) analysed Ti isotopic compositions of hibonites from the Murchison (CM2) carbonaceous chondrite. Hibonites grains were shown to vary between -42 and 8 permil for ^{50/49}Ti_{47/49} when measured by Secondary Ion Mass Spectrometry (SIMS). The magnitude of the variations seems explicable only in terms of nucleosynthetic processes, which produced extremely variable Ti isotopic abundances in the hibonite source material (Ireland et al., 1985). Ireland et al. (1985) advocated a supernova source as the cause of the large variations observed as proposed by the cosmic chemical memory theory set forward by Clayton (1978) and further supported by Niemeyer and Lugmair (1984b). The cosmic chemical memory theory argues that the processes at work in the early solar system were not hot enough to entirely vaporise all solids. The cosmic chemical memory proposes that solar system refractory components retain the isotopic signature of the nucleosynthetic source which created them. In 1988 Niemeyer (Niemeyer, 1988a, b) set out to analyse the distribution of Ti isotope variations among the different components of meteorites such as matrix, CAIs and chondrules. They argued that from the correlation with other Fe-peak elements of Ca, Cr and Ni and evaluation of nucleosynthetic models that the constituents formed from precursor assemblages in which some chemical memories remained intact. The differences observed were due to fractionations among the carrier phase of the different isotopic components. The larger Ti isotope anomalies in CAIs compared to the matrix and chondrules were ascribed to a primarily open system during processing of the CAI precursors (Niemeyer, 1988a; b). The diversity of Ti isotope compositions in chondrules is thought to be an inherited feature from their precursor assemblage of dust (Niemeyer, 1988a; b).

In recent years with the development of ever more sophisticated instruments such as the multiple-collector inductively coupled plasma-mass spectrometers (MC-ICPMS) isotope studies have been able to produce ever more accurate and reproducible results. Jarvis and Gray (2001) showed that the ionization yield of Ti on an MC-ICPMS is over 90%. The effects of Al, W and P on the mass fractionation during analysis were investigated and shown to be negligible (Zhu et al., 2002) due to effective anion exchange chemistry techniques that removed these elements (Makishima et al., 2002). Zhu et al. (2002) presented high precision mass dependent measurements of Ti isotope ratios in natural materials using MC-ICPMS. By utilising sample standard bracketing techniques, effects due to concentration could be effectively cancelled out. Leya et al. (2007) presented a new method for Ti isotope analysis. The authors were able to develop a precise and reproducible way of measuring isotopes by utilising anion exchange chemistry techniques adapted from Schönbächler et al. (2003). Terrestrial rock samples were

analysed using a Nu Plasma large geometry high resolution MC-ICPMS (Nu 1700). Instrumental mass fractionation was internally corrected using ⁴⁹Ti/⁴⁷Ti resulting in a long-term reproducibility of 0.28 ε , 0.34 ε and 0.28 ε for ^{50/47}Ti_{49/47}, ^{48/47}Ti_{49/47} and ^{46/47}Ti_{49/47}, respectively for the terrestrial standard solutions. Leya et al. (2007) calculated the atomic weight of Ti to be 47.877, which differs from the published value of 47.867 found by Shima and Torigoye (1993). Subsequently, Leya et al. (2008) investigated Ti isotopes within a wide range of solar system materials and reported that the Ti isotope composition of carbonaceous chondrites differ from those of ordinary chondrites, eucrites, mesosiderites, and ureilites (Fig. 1.10). Additionally, the study revealed that the Earth, Moon and Mars were indistinguishable from each other in their Ti isotope compositions within uncertainties.



Figure 1.10 Titanium isotope compositions of carbonaceous chondrites, achondrites and ordinary chondrites. From Leya et al. (2008)

Leya et al. (2008) inferred that the region of protostellar disk from which the Earth, Moon, Mars and the parent bodies of ordinary chondrites, eucrites, ureilites and mesosiderites formed displayed a homogenous Ti isotope composition. This contrasted, with the finding of a different Ti isotopic composition for carbonaceous chondrites. The latter originate from parent bodies that likely formed beyond 2.7 AU consistent with their lack of depletion in volatile elements and late formation. Trinquier et al. (2009) developed a purification procedure consisting of a three-step ion exchange chromatography procedure for the separation of Ti from matrix elements. By utilising a Thermo Fischer Neptune MC-ICPMS, Trinquier et al. (2009) improved the analytical uncertainties and this allowed them to show that Ti isotope variations exist even among the inner solar system solids, planets and asteroids. A suite of materials were analysed including CAIs, carbonaceous, enstatite, and ordinary chondrites as well as achondrites, lunar, martian and terrestrial samples. All samples apart from enstatite chondrites, achondrites and lunar meteorites showed correlated variations in $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{46/47}$ Ti_{49/47} (Fig 1.11).



Figure 1.11. The Ti isotope composition of solar system material. From Trinquier et al. (2009)

Trinquier et al. (2009) inferred that the $\varepsilon^{50/47}$ Ti_{49/47} - $\varepsilon^{46/47}$ Ti_{49/47} correlation is due to thermal processing events which resulted in preferential loss by sublimation of thermally unstable presolar silicates with ⁴⁶Ti and ⁵⁰Ti excesses. This implies that nucleosynthetic anomalies in meteorites may reflect the degree of thermal processing experienced by their precursor material and not initial disk heterogeneity (Trinquier et al., 2009). In the same year Leya et al. (2009) published a study on CAIs in Allende and Efremovka (CV3) respectively. The study found excesses in ⁵⁰Ti correlated with nucleosynthetic anomalies found in ⁶²Ni and ⁹⁶Zr indicating an origin from a neutron rich stellar source. Mass balance considerations suggest that bulk Allende Ti possibly consists of a mixture of at least two Ti components, anomalous Ti located in CAIs and a normal component possibly for matrix and chondrules. This argues for a heterogeneous distribution of Ti isotopes in the solar system (Leya et al., 2009). Zhang et al. (2011) developed new separation technique utilising Todga and AG1-X8 resins to remove isobaric interfering elements from Ti. The authors examined established ratios of ^{46/44}Ca, ^{48/44}Ca, ^{50/51}V and ^{50/53}Cr from literature and adapted the values to obtain a better correction of isobaric interferences on ⁴⁶Ti, ⁴⁸Ti and ⁵⁰Ti. Measurements conducted on geostandards and carbonaceous chondrites correlate well with those from Trinquier et al. (2009).

1.5.2. Other important isotope systems

Below I shall outline the previous isotope analysis work carried out on elements complimentary to Ti on solar system materials. It is important to give an overview of studies conducted on complimentary elements to Ti in order to be able to evaluate similarities and difference in findings from those elements studied.

1.5.3. Zirconium

Zirconium is an important complimentary element to Ti as it is also a refractory lithophile with similar condensation temperature. Zirconium also has five stable isotopes (relative abundance) ⁹⁰Zr (51.45%), ⁹¹Zr (11.22%), ⁹²Zr (17.15%), ⁹⁴Zr (17.38%) and ⁹⁶Zr (2.80%). Within this study of Ti, samples previously analysed for Zr are directly compared and contrasted. The Zr isotopic composition within solar system materials has been a focus of study in cosmochemistry for some time (Minster and Allègre, 1982). Early investigations concentrated on the detection of the products of short-lived radionuclide ${}^{92}Nb$ (t_{1/2}=3.3x10⁷ ± 0.5 Ma (Makino and Honda, (1977)) which decays to 92 Zr (e.g. (Münker et al., 2001; Sanloup et al., 2000; Schönbächler et al., 2002)). As precision and sensitivity within MC-ICPMS increased, studies were broadened to include the application of Zr to nucleosynthetic anomalies (e.g. (Akram et al., 2013; Akram et al., 2011a; Schönbächler et al., 2003; Schönbächler et al., 2005; Schönbächler et al., 2004). The majority of Zr isotopes are produced by the s-process but ⁹⁶Zr can also be produced by the r-process ((Nicolussi et al., 1998)). Schönbächler et al. (2003) found small Zr isotope anomalies in bulk chondrite analyses at the level of 0.6 ε , 0.4 ε and 1.2 ε for $\varepsilon^{91/90}$ Zr_{94/90}, $\varepsilon^{92/90}$ Zr_{94/90} and $\varepsilon^{96/90}$ Zr_{94/90}, respectively. However, recent studies ((Akram et al., 2013; Akram et al., 2011a, b)) found larger anomalies in $\varepsilon^{96/90}$ Zr_{94/90} with greater analytical precision obtained. Schönbächler et al. (2005) demonstrated that large anomalies are present in Zr isotopes within chondritic components by leaching experiments. Schönbächler et al (2005) found ranges of anomalies for $\varepsilon^{91/90}$ Zr_{94/90}, $\varepsilon^{92/90}$ Zr_{94/90} and $\varepsilon^{96/90}$ Zr_{94/90}, of 2.6 ± 0.6 ε , 1 ± 0.4 ε and 48.6 ± 1.4 ε , respectively from the leaches of carbonaceous chondrites Allende and Murchison. Greater anomalies were found during the complete dissolution of the residue by Parr Bomb of the CI carbonaceous chondrite Orgueil which yield deficits of -22 ± 1.2 ε , - 8.8 ± 0.5 ε and -377.5 ± 3.3 ε for $\varepsilon^{91/90}$ Zr_{94/90}, $\varepsilon^{92/90}$ Zr_{94/90} and $\varepsilon^{96/90}$ Zr_{94/90}, respectively. The large anomalies in the r-process isotope ⁹⁶Zr are consistent with the measurements of refractory inclusions by (Harper et al., 1991; Harper et al., 1990) and the correlations observed by Nicolussi et al. (1998) in pre-solar grains (Schönbächler et al., 2005).

1.5.4. Chromium

Chromium has four stable isotopes ⁵⁰Cr (4.345%), ⁵²Cr (83.789%), ⁵³Cr (9.501%), and ⁵⁴Cr (2.365%). Chromium isotope anomalies can be used as radio-chronometers as ⁵³Mn decays to ⁵³Cr in 3.7 Myears and has proved effective at determining the chronology of early planetary formation processes. However, Cr may also be utilised to investigate nucleosynthetic variations, like Ti it is an Fe-peak element and the nucleosynthetic source of the neutron rich stable isotopes of Cr and Ti has been shown to be from the same source. The first study to identify chromium isotope heterogeneity within bulk solar system materials was Rotaru et al. (1992). As part of the study, whole rock and a step wise leachate procedures were utilised on a suite of carbonaceous chondrites in order to identify carrier phases responsible for chromium isotopic heterogeneity. They inferred that the bulk solar system composition was the result of mixing of supernova components. Subsequent studies by Trinquier et al. (2007) and Qin et al. (2010) corroborated the work of Rotaru et al. (1992) and expanded the range of solar system material analysed to show that $\varepsilon^{54/50}Cr_{52/50}$ results for bulk meteorites were due to heterogeneous spatial or temporal distribution of the ε^{54} Cr carrier phase.

As an iron group element Cr anomalies in the neutron rich isotope ⁵⁴Cr have been attributed to nuclear statistical equilibrium SN Ia environment or in a high mass 15-25 M_{solar} SN II. Recent studies have attempted to identify the presolar carrier of ⁵⁴Cr and its nucleosynthetic source ((Dauphas et al., 2010; Qin et al., 2011b). It is likely that this carrier is a refractory phase such as Cr-spinel that formed in SN II (Dauphas et al., 2010).

1.5.5. Oxygen

Oxygen is an important element that can reveal information about the physical processes that occurred during the birth of the solar system (Clayton, 1993). Oxygen has three

stable isotopes, which are produced by different nucleosynthesis processes.¹⁶O (99.757%) is a primary isotope that is created by H and He burning while ${}^{17}O(0.038\%)$ and ${}^{18}O(0.205\%)$ are secondary isotopes that can only be produced in second generation stars (Clayton, 2010). Oxygen was the first element to be shown to have resolvable anomalies on the bulk sampling scale of meteoprites (Clayton et al., 1976). Oxygen isotopes have also been shown to have anomalies on all scales studied and so have become one of the major tools for classifying meteorites and investigating the early Solar System ((Clayton, 1993; Clayton and Mayeda, 1978, 1983, 1988, 1996; Clayton et al., 1991; Clayton et al., 1983; Clayton et al., 1984; Clayton et al., 1976; Rowe et al., 1994) (Russell et al., 2010). The three isotopes of O are normally represented on a δ^{17} O v.s δ^{18} O three isotope plot. Samples from one equilibrated reservoir that have only been affected by mass-dependent fractionation plot on line of slope 0.52, termed the terrestrial fractionation line (TFL) when it passes through terrestrial compositions. Anomalous samples are defined as those above or below this line and can be described by a third parameter Δ^{17} O, which is the excess of δ^{17} O relative to the terrestrial fractionation line. These anomalies display a range of around 6 ‰ in bulk chondrite samples. When first identified and for some time afterwards it was thought that O isotope anomalies represented mixing of material with a distinct nucleosynthetic history in to the Solar System ((Clayton et al., 1976) and so helped overturn the theory that the proto- solar nebula had been heated to a high enough temperature to eradicate all pre-solar signatures (Clayton et al., 1973). However recent data from the genesis sample return mission has revealed a different story. O isotope anomalies are now though to represent two component mixing between a ¹⁶O rich end-member, represented by the sun ((McKeegan et al., 2011), and ¹⁶O poor component, which manifests in the terrestrial planet forming region, that has been enriched in ¹⁷O and ¹⁸O relative to the bulk Solar System by gas phase reactions, e.g. self-shielding during CO photolysis ((Clayton, 2002; Thiemens, 1999). Therefore O isotope data cannot help identify the origins of exotic components that provide isotopic heterogeneity in the early Solar System, but can provide important constraints on mixing processes in the early Solar system.

1.6. Study outline

This study aims to investigate the processes and material that formed the solar system over 4.6 billion years ago by determining the Ti isotope composition in solar system materials at high precision. In order to achieve this goal, the study incorporates different analytical techniques regarding the precise determination of Ti isotopes within a suite of solar system materials and components. The determination of Ti isotope compositions within solar system materials enables determination of nucleosynthetic processes which created the material, and the processes at work during and after solar system formation.

Chapter 2 focuses on the analytical methods used to determine mass-independent (nucleosynthetic) and mass-dependent Ti isotope variations within geological materials. To this end a new Ti double spike method was set up and tested for accuracy and reproducibility. As author, my contribution to the study was to carry out all sample digestion procedures and achieve the separation of Ti from elements capable of causing isobaric interferences via ion exchange chromatography at the University of Manchester. Calibration of the double spike and the initial setup of the double spike method were aided by M. A. Fehr, and M. Schönbächler. All measurements utilising the Neptune MC-ICPMS were aided by M. A. Fehr and carried out under the guidance of I. J. Parkinson. Post processing of data and data interpretation were carried out by the author.

In chapter 3, whole rock Ti data are presented utilising the internal normalisation scheme relative to ⁴⁷Ti/⁴⁹Ti. The data includes a suite of solar system materials including achondrites, ordinary chondrites, eucrites, enstatite, carbonaceous chondrites, lunar, terrestrial and chondritic components such as CAIs and chondrules in order to investigate the possible nucleosynthetic processes which created the Ti isotope signature observed within the solar system. Waheed Akram provided aliquots of Ti from samples already separated from Zr in order to obtain complimentary data for both elements. As author, my contribution to the study was to further purify Ti from isobaric interferences via ion exchange chromatography at the University of Manchester. Initial calibrations of the mass independent method were aided by M. A. Fehr, and M. Schönbächler. All measurements utilising the Neptune MC-ICPMS were aided by M. A. Fehr and carried out under the guidance of I. J. Parkinson. Post processing of data and data interpretation were carried out by the author.

In Chapter 4, the results from leachates of carbonaceous chondrites Murchison (CM2), Allende (CV3),Orgueil (CI) and ordinary chondrite QUE 97008 are presented. These data are also obtained utilising the internal normalisation scheme relative to ⁴⁷Ti/⁴⁹Ti. The purpose of this study is to resolve the Ti isotope composition of different phases within the meteorite to determine the carrier phases of potential isotopic heterogeneity. This chapter contains data from various sources. Murchison, Allende and Orgueil data obtained utilising the Nu1700 were given to the author by I. Leya. The remaining fractions of Ti from the measured samples were also given to the author to carry out chemically purification techniques and re measure utilising the methods set out in chapter 2. Aliquots of the samples Murchison –(Q) and QUE 97008 (Q) utilised in the study of Qin et al (2011) were provided by Richard Carlson and Linping Qin. These aliquots required the author to carry Ti purification techniques and also measure using the Neptune MC-ICPMS. All measurements utilising the Neptune MC-ICPMS were aided by M. A. Fehr and carried out under the guidance of I. J. Parkinson.

Chapter 5 concludes the study by applying the double spike method to obtain the absolute Ti isotope compositions of a wide range of solar system materials. The data is then used to determine the true location of nucleosynthetic anomalies and can be compared to nucleosynthetic models. At the same time, the double spike procedure provides the mass-dependent Ti isotope composition of the investigated samples. Mass-dependent Ti isotope variations are identified within terrestrial samples and meteorites. Within this study mass independent and double spike data for Ti will be combined in order to determine the absolute nucleosynthetic anomalies of different solar system materials. The contributors to the work described in this chapter follow that of Chapter 2. Full sample digestion and purification was mainly carried out by the author except on samples marked as being initially processed for Zr by Waheed Akram. All measurements utilising the Neptune MC-ICPMS were aided by M. A. Fehr and carried out under the guidance of I. J. Parkinson. Post processing of data and data interpretation were carried out by the author.

Chapter 6 will state the final outcomes of the study.

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Chapter 2:

The development of a novel titanium double spike procedure by MC-ICPMS for the determination of absolute Ti isotope compositions in solar system materials.

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2.1. Abstract

A new method to determine the Ti isotope composition of solar system materials to high precision was developed by combining mass independent results with a 47 Ti – 49 Ti double spike procedure. The combination of internally normalised Ti isotope data with double-spiked analyses allows us to obtain novel mass dependent Ti isotope data for terrestrial and meteorite samples. The methods furthermore generate "absolute" Ti isotope compositions which can be used to identify the exact Ti isotopes that display nucleosynthetic isotope variations in meteorites.

Our data shows that mass-dependent fractionation of Ti isotopes is induced by the ion exchange procedure. This is demonstrated by, separately processed sample aliquots that were spiked prior and after the ion-exchange chromatographic procedure. This outcome requires the addition of the double spike before the ion exchange chemistry in order to accurately determine natural mass-dependent Ti isotope compositions. The accuracy and reproducibility of the method was verified by analyses of two Ti standards (an Alfa Aesar solution and an Alfa Aesar Ti wire standard) and three USGS rock standards (AGV-2, BHVO-2 and BCR-2). Multiple double spike analyses of the Ti wire solution over several months yielded an average reproducibility (2σ) of 17 ppm for $\delta^{48/47}$ Ti.

The terrestrial basalts (BHVO-2 and BCR-2) display an average Ti isotope composition of -0.113 ± 0.006 ‰ in $\delta^{48/47}$ Ti, while the analysed andesite AGV-2 yields a $\delta^{48/47}$ Ti of -0.081 ± 0.016 . This indicates that igneous processes induce mass-dependent Ti isotope fractionation.

Combined mass-independent and double-spike analyses of the two carbonaceous chondrites Allende (USNM 3529) and Murchison (USNM 5453) yields mass independent data that document correlated enrichments in $\varepsilon^{46/47}$ Ti values of 0.56 ± 0.20 and 0.51 ± 0.18 respectively and $\varepsilon^{50/47}$ Ti values of 3.77 ± 0.06 and 3.17 ± 0.12 relative to the terrestrial standard, while $\varepsilon^{48/47}$ Ti and $\varepsilon^{49/47}$ Ti are identical to those of the terrestrial samples. This suggests that the nucleosynthetic anomalies are located in ⁴⁶Ti and ⁵⁰Ti.

2.2. Introduction

Titanium is a refractory lithophile element, which is found abundantly (wt. % concentrations) in most solar system materials and thought to be immobile during secondary alteration processes due to its high field strength (charge/radius ratio, (Floyd and Winchester, 1978; Pearce and Norry, 1979). However more recent studies suggest that Ti can be mobilised under certain pressure and temperature conditions. (Ayers and Watson, 1991, 1993). Previous studies by Niederer et al. (1980, 1981) utilising Thermal Ionisation Mass Spectrometry (TIMS) showed that no Ti isotope variations exist among terrestrial, lunar and meteorite bulk samples. The authors demonstrated that nucleosynthetic variations are held within components of meteorites such as Calcium Aluminium rich Inclusions (CAI's), which were the first solids formed in the protoplanetary disk (Niederer et al, 1980). Further Ti isotope studies were able to resolve mass independent variations present in bulk meteorites and individual components of meteorites such as Fractionation and Unidentified Nuclear (FUN) CAI's, normal CAI's and chondrules. These variations were attributed to ⁵⁰Ti enrichments synthesized during hydrostatic burning within a massive star (Niemeyer and Lugmair, 1981, 1984). Niederer et al. (1985) utilised a ⁴⁶Ti-⁵⁰Ti double spike method in combination with TIMS to resolve absolute isotope compositions within bulk meteorites, FUN and normal CAI's, which demonstrated that clearly resolvable excesses in ⁵⁰Ti are present in whole rock meteorites.

Recent advances in mass spectrometry have led to the ability of achieving high precision and reproducibility by the use of Multi Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS). Leya et al (2007; 2008) utilised the Nu Plasma HR-MC-ICP-MS (Nu 1700) to determine the Ti isotope composition of terrestrial samples and bulk meteorites respectively, which revealed wide spread radial Ti isotope heterogeneity in bulk solar system material. Further Ti mass independent studies of solar system materials achieved higher precision through better ion chromatography techniques that were capable of enhanced purification of Ti (Trinquier et al., 2009; Zhang et al., 2011). Both studies revealed correlated enrichment and depletion among solar system materials between ⁵⁰Ti and ⁴⁶Ti (Trinquier et al., 2009; Zhang et al., 2011). However, like all mass independent data it suffers from the disadvantage of having to fix two isotopes in order to correct for instrumental mass bias. By utilising the double spike methodology which is capable of providing a precise correction for instrumental mass bias it is possible to discern laboratory induced isotope fractionation caused by ion chromatography techniques from mass dependent fractionation processes caused by kinetic and thermal fractionation (Albarede and Beard, 2004); and hence generate the first high precision Ti stable isotope data. Recent investigations of stable isotope data utilising the double spike technique have revealed that it is a useful method for the investigation of geological and biological processes (Arnold et al., 2010; Cameron et al., 2009; Gall et al., 2012; Ripperger et al., 2007; Siebert et al., 2001; Wombacher et al., 2003). Recent work on Ti stable isotope data (Millet and Dauphas, 2014) investigated stable isotope compositions of high temperature terrestrial basalts using a ⁴⁹Ti-⁴⁷Ti double spike and found stable isotope fractionation between the different measured terrestrial basalts. The authors reported an external reproducibility for all standard solutions of 20ppm (2sd) on $\delta^{49/47}$ Ti over 15 weeks. Five basaltic rock standards were analysed and displayed slightly different $\delta^{49/47}$ Ti values. W2 and BHVO-2 displayed slightly heavy compositions relative to the OL-Ti standard of 0.040 ± 0.013‰ and 0.021 ± 0.008‰ respectively while BCR-2, BIR-1 and JB-2 displayed light stable isotope compositions of terrestrial basalts and andesites within this work will allow further investigation of Ti stable isotope fractionation during high temperature igneous processes.

Trinquier et al. (2009) and Zhang et al. (2011) have already shown that solar system material display correlated enrichment and depletions for ⁵⁰Ti and ⁴⁶Ti when utilising ^{49/47}Ti for mass bias correction. The isotopes utilised for mass bias correction will be displayed as $Ti_{i/j}$ within this work. The aim of this investigation was to develop a double spike technique for the accurate, precise and reproducible determination of absolute Ti isotope compositions in terrestrial and meteorite samples that are not compromised by a mass bias correction procedure that assumes to know the abundance of two isotopes in a sample. By combining mass independent data with the double spike technique an evaluation of the nucleosynthetic Ti anomalies on all isotopes is possible, which provides further insights into the stellar sources, which produced the material that formed the solar system. The technique also yields stable isotope data for terrestrial and solar system materials enabling the examination the mass dependent isotope fractionation processes that affected Ti isotopes.

2.3. Experimental

2.3.1. Sample preparation

Sample preparation was carried out in Class 10 fume cupboards within the class 1000 clean room facility at the University of Manchester. Mineral acids except for hydrofluoric acid (HF) were purified from analaR® grade reagents by triple sub-boiling distillation in quartz

stills. Sub-distilled HF (~28 M ultrapure grade from Romil), H_2O_2 (~30% vol. ultrapure grade) and H_2SO_4 (ultrapure grade) were purchased from Sigma Aldrich. Water of >18.2 M Ω cm⁻¹ grade H_2O from a Millipore® Corporation deionising purification system was used throughout.

2.3.2. Sample digestion and Titanium separation

Samples utilised in this study include three USGS geological reference samples BHVO-2 (Hawaiian basalt), BCR-2 (Columbia river basalt) and AGV-2 (andesite) to investigate Ti stable isotope variations in different terrestrial igneous settings. Furthermore, two single element standards, a Ti Alfa Aesar reference solution (Ti AA) and an AA Ti wire of 99.99% purity (Ti wire) were analysed. To complement the study two carbonaceous chondrites Murchison (CM2) and Allende (CV3) were also analysed.

Digestion of the terrestrial rock standards and meteorites followed a modified procedure of Schönbächler et al. (2004) utilising the Parr Bomb® technique for sample digestion. A summary is given in the following: First the samples were crushed in a boron carbide mortar under a laminar flow of filtered air to avoid contamination. Terrestrial samples of up to 200 mg and meteorite samples of up to 100 mg were digested in 12 ml Savillex® vials containing 3 ml of concentrated HF and 1 ml of concentrated HNO₃. Sample vials were placed inside a 125 ml Parr Bomb and heated in an oven to 180°C for 4.5 days. After digestion the samples were dried down and completely re-dissolved in 10 ml of 6 M HCl for terrestrial rock standards, and 5 ml of 6 M HCl for meteorites. The Ti wire single element standard was prepared from a Ti wire of 99.9985% purity (Alfa Aesar) cut to a length of 68 mm. The Ti wire was then leached with 0.1 M HNO₃ for 5 minutes before being washed with water and distilled ethanol. The wire was weighed and transferred to a Savillex® vial for the digestion in 3 ml of conc. HF and 1 ml conc. HNO₃. The Ti AA standard solution only required pipetting into a Savillex® vial for weighing.

Solutions were then split into two aliquots containing 50 µg of Ti for terrestrial and single element standards, while meteorite samples aimed at containing 25 µg of Ti per aliquot. The first aliquot was put through the anion exchange chromatography procedure (described below) to purify Ti and was then analysed using the internal normalisation method. Subsequently, it was spiked and analysed again using the double spike method. The second aliquot was spiked prior to column chemistry in order to compare with the data that was spiked after the anion exchange procedure. This allowed us to evaluate any mass dependent fractionation that could occur during chemical processing of the samples.

The separation of Ti utilised a three stage ion-exchange chromatographic procedure in order to separate Ti from the sample matrix and in particular from Ca, V and Cr, whose isotopes form isobaric interferences on Ti isotopes. Fluorinated ethylene propylene (FEP) columns filled with 0.7 ml AG1-X8 200-400 mesh anion exchange resin was used for all three stages of the separation procedure. The resin was cleaned with two column volumes (7 ml) of 0.5 M HCl followed by 5 ml of 6 M HCl +1 M HF before finally washing it with 1 column volume of 18.2 M Ω H₂O.

The first anion exchange column was identical to those of Schönbächler et al. (2004). It was conditioned with 6 ml of 4 M HF. Samples were loaded utilising 5 ml of 4 M HF. If precipitate of CaF was observed, the samples were split prior to loading into two 1.5 ml centrifuge vials. The centrifuge vials were centrifuged for 20 minutes in order to separate the CaF precipitate prior to loading. This process was repeated three times such that a total volume of 5 ml of sample was produced. After the sample was loaded a further 0.5 ml of 4 M HF and 5 ml of 4 M HF were added to elute the majority of matrix elements. Titanium was eluted next in 3 ml of 6 M HCl + 1 M HF.

The second column was utilised to separate Ti from Zr and it also follows Schönbächler et al. (2004). For this procedure the resin was preconditioned using 7 ml of 0.25 M H₂SO₄ +1% H₂O₂, which was prepared on the same day in order to preserve the H₂O₂. The Ti was loaded using 1 ml of 0.25 M H₂SO₄ +1% H₂O₂ and a further 0.5 ml of 0.25 M H₂SO₄ +1% H₂O₂ was added. Titanium was eluted in the loading phase and an additional 8 ml of 0.25 M H₂SO₄ +1% H₂O₂. Zirconium was eluted using 4 ml of 6 ml HCl + 1 M HF.

The final column added to the procedure of Schönbächler et al. (2004) to improve the separation of V, Ca and Cr from Ti to reduce the impact of these isobaric interfering elements. The third column also utilised 6 ml of 4 M HF to precondition the column. The sample was loaded using 1 ml of 4 M HF. An additional 0.5 ml of 4 M HF was also added to the sample vial to take up any remaining Ti and this solution was also added to the column. A further 5 ml of 4 M HF was added to elute remaining matrix elements including Ca and Cr. This was followed by 5 ml of 0.5 M HCl + 0.5 M HF to elute V, before Ti was collected using 3 ml of 6 M HCl + 1 M HF.

The Ti fraction was then dried down and dissolved in 60 μ l conc. HNO₃ + 10 μ l 1 M HF. This solution was evaporated down to approximately 0.04 ml of solution before adding

0.96 ml of H₂O. The solutions were then ready for analysis with a Neptune Finnigan MC-ICP-MS at the Open University.

2.4. Double spike method

2.4.1. Evaluation of the double-spike procedure

The double spike technique requires four isotopes for the accurate determination of stable isotope data. Since Ti consists of five stable isotopes, ⁴⁶Ti (8.25%), ⁴⁷Ti (7.44%), ⁴⁸Ti (73.72%), ⁴⁹Ti (5.41%) and ⁵⁰Ti (5.18%) it is essential to decide which four to use. The optimal double spike composition was determined based on error propagation simulations using the double spike toolbox by Rudge et al. (2009). The intersection angle of the planes approach after Galer et al. (1999) was also utilised to identify spike compositions that provide near optimal intersection angles between the mass fractionation vectors of spiked and un-spiked samples.

Rudge et al. (2009) published a MATLAB code that evaluated all possible double spike combinations for all elements with at least four naturally occuring isotopes. The code uses real spike compositions provided by the Oak Ridge National Laboratory (ORNL) enabling the calculation of the double spike compositions that will provide the lowest errors on the fractionation factors. The code of Rudge et al. (2009) was utilised in order to identify and compare the characteristics of all possible spike combinations. The method of Rudge et al. (2009) indicates that the combination of ⁴⁷Ti-⁴⁹Ti spikes when mixed in the propotion 0.49:0.51 respectively provide the best results in terms of the lowest errors are expected (Fig. 2.1). Moreover the ⁴⁷Ti-⁴⁹Ti spike combination when mixed in the propotion 0.49:0.51 respectively provides a robust range of double spike to sample mixtures over which the error propogation remains low.


Figure 2.1. Expected errors on the fractionation factor (α) after double spike calculations are given as a function of the ratio of double spike in the double spike-sample mix for different double spike mixtures. Results were obtained by the error minimization code of Rudge et al. (2009). Coloured lines denote different double spike mixtures. The results demonstrate that the ⁴⁷Ti-⁴⁹Ti double spike mixed in the proportion 0.49:0.51 is the most favourable combination and maintains a lower error over a wide range of spike to sample ratios.

The method of Rudge et al. (2009) can also be used to indicate the optimal mixture for the spike combination (Fig. 2.2). Figure 2.2 indicates that the optimal double spike to sample mixture is 0.94, whereas the optimal ratio of ⁴⁷Ti spike in the ^{47/49}Ti double spike combination is 0.96.



Figure 2.2. Displays the optimal ratio of double spike to use in the double spike to sample mixture (x-axis) against the proportion of ⁴⁷Ti (spike $2=^{47}$ Ti, and spike $4=^{49}$ Ti) in the double spike ⁴⁷Ti-⁴⁹Ti mixture (y-axis). The contours in fig. 2.2 denote the 1% interval of the optimal error for the fractionation factor (α). Results from the evaluation of optimal Ti double spike proportions provided by the error minimization code of Rudge et al. (2009). Contours denote the 1% interval of the optimal error in Alpha up to 25% of the optimal error for the optimum proportion of ⁴⁷Ti in the ⁴⁷Ti-⁴⁹Ti double spike against the proportion of double spike in the double spike -sample mixture. The broad region around the optimum denotes the area where the lowest errors are found.

These results based on Rudge et al. (2009) were confirmed by those obtained from the evaluation of the intersection angles of the planes (Galer et al. 1999) and our own error propagation simulations. They yielded the most favourable results for a ⁴⁷Ti-⁴⁹Ti double spike mixed in the ratio (⁴⁷Ti/⁴⁹Ti) of 0.89.

2.4.2. Double spike preparation

The Ti double spike was created as a mixture from two single spike solutions enriched in ⁴⁷Ti and ⁴⁹Ti. A total of 31 mg ⁴⁷Ti oxide (94.55% purity) and 29 mg ⁴⁹Ti oxide (96.25% purity) purchased from the Oak Ridge National Laboratory (ORNL) were separately dissolved for 3 days in 3 ml concentrated HF + 1 ml concentrated HNO₃ and subsequently diluted to a concentration of around 200 ppm. The Ti concentrations of the solutions were determined using reverse isotope dilution. The two single spike solutions were then mixed in such a way that a final double spike solution was obtained, with a ${}^{47}\text{Ti}/{}^{49}\text{Ti} \sim 0.92$ and a total Ti concentration of 30.29 µg/g in 2 M HNO₃ + 0.2 M HF.

2.5. Mass spectrometry

2.5.1. Measurement protocol for internally normalised data

All isotopic measurements were performed using a Neptune MC-ICPMS instrument at the Open University, Milton Keynes. The samples were introduced into the mass spectrometer using an Aridus II desolvating sample introduction system and X-cones. The collector configuration is shown in Table 2.1. All five Ti isotopes and ⁴⁴Ca were measured simultaneously in cycle 1. The ⁴⁴Ca isotope was monitored in order to correct for isobaric interferences of Ca on ⁴⁶Ti and ⁴⁸Ti. A second cycle was configured in order to correct for isobaric interferences from V and Cr on ⁵⁰Ti (Table 2.1). Due to the interference of the argide ¹⁴N³⁶Ar on ⁵⁰Ti the position of measurement of cycle 1 had to be altered in order to measure on the shoulder of ⁵⁰Ti. In cycle 2 the interference of the argide ¹³C⁴⁰Ar on ⁵³Cr caused the position of measurement to be moved to the shoulder in order to resolve the interference.

Table 2.1. Collector configuration for Ti isotope abundances and important isobaric interferences.

		-		Cycl	e 1				Cycle	2
Mass	44	45	46	47	48	49	50	50	51	53
Collector	L4	L3	L1	С	H1	H2	H3	С	H1	H3
Isotope	⁴⁴ Ca	⁴⁵ Sc	⁴⁶ Ti	⁴⁷ Ti	⁴⁸ Ti	⁴⁹ Ti	⁵⁰ Ti	⁵⁰ Ti	⁵¹ V	⁵³ Cr
Abundances(%)	2.08%	100%	8.25%	7.44%	73.72%	5.41%	5.18%		99.75%	9.50%
Interferences										
Single charged			⁴⁶ Ca		⁴⁸ Ca		⁵⁰ V, ⁵⁰ Cr	⁵⁰ V, ⁵⁰ Cr		
Double charged atomic			⁹² Zr ²⁺	⁹⁴ Zr ²⁺	⁹⁶ Zr ²⁺					
other interferences				$^{19}\text{F}^{28}\text{Si}^{+}$		¹⁴ N ³⁵ Cl ⁺	$^{14}N^{36}Ar^{+}$			$^{13}C^{40}Ar^{+}$

The data acquisition sequence for samples and standards comprised collection of 40 ratios with 8.4 s integration for cycle 1 and 40 ratios with 4.2 s integration for cycle 2. Background analyses of the wash consisting of 0.5 M HNO₃ + 0.005 M HF included the collection of 20 ratios with integration of 8.4 s. A background analysis was performed before and after each sample and standard measurement. The on peak background correction used the average values of background measurements taken before and after the sample and standards. Every sample and standard analysis was followed by a washout, whereby the sample

introduction system was flushed with 0.5 M HNO₃ + 0.005 M HF for 240 s in order to remove potential memory effects within the system. Each complete sample analysis was preceded and followed by a standard measurement of Ti AA solution. One sample measurement required 18 minutes and consumed ~800 μ l sample solution. The Neptune MC-ICP-MS gave an average instrumental sensitivity for Ti of around 80 V/ppm.

Internally normalised (Mass-independent) Ti data are reported relative to a Ti AA standard solution using the ε notation:

$$\epsilon^{i/47} T i_{49/47} = \left(\frac{R_{sample}}{R_{standard}} - 1\right) x 10^4 \tag{2.1}$$

Where *i* denote the isotope mass being investigated (46, 48 and 50), R_{sample} and $R_{standard}$ the ⁱTi/⁴⁷Ti isotope ratio of the sample and standard, respectively and _{49/47} refers to the applied mass bias correction relative to (⁴⁹Ti/⁴⁷Ti = 0.749766 (Niederer et al. 1981)). The standard sample bracketing method was used to correct for drifts that potentially occurred over the sample measurement session. The internally normalised data (mass independent) will be used in conjunction with the double spike protocol to obtain the absolute Ti isotope composition of a sample and hence the 'true' Ti isotope composition.

2.5.2. Double spike calibration

To determine the Ti isotope composition of the double spike, two separate techniques were applied. All double spike calibrations and measurements were carried out relative to the Ti wire standard solution. The isotopic analyses of the spike were externally normalised relative to Ca for mass bias correction of ⁴⁹Ti and ⁵⁰Ti. For the correction of ⁴⁶Ti and ⁴⁸Ti external normalization relative Cr was utilised. In order check the external normalization procedure, solutions of Ti wire were run on the Neptune MC-ICPMS variably doped with Ca and Cr. Equation 2.2 -2.4 demonstrates how the interference correction was applied for Ca (Equation 2.3) and Cr (Equation 2.4).

$$R_{Ti} = r_{Ti} (\frac{mTi^{48}}{mTi^{47}})^f \tag{2.2}$$

 R_{Ti} denotes the mass bias corrected 'true' ⁴⁸Ti/⁴⁷Ti and r_{Ti} denotes the measured ⁴⁸Ti/⁴⁷Ti ratios, and *m* is the atomic mass of the relevant isotope. The fractionation factor *f* for Ca is given by:

$$f_{Ca} = \frac{\ln\left(\frac{R_{Ca}}{r_{Ca}}\right)}{\ln\left(\frac{m+2}{m+4}\right)} \tag{2.3}$$

The fractionation factor for Cr is given by:

$$f_{Cr} = \frac{\ln\left(\frac{R_{Cr}}{r_{Cr}}\right)}{\ln\left(\frac{m53}{m52}\right)} \tag{2.4}$$

Initially, R_{Ca} and R_{Cr} utilised the 'referenced ⁴²Ca/⁴⁴Ca ratio of 0.31221 (Russell et al, 1978) and ⁵³Cr/⁵²Cr ratio of 0.113386 (Shields et al. 1966) respectively for the Ca and Cr dopant. r_{Ca} and r_{Cr} are the measured ratios obtained from repeat analysis relative to the Ti wire standard which is used as a standard sample bracketing standard.

From the repeat analysis of Ti wire doped with varying amounts of Ca and Cr the ${}^{42}Ca/{}^{44}Ca$ and ${}^{53}Cr/{}^{52}Cr$ ratios utilised as R_{Ca} and R_{Cr} in equation (2.3) and (2.4) were optimized for each measurement session. This experimentally derived recalculation of the 'true' ${}^{42}Ca/{}^{44}Ca$ ratio to equal 0.3092 and ${}^{53}Cr/{}^{52}Cr$ ratio to equal 0.11336356 was necessary in order to account for the changes in the mass bias behaviour between Ti and Ca and Cr for each analysis over the measurement session. The 'true' ${}^{42}Ca/{}^{44}Ca$ and ${}^{53}Cr/{}^{52}Cr$ ratios were optimized in order that the mass bias correction procedure using the ${}^{42}Ca/{}^{44}Ca$ ratio and ${}^{53}Cr/{}^{52}Cr$ produced identical results for ${}^{46}\text{Ti}/{}^{47}\text{Ti}$; ${}^{48}\text{Ti}/{}^{47}\text{Ti}$ and ${}^{50}\text{Ti}/{}^{47}\text{Ti}$ as internal normalization to ${}^{49}\text{Ti}/{}^{47}\text{Ti} = 0.749766$ (Niederer et al. 1981) would. Finally the optimised ${}^{42}\text{Ca}/{}^{44}\text{Ca}$ and ${}^{53}\text{Cr}/{}^{52}\text{Cr}$ ratios were utilised for the mass bias correction of the pure Ti double spike solution (Table 2.2). The Ti concentrations of the standard and spike solutions were matched for all measurements in order to avoid potential matrix effects.

Table 2.2. Average Ti isotopic compositions determined for unspiked and spiked Ti wire, standard and double spike data. Data obtained from external normalization to Ca ($^{49/47}$ Ti and $^{50/47}$ Ti) and Cr ($^{46/47}$ Ti and $^{48/47}$ Ti $^{49/47}$ Ti doping

Solution	⁴⁶ Ti/ ⁴⁷ Ti	2 S.D	⁴⁸ Ti/ ⁴⁷ Ti	2 S.D	⁴⁹ Ti/ ⁴⁷ Ti	2 S.D	⁵⁰ Ti/ ⁴⁷ Ti	2 S.D
Ti wire	1.093173	0.000020	10.069413	0.000169	0.749529	0.000026	0.729573	0.000038
⁴⁷ Ti- ⁴⁹ Ti double spike	0.006118	0.000007	0.078940	0.000150	1.057969	0.002243	0.008457	0.000003
Spiked Ti wire (1:1)	1.093199	0.000058	10.069168	0.000639	0.749495	0.000077	0.729524	0.000111

2.5.3. Double spike data reduction

The double spike data reduction was performed off line, using a procedure previously described by Siebert et al. (2001). This procedure applies a geometric approach to solve the double spike equations in three dimensional isotope spaces. The three axes are defined by

isotope ratios with a common denominator, necessitating the use of four isotopes in the inversion process (Russell, 1971). For the inversion process ⁴⁶Ti, ⁴⁸Ti and ⁴⁹Ti with ⁴⁷Ti as the denominator were utilised. The data reduction procedure described by Siebert et al. (2001) was chosen over the procedure described by Galer (1999) as it does not make the simplifying assumption that the instrumental mass bias can be described by a linear law. The linear law has been used for some studies utilising TIMS; however the mass bias of MC-ICPMS analysis is an order of magnitude larger, therefore requiring an iterative procedure. The iterative procedure accounts for the curved trajectories obtained during analysis by cycling the fractionation factor through the iterations until the values converge.

The Ti stable isotope data are reported relative to the Ti wire standard using the δ notation:

$$\delta^{i/47}Ti = \left(\frac{R_{sample}}{R_{standard}} - 1\right) x 10^3 \tag{2.5}$$

Where *i* denote the isotope masses 46 Ti, 48 Ti, 49 Ti and 50 Ti; R_{sample} and R_{standard} the isotope ratio of the sample and standard, respectively.

The sample standard bracketing method was used and R_{standard} was calculated using the average of the standards run before and after the sample. The spiked standard measurements were used to correct for the daily variability observed among measurement sessions through the sample standard bracketing technique method.

2.5.4. Combining mass independent and double spike data

In order to evaluate solar system materials that contain mass-dependent and mass independent (nucleosynthetic) variations, mass-independent data and double spike data are combined. Firstly the unspiked mass independent data for the sample was determined according to section 2.5.1, while the spiked data was measured and corrected for background and inferring elements according to the above described data evaluation (section 2.5.3). The results of the unspiked analyses are then used as the natural composition in the double spike data reduction scheme. In addition to the iterative data reduction procedure, a thousand random values were used to create an error propagation procedure which enabled the production of the reported 2. S.D values quoted. The results obtained with this procedure are the absolute Ti isotope composition. For solar system materials the absolute Ti isotope compositions contain mass dependent and nucleosynthetic anomaly data.

2.5.5. Kinetic fractionation equation

In order to evaluate the nucleosynthetic variations that are carried within solar system materials such as Allende and Murchison, the absolute Ti isotope compositions needs to be split into the mass-dependent and the mass-independent (nucleosynthetic) portion. Once the mass-dependent value for one ratio is known, the values of other ratios can be calculated with the following equation by Wombacher and Rehkämper. (2004).

$$\varepsilon^{i/48}Ti = \left[\left(\frac{\varepsilon^{48/49}}{10^4} + 1 \right)^{\beta} - 1 \right] x 10^4 \tag{2.6}$$

Where, *i* represents the isotope of mass m_i , and β is given by $[\ln (m_i/m_{48})]/ [\ln (m_{48}/m_{49})]$. The $\varepsilon^{48/49}$ Ti values were utilised to calculate the mass dependent data from the Ti isotope compositions as $\varepsilon^{48/49}$ Ti was shown to have no nucleosynthetic anomaly effects within the data and displayed only mass dependent signatures.

2.6. Results and discussion

2.6.1. Mass independent Titanium data

The mass independent (internally normalised) data for the three USGS geo standards BHVO-2, BCR-2 and AGV-2, the Ti wire and Ti AA standards and two carbonaceous chondrite Allende and Murchison are reported in Table 2.3 displayed with the 2 standard error (2S.E) values calculated from the combination of all measured individual samples. All mass independent measurements utilise the Ti AA standard solution as the standard bracketing solution. Also displayed are the average uncertainty values given as 2SE spanning all samples and measurement sessions over 8 months. The results for the three USGS geostandards and single element Ti solutions show normal values within total analytical uncertainty and agree well with previous Ti work by Leya et al (2007), Trinquier et al (2009) and Zhang et al. (2012). The results for the two carbonaceous chondrites Allende and Murchison agree well (within analytical uncertainty) with the work of Zhang et al. (2011) and Leya et al. (2007; 2008). The Murchison data also agrees well with the data reported by Trinquier et al. (2009) but the values of Allende do not overlap. The discrepancy is best explained by sample heterogeneity or incomplete dissolution of presolar phases with anomalous Ti isotope composition during the digestion process.

Table 2.3. Ti isotope results for mass independent data internally normalised relative to ^{49/47}Ti. Mass independent data is given relative to Ti AA standard solution. Uncertainties are reported as 2 S.E for individual samples. Also displayed are the total reproducibility values for all samples given also as 2 S.E.

Sample	Туре	Number	ε ^{46/47} Ti _{49/47}	2 SE	$\epsilon^{48/47} Ti_{49/47}$	2 SE	$\epsilon^{50/47} Ti_{49/47}$	2 SE
Terrestr	ial and laboratory standards							
BHVO-2	Basalt	2	-0.19	0.04	-0.08	0.10	0.01	0.03
BHVO-2 *	Basalt	2	0.06	0.10	-0.03	0.16	-0.01	0.32
BCR-2	Terrestrial Basalt	2	-0.06	0.10	-0.19	0.13	-0.04	0.03
BCR-2 *	Terrestrial Basalt	4	-0.09	0.05	0.09	0.08	0.01	0.07
AGV-2	Andesite	3	-0.16	0.02	0.01	0.18	0.03	0.05
AGV-2 *	Andesite	2	-0.05	0.05	-0.04	0.16	0.04	0.04
Tiwiro	Laboratory standard	2	0.09	0.21	0.25	0.20	0.09	0.00
Tiaa		2	-0.08	0.51	-0.25	0.29	-0.06	0.09
ПАА	Laboratory standard	2	-0.07	0.04	-0.10	0.21	-0.09	0.04
Ca	rbonaceous chondrites							
Murchison	Carbonaceous chondrite CM2	3	0.51	0.18	-0.04	0.15	3.17	0.12
Murchison *	Carbonaceous chondrite CM2	6	0.32	0.11	-0.03	0.08	2.94	0.10
Murchison ^T	Carbonaceous chondrite CM2		0.35	0.17	0.01	0.11	3.06	0.33
Murchison ^z	Carbonaceous chondrite CM2		0.45	0.15	-0.06	0.09	2.83	0.19
Allende	Carbonaceous chondrite CV3	4	0.56	0.20	0.03	0 09	3 77	0.06
Allende *	Carbonaceous chondrite CV3	4	0.62	0.05	0.03	0.11	3.39	0.18
Allende *	Carbonaceous chondrite CV3	2	0.57	0.17	-0.05	0.14	3.25	0.10
Allende ^T	Carbonaceous chondrite CV3		0.94	0.11	0.12	0.12	5.01	0.29
Allende ^L	Carbonaceous chondrite CV3		0.33	0.78	0.25	0.44	3.37	0.74
Allende ^Z	Carbonaceous chondrite CV3		0.68	0.11	-0.10	0.08	3.68	0.25
Allenue	carbonaceous chonuille CV3		0.00	0.11	0.10	0.00	5.00	0.20
	Mean reproducibility			0.22		0.23		0.22

*sample aliquots taken from Zr study of Akram et al. (2013)

^T obtained by Tringuier et al (2009)

^L obtained by Leya et al (2007)

^z obtained by Zhang et al (2011)

2.6.2. Titanium double spike analyses

Repeated measurements of Ti wire solution standard mixtures with near-optimal molar proportions of spike to standard ratios of 1:1 were carried out prior to each analytical session to check the performance of the instrument on any given day. The Ti wire standard solution was also used for the standard sample bracketing solution and displayed small deviations from δ^{46} Ti = 0, which was in line with previous double spike studies utilising MC-ICPMS (Arnold et al., 2010; Ripperger et al., 2007). Daily variations in the measured and mass bias corrected ratios of around 0.02‰ (2sd) for $\delta^{46/47}$ Ti were observed. These small variations reflect the deviations in the instrumental mass bias, which in turn produce fractionation patterns that deviate from exponential law behaviour (Wombacher et al., 2003). Over one measurement session, the Ti double spike-Ti wire mixtures displayed isotope compositions that were within the measurement precision (Figure 2.3A). Over several measurement sessions the same small deviations were observed for the standard measurements. By taking the mean value of several sessions of Ti double spike-Ti wire mixtures (Figure 2.3B); we were able to improve the precision of the correction applied to the data reduction procedure. The correction applied used the mean isotopic composition of the spiked standard which was determined from repeated analysis of a Ti double spike-Ti wire mixture over several measurement sessions. The offset was calculated by referencing the measured sample data of a session to the mean composition of the Ti double spike-Ti wire mixture:

$$\delta^{i/47} Ti_{sample(true)} = \delta^{i/47} Ti_{sample(measured)} - \delta^{i/47} Ti_{wire(mean)}$$
(2.7)





Figure 2.3. The Ti isotope data ($\delta^{46/47}$ Ti values) determined for Ti wire - double spike mixtures (in proportion of 1:1) utilising sample standard bracketing technique for (a) one measurement session displaying individual offsets (1-5) and daily average (average) (uncertainties for individual measurements are displayed as per mil and the uncertainty of the average measurement is displayed as the 2SD of the individual measurements). (B) average offset of all measurements taken from multiple measurement sessions (uncertainties are given as 2SD for each measurement session). Plots demonstrate the increase in precision when taking the average of all measurement sessions over individual measurement sessions.

Samples were measured at least twice during an analytical session, and the combined precision of the analyses yielded precisions (2 SD) for $\delta^{46/47}$ Ti of between 0.01 ‰ and 0.05 ‰ (Table 2.4). The average uncertainty of sample measurements was similar to the external precision (2 SD) obtained for multiple analyses of spiked Ti wire solution for $\delta^{46/47}$ Ti of 0.02 ‰ conducted over one measurement session.

In order to investigate the robustness of the proportion of double spike used in the double spike standard mixture; the Ti isotope composition of Ti double spike – Ti wire mixtures were analysed with variable proportions of double spike (f = 0.25 - 3) relative to a mixture with the previously determined optimal proportion of double spike (f =1) (Fig. 2.4). The results indicate that the double spike methodology yields reproducibility comparable to the average uncertainty found over one measurement session ($\delta^{46/47}$ Ti of 0.02 ‰) when the proportion of the double spike in the double spike – standard mixture is between 0.5 and 2. At higher and lower proportions of double spike in the measured solutions, the precision and accuracy of the data appear to deteriorate beyond $\delta^{46/47}$ Ti of 0.02 ‰ found for multiple analysis of the standard over one measurement session.



Figure 2.4. The Ti isotope data for various mixtures of double spike and Ti wire standard. The results are reported relative to data acquired at optimal proportion (1:1). The grey rectangle denotes the range of mixtures, which are robust and produce errors comparable with those of spike Ti wire standards over one analytical session (dashed lines) The error bars denote the internal precision (2 SE) of the analyses.

2.6.3. Titanium stable isotope data

2.6.3.1. Isotope fractionation due to laboratory chemical processing

In order to investigate the possible fractionation due to the chemical separation technique, aliquots of samples spiked before column chemistry were processed and compared to the same samples spiked after column chemistry. Table 2.4 gives the $\delta^{i/47}$ Ti isotope composition of the samples relative to Ti wire double spike solution for samples spiked before column chemistry (BCC-blue) and those of a different aliquot of the same sample spiked after column chemistry (ACC-black).

Table 2.4. Mass dependent Ti isotope data relative to the Ti wire standard displayed as $\delta^{i/47}$ Ti which is the deviation in parts per ten thousand of the sample from the referencing standard Ti wire.

Samples # (of measurements	δ ^{46/47} Ti	2 S.D	δ ^{48/47} Ti	2 S.D	δ ^{49/47} Ti	2 S.D	δ ^{50/47} Ti	2 S.D
	Terrestria	l and laboi	ratory sta	andards					
BHVO-2	6	0.10	0.02	-0.10	<i>0.0</i> 2	-0.20	0.04	-0.34	0.04
BHVO-2*	2	0.09	0.00	-0.08	0.00	-0.17	0.00	-0.30	0.02
BCR-2	6	0.11	0.02	-0.11	0.02	-0.22	0.03	-0.36	0.02
BCR-2*	2	0.12	0.02	-0.12	0.02	-0.24	0.04	-0.37	0.02
	_								
AGV-2	5	0.06	0.01	-0.06	0.01	-0.13	0.02	-0.22	0.03
AGV-2*	2	0.04	0.01	-0.04	0.01	-0.08	0.01	-0.13	0.04
Ti AA +		0.16	0.02	-0.17	0.00	-0.30	0.04	-0.45	0.06
Processed through colu	<u>imn</u>								
Ti AA #	2	0.01	0.03	-0.01	0.03	-0.01	0.07	-0.02	0.01
Ti Wire	2	0.02	0.05	-0.02	0.05	-0.04	0.09	-0.02	0.01

Ti AA solution measured relative to Ti AA

* Denotes samples spiked after column chemistry

+ measured relative to Ti wire and not processed through column

All 2 S.D values of 0.00 are less than 0.005

Table 2.5 displays the $\delta^{i/48}$ Ti isotope composition of the samples relative to Ti wire double spike solution for samples spiked before column chemistry (BCC-blue) and those of a different aliquot of the same sample spiked after column chemistry (ACC-black). The results of Ti AA+ and Ti AA# within tables 2.4 and 2.5 demonstrate that the Ti AA+ which was not processed through the column displays the true stable composition as column induced fractionation has not occurred.

Samples #	# of measurements	$\delta^{46/48}$ Ti	2 S.D	δ ^{47/48} Ti	2 S.D	δ ^{49/48} Ti	2 S.D	δ ^{50/48} Ti	2 S.D	
Terrestrial and laboratory standards										
BHVO-2	6	0.20	0.03	0.10	0.01	-0.10	0.01	-0.19	0.03	
BHVO-2*	2	0.17	0.00	0.08	0.00	-0.08	0.00	-0.16	0.00	
BCR-2	6	0.22	0.03	0.11	0.02	-0.11	0.02	-0.21	0.03	
BCR-2*	2	0.25	0.04	0.12	0.02	-0.12	0.02	-0.24	0.03	
AGV-2	5	0.13	0.01	0.06	0.01	-0.06	0.01	-0.13	0.01	
AGV-2*	2	0.08	0.01	0.04	0.01	-0.04	0.01	-0.08	0.01	
Ti AA +	2	0.34	0.00	0.17	0.00	-0.16	0.00	-0.33	0.00	
Processed through co	lumn_									
Ti AA #	2	0.01	0.07	0.01	0.03	-0.01	0.03	-0.01	0.06	
Ti Wire	2	0.04	0.09	0.02	0.05	-0.02	0.05	-0.04	0.09	

Table 2.5. Titanium stable isotope data relative to the Ti wire standard displayed as $\delta^{i/48}$ Ti.

Ti AA solution measured relative to Ti AA

* Denotes samples spiked after column chemistry

+ measured relative to Ti wire and not processed through column

All 2 S.D values of 0.00 are less than 0.005

2.6.3.2. Mass dependent Ti isotope analysis of single-element standards and terrestrial standards

Several measurements were made in order to calibrate the Ti isotope composition of Ti wire relative to the Ti AA solution (Table 2.4 and 2.5, Fig. 2.5). Analysis reveals that the isotopic composition of Ti wire is similar to Ti AA # within analytical uncertainty. However Ti AA + which was not passed through the column procedure displayed $\delta^{49/47}$ Ti of -0.30 ± 0.04 which is the true stable Ti composition of the Ti AA standard solution. The two basalts BHVO-2 and BCR-2 display stable Ti isotope compositions of $\delta^{49/47}$ Ti of -0.20±0.04 and -0.22±0.03 respectively compared to a $\delta^{49/47}$ Ti of -0.13±0.02 for AGV-2. The data indicates that the andesite AGV-2 experienced a different fractionation process compared to the two terrestrial basalts.

2.6.3.3. Analysis of terrestrial standards

From Figure 2.5 we observe that significant fractionation has occurred to the laboratory standards as would be expected from purified laboratory standards. Figure 2.5 shows the double spike results for the Ti single element standards and terrestrial standards.



Figure 2.5. Displays the $\delta^{49/47}$ Ti isotope compositions of Ti AA standard solution and Ti wire along with the terrestrial rock standards. The error bars denote the (2 SE) uncertainty limits associated with the combination of mass independent and double spike procedure. All samples displayed were spiked Before Column Chemistry (BCC) except for Ti + which was not put through column chemistry. Ti AA was measured relative to Ti AA. Ti AA + was measured relative to Ti wire.

The following data was obtained from the procedure set forward in section 2.5.4 where mass independent data is combined with the double spike data to produce mass dependent data for terrestrial and laboratory standards and absolute nucleosynthetic data for meteorite data. The data is displayed in the ε notation and is the deviation in parts per ten thousand from the measured standard. From table 2.6 and table 2.7 it is evident that mass dependent variations exist between the two investigated basalts (BHVO-2 and BCR-2) and the andesite AGV-2.

Table 2.6. Evaluated double spike data displaying mass dependent fractionation data for terrestrial standards as $\epsilon^{i/47}$ Ti. Solar system materials display both mass dependent

Sample	Туре	Number	ε ^{46/47} Ti	2 SE	ε ^{48/47} Ti	2 SE	ε ^{49/47} Ti	2 SE	ε ^{50/47} Ti	2 SE
Terrestrial a	nd laboratory standards				-		-			
BHVO-2	Basalt	6	0.96	0.08	-1.16	0.04	-2.23	0.03	-3.23	0.08
BHVO-2 *	Basalt	2	1.02	0.07	-0.99	0.03	-2.01	0.20	-3.06	0.02
BCR-2	Terrestrial Basalt	6	1.12	0.16	-1.21	0.06	-2.22	0.01	-3.34	0.01
BCR-2 *	Terrestrial Basalt	2	1.33	0.04	-1.25	0.02	-2.60	0.10	-3.86	0.08
AGV-2	Andesite	5	0.60	0.03	-0.78	0.18	-1.55	0.23	-2.38	0.20
AGV-2 *	Andesite	2	0.41	0.18	-0.47	0.07	-0.90	0.41	-1.39	0.49
Ti wire	Laboratory standard	2	0.20	0.15	-0.29	0.35	-0.42	0.26	-0.69	0.43
Ti AA	Laboratory standard	2	-0.01	0.14	-0.16	0.35	-0.06	0.22	-0.10	0.32
Ti AA #*	Laboratory standard	2	0.26	0.04	-0.42	0.25	-0.57	0.01	-0.87	0.02
Carbonaceo	us chondrites									
Murchison	Carbonaceous chondrite CM2	3	1.21	0.04	-0.82	0.11	-1.53	0.16	0.94	0.16
Murchison *	Carbonaceous chondrite CM2	2	1.30	0.13	-1.08	0.11	-2.07	0.01	0.06	0.18
Allende	Carbonaceous chondrite CV3	4	1.32	0.19	-0.72	0.11	-1.38	0.25	1.40	0.16
Allende *	Carbonaceous chondrite CV3	2	0.95	0.18	-0.37	0.14	-0.65	0.28	2.35	0.42
Allende *	Carbonaceous chondrite CV3	2	0.57	0.10	-0.04	0.13	-0.10	0.15	3.36	0.01

fractionation and nucleosynthetic anomalies. All samples except Ti AA are measured relative to Ti wire.

* Denotes samples spiked after column chemistry

Ti AA solution measured relative to Ti AA

Table 2.7. Mass dependent Ti isotope data for terrestrial standards expressed in	ε ^{i/48} Ti.
All samples except Ti AA are measured relative to Ti wire.	

Sample	Туре	Number	ε ^{46/48} Τί	2 SE	ε ^{47/48} Ti	2 SE	ε ^{49/48} Ti	2 SE	ε ^{50/48} Ti	2 SE
Terrestrial a	nd laboratory standards									
BHVO-2	Basalt	6	2.12	0.04	1.16	0.04	-1.07	0.01	-2.07	0.12
BHVO-2 *	Basalt	2	2.00	0.04	0.99	0.03	-1.02	0.23	-2.07	0.04
BCR-2	Basalt	6	2.32	0.10	1.21	0.06	-1.01	0.05	-2.13	0.05
BCR-2 *	Basalt	2	2.58	0.01	1.25	0.02	-1.35	0.13	-2.60	0.06
AGV-2	Andesite	5	1.38	0.15	0.78	0.18	-0.77	0.23	-1.60	0.04
AGV-2 *	Andesite	2	0.88	0.25	0.47	0.07	-0.43	0.34	-0.91	0.42
Ti wire	Laboratory standard	2	0.49	0.35	0.29	0.35	-0.13	0.28	-0.40	0.37
Ti AA	Laboratory standard	2	0.15	0.49	0.16	0.35	0.10	0.13	0.06	0.03
Ti AA #	Laboratory standard	2	0.68	0.28	0.42	0.25	-0.16	0.23	-0.45	0.23
Carbonaceo	us chondrites									
Murchison	Carbonaceous chondrite CM2	3	2.03	0.15	0.82	0.11	-0.70	0.05	1.77	0.06
Murchison *	Carbonaceous chondrite CM2	2	2.39	0.05	1.08	0.11	-0.99	0.10	1.15	0.26
Allende	Carbonaceous chondrite CV3	4	2.04	0.31	0.72	0.11	-0.66	0.16	2.12	0.09
Allende *	Carbonaceous chondrite CV3	2	1.33	0.31	0.37	0.14	-0.28	0.15	2.73	0.30
Allende *	Carbonaceous chondrite CV3	2	0.61	0.02	0.04	0.13	-0.06	0.02	3.40	0.11

* Denotes samples spiked after column chemistry

Ti AA solution measured relative to Ti AA

2.6.3.4. Analysis of carbonaceous chondrites

Tables 2.6 and 2.7 display the results of combining the the mass independent and double spike data for the different aliquots of Allende and Murchison. The results for samples spiked before column chemistry and the results for samples spiked after column chemistry are significantly different due to column chemistry induced fractionation processes. The amount of fractionation caused to the samples spiked after column chemistry varies and therefore only samples spiked before column chemistry can be evaluated for mass dependent fractionation effects. Figure 2.6 displays the effects of mass dependent fractionation and nucleosynthetic anomalies. The two carbonaceous chondrites display significant positive deviations on $\varepsilon^{50/48}$ Ti (Table 2.7) on which nucleosynthetic anomalies are known to reside (Chapter 2.6, Leya et al., 2008; Trinquier et al., 2009; Zhang et al., 2011). The data indicates that the Ti isotope data obtained in this study are more precise due to the increase in precision to less than 20ppm achieved utilising a modern MC-ICPMS for the isotope analyses compared to 300ppm with a thermal ionization mass spectrometer (TIMS) utilised by Niederer et al. (1985).



Figure 2.6. The Ti isotope compositions obtained by double spike analysis of the carbonaceous chondrites Allende and Murchison. The data shows the mass dependent fractionation and nucleosynthetic anomaly data for the carbonaceous chondrites. Error bars denote the 2 SE uncertainties in the combination of mass independent and double spike data. Data from Niederer et al. (1985) also displayed for comparison. Dashed black line indicates mass dependent fractionation of 1 Epsilon unit per amu.

By utilising the kinetic fractionation equation by Wombacher and Rehkämper (2004) described in Section 2.5.5 it is possible to isolate the effects of the nucleosynthetic anomalies from the mass dependent fractionation to display the absolute nucleosynthetic anomalies that occur within solar system material. The absolute nucleosynthetic variations found by utilising the double spike technique for Allende and Murchison are within error of the values found using the mass independent technique. The new absolute nucleosynthetic variations within the carbonaceous chondrites Allende and Murchison are displayed in Figure 2.7 in which the data has been modified to utilise the ⁴⁸Ti as the denominator. The data reported within this study demonstrates that $\varepsilon^{46/48}$ Ti and $\varepsilon^{50/48}$ Ti are enriched relative to all other Ti stable isotopes.



Figure 2.7. The absolute nucleosynthetic anomaly data for Allende and Murchison from this study (Black symbols). Uncertainties are reported as 2.S.E

2.7. Conclusion

The double spike technique was utilised for the analysis of Ti isotopes within terrestrial and solar system materials. The main aim of the study was to overcome the instrumental mass bias problems encountered during mass independent analysis and isolate the absolute nucleosynthetic variations that exist among solar system materials. Two single element laboratory standards Ti AA and Ti wire as well as three terrestrial reference samples were analysed to test the method. Relative to previous Ti tracer method by Niederer et al. (1985), this technique makes significant improvements regarding both the ease of measurement and the precisions obtained which are an order of magnitude better, as is evident from the analysis of the whole rock carbonaceous chondrites Allende and Murchison which have precisions greater than 20ppm in this study compared to less than 200ppm in the study by Niederer et al. (1985). Results obtained from repeated measurements of the Ti Wire standard solutions were consistent over several measurement sessions giving an average precision for $\delta^{49/47}$ Ti of 0.02.

The results obtained for the terrestrial reference samples showed that mass dependent fractionation effects do exist between the two terrestrial basalts BHVO-2 and BCR-2 and the andesite AGV-2 indicating that the Ti double spike procedure is a valid technique to study igneous processes.

The double spike methodology was used in conjunction with the kinetic fractionation equation of Wombacher and Rehkämper. (2004) in order to isolate absolute nucleosynthetic variations that exist among solar system materials. The two carbonaceous chondrites Allende and Murchison both displayed positive nucleosynthetic anomalies for $\varepsilon^{46/48}$ Ti and $\varepsilon^{50/48}$ Ti and correlates well with the previous mass independent Ti studies of Trinquier et al. (2009) and Zhang et al. (2012).

2.8. Acknowledgements

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Chapter 3:

Nucleosynthetic sources of titanium and zirconium isotope variations within solar system materials

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3.1. Abstract

The Ti isotope composition of calcium-aluminium rich-refractory inclusions (CAI's) and a suite of whole rock solar system materials were investigated in order to identify nucleosynthetic variations arising from particular stellar sources. These new Ti isotope data are combined with previously published Zr isotope data that were obtained on the same sample aliquots in order to determine the nucleosynthetic origin of the nucleosynthetic Zr and Ti anomalies.

Whole rock analysis of Ti utilising the ⁴⁹Ti/⁴⁷Ti ratio for internal mass bias correction revealed a best fit line with a slope of 5.34 \pm 0.34 in the $\epsilon^{50/47}$ Ti_{49/47} versus $\epsilon^{46/47}$ Ti_{49/47} diagram for carbonaceous chondrites, achondrites, eucrites, enstatite, ordinary chondrites and components digested using the Parr Bomb[®] technique and the results are in good agreement with the previous studies (Trinquier et al., (2009), Zhang et al., (2011)). The carbonaceous chondrite Murchison was digested using the microwave and the Parr Bomb techniques. The results show a larger Ti isotope anomaly for $\varepsilon^{50/47}$ Ti_{49/47} of 5.12 ± 0.14 compared to 3.03 ± 0.08 when using the microwave digestion technique. This suggests that the microwave technique was unable to completely dissolve all the presolar refractory phases. The CAI's display the largest positive anomalies for $\epsilon^{50/47}$ Ti_{49/47} of 9.54 ± 0.02 and $\epsilon^{46/47}$ Ti_{49/47} of 1.74 ± 0.05. Carbonaceous chondrites display a positive trend principally controlled by the CAI content. Enstatite chondrites overlap terrestrial Ti isotope ratios within uncertainty, as do lunar samples. Ordinary chondrites and achondrites exhibit negative Ti isotope variations. Plotting the results of ^{96/90}Zr_{94/90} from the corresponding Zr study (Akram et al., 2014, submitted) against ^{50/47}Ti_{49/47} confirmed that one carrier phase of the Ti and Zr bulk rock anomalies are the CAIs, although these inclusions are not the only carrier that generates nucleosynthetic anomalies in Ti and Zr isotopes.

Nucleosynthetic models were evaluated and the results show that the whole rock $\epsilon^{50/47}$ Ti_{49/47} - $\epsilon^{46/47}$ Ti_{49/47} correlation can be produced in the He/C, O/Ne and O/C zones of a 25M₀ SN II core collapse supernovae. Models of the total yields for AGB and SNIa stars were also evaluated. Whereas the SNIa models were unable to reproduce the whole rock Ti correlation, a three solar mass AGB star (where the *s*-process is likely to occur) was able to reproduce the whole rock Ti correlation. However, the observed correlation of Zr and Ti enrichment cannot be solely explained by one stellar model.

3.2. Introduction

Calcium aluminium rich inclusions (CAI's) were likely the first materials to form in the protoplanetary disk by condensation and evaporation (Gray et al., 1973). They were created over 4.568 billion years ago (Bouvier and Wadhwa, 2010) and are major components within chondritic materials (Rubin et al., 2011). These early solar system components formed from material with a chemical memory of the nucleosynthetic processes which created them (Clayton, 1982). Each stellar source produces a unique isotopic signature as different nuclear fusion processes occur within them (Burbidge et al., 1957; Cameron, 1957). These isotopic signatures were then preserved within the dust that was further mixed and heated during the collapse of the protostellar cloud from which then the first solar system components were formed via condensation (Alexander, 2004).

Titanium is a refractory lithophile element that is part of the iron group of elements that have nuclear binding energies close to the maximum and provide clues to understanding late stage hydrostatic and/or explosive burning phases in stellar interiors (Meyer et al., 1995). Previous studies have examined isotopic anomalies within different types of CAI's and chondritic material for a variety of elements such as O (Clayton, 1993), Cr (Trinquier et al., 2007), Ni (Steele et al., 2010), and Zr (Akram et al., 2013; Akram et al., 2011b; Schönbächler et al., 2003) in order to identify their nucleosynthetic source. The correlations observed for the neutron rich isotopes of ⁴⁸Ca (Lee et al., 1978), ⁵⁴Cr (Papanastassiou, 1989), ⁵⁸Fe ((Volkening and Papanastassiou, 1989)) and ⁵⁰Ti (Niederer et al., 1980) within the fractionated unknown nuclear (FUN) CAI EK-1-4-1 have pointed to a common nucleosynthetic source. The unique isotopic pattern found within FUN inclusions is mixed with a variety of other possible carrier phases from other early solar system condensates to create the isotopic signature found in bulk solar system materials. It was proposed that the neutron rich isotopes of ⁵⁰Ti, ⁵⁴Cr, ⁶⁴Ni and ⁵⁸Fe were produced in large quantities by nuclear statistical equilibrium and quasi statistical equilibrium within SN Ia stars (Woosley, 1997). Recent studies of Zr isotopes (Akram et al., (2011a), Schönbächler et al., (2003)) also revealed excesses in the neutron rich isotope ⁹⁶Zr for bulk solar system material. The ⁹⁶Zr isotope is unlikely to be produced in SN Ia stars (Meyer et al., 1996). Hence potential correlations of ⁵⁰Ti and ⁹⁶Zr allow us to distinguish between the nucleosynthetic sources that generated the bulk rock anomalies.

Previous work (Leya et al., 2007; Trinquier et al., 2009; Zhang et al., 2011) showed that Ti isotope variations exist among inner solar system solids, planets and asteroids. Former studies report data for CAIs, carbonaceous chondrites, enstatite, ordinary chondrites,

achondrites, samples from the Moon, from Mars and terrestrial standards. All samples apart from enstatite chondrites and lunar samples display correlated variations in $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{46/47}$ Ti_{49/47} (Trinquier et al., 2009; Zhang et al., 2012). Trinquier et al. (2009) inferred that the $\varepsilon^{50/47}$ Ti_{49/47} v $\varepsilon^{46/47}$ Ti_{49/47} correlation resulted from thermal processing events also responsible for the depletion of moderately volatile elements in the matrices of carbonaceous chondrites. The thermal processing would also result in preferential loss by sublimation of thermally unstable presolar silicates which contained the ⁴⁶Ti and ⁵⁰Ti excesses. This implies that nucleosynthetic anomalies in meteorites may reflect the degree of thermal processing experienced by their precursor material and not initial disk heterogeneity. In addition Leya et al. (2009) reported ⁵⁰Ti excesses in oxidised and reduced CAIs of Allende and Efremovka that correlated with variations in ⁹⁶Zr (Schönbächler et al., 2003) and ⁶²Ni (Quitte et al., 1997) indicating an origin from a neutron rich stellar source.

The energies required for the production of Zr and Ti isotopes can be found in thermally pulsing asymptotic giant branch (TP-AGB) stars through the *s*-process. The *s*-process requires environments with neutron densities of typically $10^{6}-10^{11}$ cm⁻³ to occur (Lugaro et al., 2003). The *s*-process is predicted to predominantly occur in the He-burning shells of TP-AGB stars (Burbidge et al., 1957). At this site the reaction 22 Ne (α , n) 25 Mg occurs that releases abundant amounts of neutrons to fuel the creation of 46 Ti, 47 Ti, 48 Ti 49 Ti and even 50 Ti (Gallino et al., 1998). The activation of 22 Ne (α , n) 25 Mg within TP-AGB also results in significant production of 96 Zr (Akram et al., 2013) with Travaglio et al. (2011) accrediting 82% of the solar systems 96 Zr to low and intermediate mass AGB stars. Thermally pulsing asymptotic giant branch stars experience thermal pulses due to helium flashes (Schwarzschild and Harm, 1965). During the TP-AGB phase stars suffer significant mass loss through stellar winds, providing suitable conditions for the formation of dust. This dust contains isotopic and elemental signatures that reflect the composition of the star when the thermal pulsing occurs (Ferrarotti and Gail, 2006; Gail et al., 2009).

Stars whose mass is $< 8 \text{ M}_{o}$ (where $\text{M}_{o} =$ solar mass) are not large enough to produce the temperatures and densities required for further hydrostatic mainstream burning beyond the iron peak evolve into white dwarfs. They eject so much material during the planetary nebula phase that their lives end as electron degenerate C-O white dwarfs. In a binary system the C-O white dwarf may accrete enough mass to initiate explosive C and O burning where the main components C and O making up the star fuse. These violent events are termed Type Ia supernovae (Whelan and Iben, 1973). Disintegration reactions break some of the nuclei down

to fundamental alpha, proton and neutron particles. The temperature and pressures involved in Si burning allow equilibrium conditions to develop were nuclear reactions occur quickly between all nuclear species and light particles. Quasi statistical equilibrium (QSE) develops when all nuclear species heavier than C are in equilibrium under exchange of light particles (Meyer and Zinner, 2006). In such equilibrium conditions neutron rich iron group elements such as ⁵⁰Ti, ⁵⁴Cr, ⁵⁸Fe and ⁶⁴Ni isotopes increase in abundance (Meyer et al., 1996). As an iron core has now developed in the star, further synthesis of elements does not occur by hydrostatic equilibrium. Shock heating of the Si-rich layer drives explosive Si burning. In the innermost regions where extreme densities exist, the heating is sufficient for the matter to achieve NSE. The expansion and cooling is sufficiently rapid to leave a large abundance of free alpha particle. This expansion is thus known as the alpha rich freeze out from NSE, some reassembly of the free alpha particles occurs in the late stages of the freeze-out, which creates abundant ⁴⁴Ti. In the outer layers of the Si shell, the matter is less heated from the passing of the shock. In the oxygen rich layers explosive burning occurs at even lower temperatures than explosive Si burning. These regions can develop significant production of the isotopes ⁴⁴Ti and ⁴⁸Ti. Niederer et al. (1980) inferred from the distinct correlation between the neutron rich isotopes of Ca and Ti and the absence of substantial effects in ⁴⁶Ca in the FUN samples EK-1-4-1 and C-1, that the effects reflect QSE and NSE nucleosynthesis in the outer layers of a supernova core.

Massive stars ($M_{\odot}>8$) can end their lives by a second type of explosion, termed gravitational collapse in which part of the star falls down and transfers energy to the remaining layers. Filippenko (1997) classified the supernovae as Type II, Ib, Ic based on their light curves. Stars with masses greater than $M_{\odot}>8$ have large enough temperatures and pressures to hydrostatically process H all the way to Fe which leads to the classical 'onion' shape model for large stars (Fig. 3.1). Niemeyer and Lugmair (1981; 1984) inferred the sources of the excesses in $^{50/46}$ Ti_{48/46} were due to relative enrichment of isotopes synthesized during hydrostatic burning in or near the core of a massive star, while an s-process mechanism was proposed as a viable source for the anomalies on the neutron poor Ti isotopes. The authors argue that the Ti isotope anomalies are linked to the diversity of nucleosynthetic sources found in the interstellar medium rather than a late stage supernova injection model that is responsible for the preservation of observed isotopic heterogeneities.



Figure 3.1. Schematic illustration of the 'onion' like shell structure of the interior of a $25M_{\odot}$ SNII core collapse Supernova pre collapse. The red mass numbers relate to the cumulative remnant mass below that zone. From Meyer. (1995) and Rauscher et al. (2012) data

Correlations between anomalies in ⁹⁶Zr and ⁵⁰Ti within CAI's were identified by several authors (Akram et al., 2013; Harper et al., 1990; Leya et al., 2009) which possibly indicates a common stellar source for their production. An initial objective of this study is to obtain high precision Ti isotope data of carbonaceous chondrites, ordinary chondrites, eucrites, enstatite, ureilites, lunar, terrestrial and early solar system components and identify potential correlations between Ti and Zr isotopes in other solar system materials than CAIs. Subsequently nucleosynthetic models were evaluated to determine the stellar origin of the correlated Ti and Zr isotope variations. We address this issue by utilising various nucleosynthesis models of SNII, SN Ia and AGB stars to recreate the observed isotopic signature found in CAI's and solar system materials.

3.3 Analytical Procedure

3.3.1. Sample Preparation

All chemical procedures were undertaken in a class 1000 clean room at the University of Manchester. Fragments weighing approximately 100 to 300 mg were extracted from meteorite samples and then crushed to a fine powder with an agate pestle and mortar under

laminar air flow. Samples were then digested using HF-HNO₃ acid mixtures (3:1) in Teflon beakers in a Parr Bomb[®] at 170°C in the framework of the study of Akram et al. (2014). A modified ion exchange chromatographic procedure from Schönbächler et al. (2004) was used to separate both Ti and Zr from the sample aliquot. The method is described in section 2.3.2. The Ti chemical separation procedure employed ensured yields in excess of 90% which was calculated by comparing referenced Ti content within individual meteorite samples and against the measured Ti content of aliquots obtained from the final ion exchange step. Full procedural blanks averaged 3 ng with a range of between 0.6 and 16ng. This is negligible compared to the 100 μ g of Ti typically processed through the column for a single sample.

3.3.2. Mass spectrometry

High precision Ti isotope measurements were performed on a suite of solar system materials utilising a Neptune multiple collector ICP mass spectrometer (MC-ICPMS) at the Open University. Measurements were recorded using the sample standard bracketing technique, where a Ti Alfa Aesar solution (Ti AA) was used as a terrestrial standard, in 500ppb solution. Samples and standards were introduced via an Aridus II desolvating nebuliser system in dilute HNO₃-HF mixtures using argon as sweep gas. Measurements were carried out over 2 cycles to allow for interference corrections from V, Cr and Ca. This corresponded to using ⁴⁷Ti and ⁵⁰Ti as axial masses in cycle 1 and 2, respectively. In the main cycle ⁴⁴Ca, ⁴⁵Sc, ⁴⁶Ti, ⁴⁷Ti (axial), ⁴⁸Ti, ⁴⁹Ti and ⁵⁰Ti were measured with an integration time of 8.4s comprising of 40 blocks of measurements. In the second cycle ⁵⁰Ti (axial), ⁵¹V and ⁵³Cr were collected with an integration time of 4.2s comprising of 40 blocks of analysis. Measurements were conducted in medium resolution (MR) and high resolution (HR) modes, where MR typically gave a mass resolution of M/ Δ M <10000 while HR gave a mass resolution of M/ Δ M>10000. On peak backgrounds were measured in 0.5 M HNO₃ + 0.005 M HF wash solutions and were subtracted from the analyte beam intensities during data processing. The Ti isotope ratios were internally normalised to ${}^{49}\text{Ti}/{}^{47}\text{Ti}=0.749766$ (Niederer et al., 1981) with results reported in the ε notation using the sample standard bracketing technique relative to the Alfa Aesar standard (equation 3.1).

$$\varepsilon^{i/47} \mathrm{Ti}_{49/47} = \left(\left(\frac{i^{47} \mathrm{Ti}_{49/47} \, \mathrm{Sample}}{\left(\frac{i^{47} \mathrm{Ti}_{49/47} \, \mathrm{Sample} \, (B) + i^{47} \mathrm{Ti}_{49/47} \, \mathrm{Sample} \, (A) \right)/2} \right) - 1 \right) * 10,000$$
(3.1)

The ε notation is defined as the difference in parts per ten thousand between the sample and the standards. The average of the standards measured before (B) and after (A) are used to correct for drift during the measurements. Uncertainties are reported as 2SE, were the 2 x standard deviation value from multiple analyses over several measurement sessions are divided by the square root of the number of analysis. The analytical procedure for the complementary study of Zr isotopes is described in Akram et al. (2013a). For comparison of the Ti data from this study with the Zr data of Akram et al. (2011a) weighted averages of meteorites classes were calculated utilising equation (3.2), where x is the weighted average of individual meteorites within the class and where e is the 2 standard error value of the corresponding individual meteorites within the class:

$$\overline{\mathbf{X}} = \frac{\left(\frac{\mathbf{x}_1}{\mathbf{e}_1^2} + \frac{\mathbf{x}_2}{\mathbf{e}_2^2} + \dots + \frac{\mathbf{x}_n}{\mathbf{e}_n^2}\right)}{\left(\frac{1}{\mathbf{e}_1^2} + \frac{1}{\mathbf{e}_2^2} + \dots + \frac{1}{\mathbf{e}_n^2}\right)}$$
(3.2)

The corresponding weighted uncertainty calculated for the associated errors were derived by using equation (3.3),

$$2\sigma = 1/\sqrt{\left(\frac{1}{e_1^2} + \frac{1}{e_2^2} + \dots + \frac{1}{e_n^2}\right)}$$
(3.3)

3.3.3. Interference correction

This study investigated the effect of adapting established ratios used by Leya et al. 2009 and Trinquier et al., 2009 as opposed to those set forward by Zhang et al. (2011) for the isobaric interferences in order to obtain precise and reproducible results. Zhang et al. (2011) examined established ratios of ^{46/44}Ca, ^{48/44}Ca, ^{50/51}V and ^{50/53}Cr from literature and adapted the values to improve the correction procedure for isobaric interferences on ⁴⁶Ti, ⁴⁸Ti and ⁵⁰Ti. To check the accuracy of interference corrections on the Neptune MC-ICPMS, solutions of our Ti standard were run variably doped with 10 ppb, 25 ppb and 50 ppb of Ca, V and Cr (Fig. 3.2). We explored the influence of altering interference ratios from those stated by Trinquier et al. (2009) for ^{46/44}Ca, ^{48/44}Ca, ^{50/51}V and ^{50/53}Cr of 0.0019175, 00.0896453, 0.002506 and 0.45732 respectively to the ratios proposed by Zhang et al. (2011) of 0.001522, 0.089765, 0.002309 and 0.45791. As seen in figure 3.1 the results were identical for the $\varepsilon^{46/44}$ Ca, ^{48/44}Ca, ^{48/44}Ca ratios. However, the $\varepsilon^{50/47}$ Ti_{49/47} differs when the two different sets of ratios are utilised for ^{50/51}V and

^{50/53}Cr. The natural ratios used by Trinquier et al. (2009) gave more reproducible results at higher interference levels than those proposed by Zhang et al. (2011).



Figure 3.2. The $\epsilon^{46/47}$ Ti49/47, $\epsilon^{48/47}$ Ti49/47 and $\epsilon^{50/47}$ Ti49/47 values for doped Ti AA standard. The data illustrates the influence of the two different interference correction ratios proposed by Trinquier et al. (2009) (squares) to Zhang et al. (2011) (triangles) when doping terrestrial 1 ppm Ti standards with 10 ppb, 25 ppb and 50 ppb solutions of V, Cr and Ca.

When utilising the natural ratios stated by Trinquier et al. (2009) the isobaric correction procedure was able to correct for impurity ratios as high as ${}^{44}\text{Ca}+/{}^{48}\text{Ti}+$ = 0.0048, ${}^{51}\text{V}+/{}^{48}\text{Ti}+$ = 0.13, ${}^{53}\text{Cr}+/{}^{48}\text{Ti}+$ = 0.0178. Therefore the natural ratios stated by Trinquier et al. (2009) were used in this study. Sample solutions with high concentrations of Ca, V and Cr for which the correction scheme breaks down where passed through the first column of the ion exchange procedure again to separate the interfering element from Ti.

3.4. Results

Table 3.1. Displays the $\varepsilon^{46/47}$ Ti_{49/47}, $\varepsilon^{48/47}$ Ti_{49/47} and $\varepsilon^{50/47}$ Ti_{49/47} results for all terrestrial and meteorite samples measured.

Sample	Type	N	s ^{46/47} Ti.ou-	2 SE	s ^{48/47} Ti	2 SF	s ^{50/47} Ti	2 SF
Sampie	Турс		E 1149/47	2 5 E	с 11 <u>49/4</u> 7	236	с 1149/47	236
	64 J J J 4	<u>Terrestrial sa</u>	<u>mples</u>	0.04	0.16	0.01	0.00	0.04
Titanium Alfa Aesar standard Titanium wire Alfa Aesar	Standard solution	2	-0.07	0.04	-0.16	0.21	-0.09	0.04
Frantum wite Ana Aesar	Standard Solution	2	-0.00	0.51	-0.25	0.27	-0.00	0.07
BHVO-2 *	Basalt (USGS)	2	0.05	0.10	-0.03	0.16	-0.01	0.32
BHVO-2	Basalt (USGS)	2	-0.19	0.04	-0.08	0.10	0.01	0.03
weighted mean BHVO-2			-0.16	0.04	-0.07	0.09	0.01	0.03
BCR-2 *	Basalt (USGS)	4	-0.09	0.05	0.09	0.08	0.01	0.07
BCR-2	Basalt (USGS)	2	-0.06	0.10	-0.19	0.13	-0.04	0.03
weighted mean BCR-2			-0.08	0.04	0.01	0.07	-0.03	0.03
ACV 2 *	Andesite (USCS)	2	0.05	0.05	0.03	0.16	0.04	0.04
AGV-2 AGV-2	Andesite (USGS)	23	-0.16	0.02	0.01	0.10	0.04	0.04
weighted mean AGV-2			-0.14	0.02	-0.01	0.12	0.03	0.03
Cody Shale *	Shale (USGS) Shale (USCS)	4	-0.01	0.04	0.01	0.06	-0.06	0.16
Cody Shale *	Shale (USGS)	2	-0.05	0.15	0.06	0.11	-0.10	0.12
weighted mean Cody Shale			-0.06	0.01	0.01	0.05	-0.04	0.09
Weighted mean Earth			-0.08	0.01	0.00	0.03	0.00	0.02
		Lunar sam	nles					
15555	Olivine norm mare basalt	3	0.01	0.12	0.09	0.16	-0.11	0.09
		Carbonaceous c	hondrites					
Orgueil *	CI	4	0.28	0.09	0.04	0.15	2.01	0.15
Orgueil *	CI	4	0.21	0.13	-0.10	0.10	1.79	0.12
weighted mean Orgueil and CI			0.26	0.07	-0.05	0.08	1.8/	0.09
Murchison *	CM2	6	0.32	0.11	-0.03	0.08	2.94	0.10
Murchison	CM2	3	0.51	0.18	-0.04	0.15	3.17	0.12
Weighted mean Murchison			0.37	0.09	-0.03	0.07	3.03	0.08
Murchison (Microwave)			0.50	0.17	-0.06	0.12	5.12	0.14
Murray *	CM2	4	0.45	0.09	-0.05	0.11	3.01	0.14
Murray *	CM2	2	0.54	0.19	0.10	0.19	3.42	0.03
weighted mean Murray			0.47	0.08	-0.01	0.10	3.40	0.03
Cold Bokeveld	CM2	4	0.50	0.10	-0.06	0.12	3.25	0.04
Weighted mean group CM			0.45	0.05	0.03	0.05	3 3 2	0.02
Weighten mean group CM			0.45	0.05	-0.05	0.05	5.52	0.02
Allende *	CV3	4	0.62	0.05	0.03	0.11	3.39	0.18
Allende	CV3	3	0.56	0.20	0.03	0.09	3.77	0.06
Allende * weighted mean Allende	CV3	2	0.57	0.17	-0.05	0.14	3.25	0.10
"eightea mean rhienae			0101	0100	0101	0100	5101	0100
Grosnaja*	CV3	4	0.46	0.05	-0.03	0.06	2.80	0.10
Vigarano*	CV3	4	0.55	0.14	-0.10	0.05	3.43	0.13
Weighted mean CV			0.53	0.03	-0.05	0.03	3.44	0.04
CRA 06100*	CR2	4	0.37	0.07	-0.05	0.15	2 19	0.20
EET 92159*	CR2	4	0.41	0.04	-0.07	0.07	1.66	0.18
Renazzo*	CR2	4	0.39	0.13	-0.06	0.13	1.59	0.13
Waiahtad maan CB			0.40	0.02	0.07	0.06	1.74	0.00
meignieu meun CR			0.40	0.03	-0.07	0.00	1./4	0.09
Bencubbin *	CB-A	4	0.29	0.16	-0.26	0.10	1.66	0.12
Bencubbin *	CB-A	2	0.34	0.05	-0.30	0.01	1.45	0.09
weighted mean Bencubbin and CB			0.33	0.05	-0.30	0.01	1.52	0.07
		Enstatite cho	ndrites					
Indarch*	EH4	4	-0.17	0.13	-0.08	0.04	-0.15	0.07
	FW4		0.07	0.12	. · · ·	0.00		0.17
Abee *	ЕН4 ЕН4	4	-0.06	0.12	0.11	0.09	-0.01	0.15
Weighted mean Abee		2	-0.10	0.11	0.12	0.02	-0.11	0.11
Weighted mean Enstatite		~ ~ ~	-0.13	0.08	0.08	0.02	-0.14	0.06
		<u>CAI's and cho</u>	ndrules	0.07	0.12	0.00	0.51	0.02
CALNVI CALNVI*	Allende CAI Allende CAI	3	1.73	0.05	0.42	0.09	9.54 9.52	0.02
Weighted mean CAI 1 NV	include 0.11	7	1.74	0.05	0.41	0.07	9.54	0.02
CAI NV 2* CAI NV 3*	Allende CAI	4	1.58	0.06	0.46	0.08	9.42	0.07
Allende Chondrules*	Allende chondrule separate	2	0.90	0.11	0.12	0.04	4.64	0.10

Sample	Туре	Ν	$\epsilon^{46/47} Ti_{49/47}$	2 SE	$\epsilon^{48/47} Ti_{49/47}$	2 SE	$\epsilon^{50/47} Ti_{49/47}$	2 SE
		Ordinary cho	ndrites					
St Severin*	LL6	2	-0.10	0.09	-0.01	0.04	-0.63	0.17
Forest Vale*	H4	4	-0.13	0.13	0.02	0.14	-0.56	0.11
Richardton	Н5	4	-0.15	0.19	-0.07	0.09	-0.46	0.14
Richardton*	Н5	2	-0.18	0.07	-0.02	0.07	-0.46	0.12
Weighted mean Richardton			-0.17	0.07	-0.04	0.05	-0.46	0.09
Allegan	Н5	4	-0.18	0.08	-0.07	0.13	-0.48	0.10
Weighted mean OC			-0.15	0.04	-0.02	0.03	-0.51	0.05
		<u>R-chondr</u>	<u>ite</u>					
NWA 755	R-chondrite 3.7	4	-0.07	0.07	-0.05	0.04	-0.47	0.04
NWA 753	R-chondrite 3.9	4	-0.03	0.09	-0.11	0.09	-0.41	0.14
Weighted mean R-chondrite			-0.05	0.06	-0.06	0.04	-0.47	0.04
		Achondri	tes					
Bouvante*	Eucrite-M	4	-0.27	0.04	-0.06	0.08	-1 33	0.09
Bereba*	Eucrite-M	6	-0.18	0.11	0.00	0.12	-1.35	0.14
Sioux county*	Eucrite-M	4	-0.20	0.10	0.12	0.11	-1.27	0.13
Juvinas	Eucrite-M	2	-0.39	0.02	0.13	0.08	-1.22	0.07
Juvinas*	Eucrite-M	2	-0.28	0.03	0.04	0.21	-1.31	0.01
Juvinas *	Eucrite-M	4	-0.47	0.22	0.03	0.16	-1.24	0.17
Weighted mean Juvinas			-0.36	0.02	0.10	0.07	-1.31	0.01
Cachari*	Eucrite-M	4	-0.18	0.11	0.10	0.15	-1.17	0.05
Pasamonte	Eucrite-P	2	-0.38	0.19	-0.10	0.24	-1.20	0.02
Pasamonte *	Eucrite-P	4	-0.29	0.14	0.00	0.07	-1.26	0.09
Weighted mean Pasamonte			-0.32	0.11	-0.01	0.07	-1.20	0.02
Weighted mean Eucrite			-0.33	0.01	0.03	0.04	-1.28	0.01
EET 96042	Ureilite	4	-0.35	0.05	-0.01	0.11	-2.05	0.06
Dhofar 125	Acapulcoite	4	-0.30	0.22	-0.04	0.03	-1.39	0.18
NWA 7325	Mercury**	3	-0.52	0.03	0.00	0.05	-1.74	0.11

* Sample aliquots taken from study of Zr by Akram et al (2013) **Classification taken from Irving et al (2014) in preparation N= Number of analysis

Table 3.2. Displays the $\varepsilon^{91/90}$ Zr_{94/90}, $\varepsilon^{92/90}$ Zr_{94/90} and $\varepsilon^{96/90}$ Zr_{94/90} results for all terrestrial and meteorite samples measured for Zr isotopes. Results from the complimentary study by Akram et al. (2013)

Sample	Туре	$\epsilon^{91/90}$ Zr _{94/90}	2 SE	$\epsilon^{92/90} Zr_{94/90}$	2 SE	$\epsilon^{96/90} Zr_{94/90}$	2 SE
				<u>Terrestrial sa</u>	mples		
BHVO-2	Basalt	-0.12	0.04	-0.08	0.03	0.18	0.08
AGV-2	Andesite	-0.01	0.11	-0.09	0.1	0.22	0.3
Cody Shale	Cody Shale	-0.06	0.02	-0.06	0.02	0.02	0.04
Weighted mean Earth		-0.07	0.02	-0.06	0.02	0.06	0.04
				I unar san	nlag		
15555	Olivine norm mare basalt	-0.07	0.07	-0.01	0.04	-0.06	0.15
			C	~~ b ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	h an duite		
Weighted mean Orqueil and (T.	-0.15	<u>0 12</u>	<u>urbonaceous c</u>	<u>nonariie</u> 01	<u>03</u>	0.22
Weighten mean Orguen and C	.1	-0.15	0.12	-0.05	0.1	0.5	0.22
Murchison (Parr bomb)	CM2	-0.02	0.05	-0.01	0.05	0.73	0.16
Murchison (Microwave)	CM2	-0.11	0.10	-0.27	0.14	0.19	0.36
Murray *	CM2	-0.01	0.12	0.12	0.15	0.58	0.29
Cold Bokeveld	CM2	-0.07	0.26	-0.2	0.21	1.18	0.63
Weighted mean group CM		-0.01	0.05	-0.01	0.04	0.72	0.14
Allende	CV3	0.13	0.05	0.02	0.04	1.11	0.11
Grosnaja	CV3	-0.18	0.3	-0.08	0.15	1.01	0.4
Weighted mean CV		0.12	0.05	0.02	0.04	1.1	0.11
FFT 02150	CD2	0.15	0.11	0.27	0.17	0.72	0.71
Renazzo	CR2	-0.13	0.08	-0.27	0.17	1.33	0.71
Weighted mean CR		-0.16	0.06	-0.12	0.09	1.16	0.38
Weighted mean Bencubbin an	d CB	-0.19	0.11	-0.08	0.12	0.96	0.24
				Enstatite cho	ndrites		
Indarch	EH4	0.09	0.15	-0.07	0.13	0.22	0.3
Abee	EH4	-0.09	0.08	-0.2	0.14	-0.25	0.38
Weighted mean Enstatite		-0.07	0.07	-0.13	0.1	0.04	0.23
Heighten menn Enstante		0.07	0.07	CAI's and cho	ndrules	0.04	0.25
Weighted mean CAL1 NV		0.06	0.05	-0.01	0.04	1.95	0.15
CALNV 2	Allende CAI	0.02	0.00	-0.04	0.07	2.27	0.32
CAI NV 3	Allende CAI	-0.11	0.07	-0.21	0.07	0.86	0.15
Allende Chondrules*	Allende chondrule separate	-0.08	0.37	-0.11	0.2	1.24	0.45
				Ordinary cha	ndrite		
St Severin*	LL6	-0.16	0.09	-0.15	0.1	0.34	0.17
Forest Vale*	H4	-0.16	0.12	-0.07	0.14	0.74	0.26
Richardton	H4	-0.19	0.08	-0.29	0.07	0.32	0.2
Weighted mean OC		-0.17	0.05	-0.22	0.05	0.41	0.12
				A chord-	tas		
Bouvante	Eucrite-M	-0.14	0.07	_0 19	0.06	0.5	0.16
Bereha	Eucrite-M	-0.14	0.07	-0.19	0.00	0.73	0.10
Sioux county	Eucrite-M	-0.13	0.00	-0.07	0.05	0.41	0.13
Juvinas	Eucrite-M	-0.09	0.09	-0.06	0.1	0.43	0.18
Pasamonte	Eucrite-P	0.02	0.08	-0.07	0.04	0.27	0.11
Weighted mean Fucrite		-0.11	0.03	-01	0.02	0.41	0.06

All measured meteorite samples display correlated variations in $\epsilon^{46/47} Ti_{49/47}$ and $\epsilon^{50/47}$ Ti_{49/47}, defining a best fit line with a slope of 5.34 ± 0.34 and intercept 0.19 ± 0.19 (Fig. 3.3). The correlation found by this study is in good agreement to previous works by Trinquier et al. (2009) and Zhang et al. (2011). Lunar and enstatite chondrites plot within uncertainty of the terrestrial smaples. Calcium aluminium rich inclusions display the largest excesses in $\epsilon^{50/47}$ Ti_{49/47} and $\epsilon^{46/47}$ Ti_{49/47} with a range of $\epsilon^{50/47}$ Ti_{49/47} values from 5.11 ± 0.15 to 9.54 ± 0.02. The analysed ureilites shows the largest deficit in $\varepsilon^{50/47}$ Ti_{49/47} and second largest deficit in $\epsilon^{46/47} Ti_{49/47}$ with -2.05 ± 0 .06 and -0.35 ± 0.05 respectively. Whole rock carbonaceous chondrites record a range of positive excesses in $\epsilon^{46/47}Ti_{49/47}$ and $\epsilon^{50/47}Ti_{49/47}$ with CI, CR and CB grouping together while CM and CV chondrites form another group (Fig. 3.3, 3.4). The largest Ti isotope variations within samples digested in a Parr Bomb are in the carbonaceous chondrites CV3 group and then decrease in the order CV3, CM2, CI, CR to CB-A. The ordinary chondrites and eucrites both display deficits in $\varepsilon^{46/47} Ti_{49/47}$ and $\varepsilon^{50/47} Ti_{49/47}$. Titanium isotope data of enstatite chondrites and one lunar sample plot within uncertainty of the terrestrial standard values around the origin at $\epsilon^{i/47}$ Ti_{49/47}=0. The chondrule separates from Allende displays an $\varepsilon^{50/47}$ Ti_{49/47} of +4.64 ± 0.10, which is close to the lowest $\varepsilon^{50/47}$ Ti_{49/47} of 5.11 ± 0.15 measured for CAI 3 NV. Refractory inclusions display $\varepsilon^{48/47}$ Ti_{49/47} values different to all bulk meteorites, which display a terrestrial $\epsilon^{48/47}$ Ti_{49/47} value when the ⁴⁹Ti/⁴⁷Ti ratio is utilised to correct for instrumental mass fractionation. Figure 3.5 displays $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} for the weighted means of the meteorite groups where clear sorting of classes and groups can be observed.



Figure 3.3. Plot displaying Ti isotope data for $\varepsilon^{50/47}$ Ti_{49/47} (y-axis) versus $\varepsilon^{46/47}$ Ti_{49/47} (x-axis) of individual solar system samples. Sample symbols are grouped to display meteorite classification. The data reveals the correlation found for solar system materials. Carbonaceous chondrites are divided into their classes of CI, CM, CV, CR and CB. The CM Murchison digested using the microwave digestion (grey) procedure is shown for comparison. Uncertainties are 2SE values and are only shown for $\varepsilon^{46/47}$ Ti_{49/47} as $\varepsilon^{50/47}$ Ti_{49/47} error values plot within symbols.

The $\varepsilon^{50/47}$ Ti_{49/47} isotope data for carbonaceous chondrites, chondrules and CAIs show similar behaviour as $\varepsilon^{96/90}$ Zr_{94/90} compositions for the same meteorites studied by Akram et al. (2011b) (Table 3.1 and Table 3.2). In figure 3.4, model abundances of refractory inclusions within chondrites from the work of Hezel et al. (2008) were plotted against the weighted mean values of $\varepsilon^{50/47}$ Ti_{49/47} from this study. The modal abundance data was then utilised within a mixing model to investigate the influence of the refractory inclusions on the variations observed for Ti and Zr isotopes. A mixing line was produced starting with the Ti isotope composition of the Earth with zero CAI content and finishing with the Ti isotope composition of CAI NV 1 and as 100% CAI content. The variations observed within all carbonaceous chondrite groups analysed for Ti and Zr do scale with CAI content; however the carbonaceous chondrite groups CR, CB and CV plot off the line suggesting the presence of an additional smaller component (Fig. 3.6).



Figure 3.4. Plot displaying Ti isotope data for $\varepsilon^{50/47}$ Ti_{49/47} (y-axis) for CAI's and different meteorite classes. The CAI modal abundance is displayed as a % beneath each class. CAI content data is from Hezel et al (2008).



Figure 3.5. Plot displaying Ti isotope data for $\varepsilon^{50/47}$ Ti_{49/47} (y-axis) versus $\varepsilon^{46/47}$ Ti_{49/47} (x-axis) of weighted mean values for the different meteorite groups, with the exception of CAI and chondrule data which are reported as individual data points. Uncertainties are reported as weighted means of the 2stdev.



Figure 3.6. Plot displaying the $\varepsilon^{50/47}$ Ti_{49/47} (This study, y-axis) against $\varepsilon^{96/90}$ Zr_{94/90} (Akram et al. 2011b, x-axis) of the results for the complementary studies on solar system materials. The weighted mean results for different meteorite groups are given for both $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{96/90}$ Zr_{94/90}. Two mixing lines are plotted: Earth-CAI (dots) and Eucrite-Earth (dash-dots) describing various admixing of CAI content to give correlated $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{96/90}$ Zr_{94/90}; Earth-Eucrite mixing line demonstrates a negative correlation possibly due to thermal modification of the carrier phases of the isotopic anomaly.

3.5. Discussion

3.5.1. Solar system material

Sample aliquots of the Murchison CM2 meteorite that were digested using a microwave revealed larger anomalies on $\varepsilon^{50/47}$ Ti_{49/47} than the corresponding sample that was digested utilising a Parr Bomb[®] (Table 3.1). We infer that the difference was caused by incomplete digestion of refractory grains within the matrix. The $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} data for the Murchison CM2 meteorite digested using the microwave does not plot on the solar system correlation line also indicating that the there is an additional presolar component possibly undissolved and missing from the result.

Measurements of CAIs lie on an extension of the Ti and Zr isotopic array defined by bulk meteorite data (Fig. 3.6). By modelling the mixing of variable amounts of CAIs to
terrestrial samples a correlation through the carbonaceous chondrites is observed via the hyperbola Earth - CAI mixing curve (Fig. 3.6). Figure 3.4 demonstrates that the variations observed for Ti for the different carbonaceous chondrite groups scale with CAI content. Therefore it can be inferred that the Ti and Zr isotope anomalies found within carbonaceous chondrites can mostly be explained by variable proportions of this isotopically anomalous component. An additional component is also required to account for the deviation off the mixing line observed for CR, CB and CV chondrites, most likely a presolar refractory component. The variable CAI content within different carbonaceous chondrite groups also explains the solar system heterogeneity evident in $\epsilon^{50/47}$ Ti_{49/47} versus $\epsilon^{46/47}$ Ti_{49/47} (Fig. 3.3 and 3.5). Leya et al. (2009) reported data for $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{96/90}$ Zr_{94/90} and inferred that ⁹⁶Zr, ⁶²Ni and ⁵⁰Ti display correlated anomalies in Allende CAI's, and also concluded that carbonaceous chondrites and CAI's sampled a different Ti isotope composition than the Bulk Silicate Earth (BSE). However the new data presented here clearly shows the existence of an additional component as new $\epsilon^{96/90}$ Zr_{94/90} Akram et al. (2011b) and $\epsilon^{50/47}$ Ti_{49/47} data obtained in this study on the same samples aliquots show that eucrites and ordinary chondrites are not identical to the Earth, Moon and Mars.

The CI carbonaceous chondrites have the lowest abundance of CAI's (; >1vol %) amongst the carbonaceous chondrites and display relatively small isotope variations within the Ti and Zr isotopic systems, whereas in the Cr (Trinquier et al., 2007) and Ni (Steele et al., 2012) isotope systems they display the largest anomalies amongst the carbonaceous chondrites. It can be inferred that CAIs are not a dominant repository of Ni or Cr anomalies and that the carrier phase of Ni and Cr isotope anomalies resides at least partly in different chondritic components.

The timing by which inherited Ti nucleosynthetic components were delivered into the solar system before its formation remains unclear. However, the patterns that are found between neutron rich Ti and other neutron rich isotopes of refractory elements such as Cr and Zr allow us to hypothesis models for the processes which occurred during solar system formation. Two simple scenarios are possible: incomplete homogenization of anomalous material in the protosolar nebula and unmixing of anomalous material from a previously well-mixed molecular cloud during nebula formation and processing. The finding that the neutron rich isotopes for Ti and Zr exhibit correlated large anomalies in CAIs, and by admixing variable amounts can account for the anomalies found for bulk carbonaceous chondrite groups, this strongly suggests that an important control on the presence of isotopic anomalies is the amount

of the carrier phase component in a particular chondritic group. Hence, it may be more plausible that the correlations represent differences in mixing processes found at different heliocentric distance for meteorite parent bodies. The ordinary and enstatite chondrites and eucrites display a negative correlation from the Earth value, which indicates that their accretion regions were either free of CAIs or their signature was thermally vaporised during accretionary processes. We also infer that the highly refractory CAIs, thought to have formed close to the proto-sun were preferentially removed from its close proximity to beyond the snow line by the X-wind perturbations to be incorporated within carbonaceous chondrites. The CAIs processed by the X-wind perturbations would have transported the enriched isotopic anomalies of ⁵⁰Ti and ⁹⁶Zr in CAIs to the carbonaceous chondrite formation zone whilst also depleting the anomalies within ordinary chondrites that formed at closer heliocentric distance.

3.5.2. Nucleosynthesis

The elements of the iron abundance peak are produced in large quantities in SN Ia stars with high central densities by NSE, (the e-process in (Burbidge et al., 1957). Nuclear statistical equilibrium and QSE can however also occur in SN II stellar interiors and these different nucleosynthetic environments will produce very large and contrasting isotope anomalies compared to the SN Ia environment (Meyer et al., 1996; Rauscher et al., 2002). Such nucleosynthetic components are recorded within presolar grains, which display isotopic anomalies many orders of magnitude larger than the solar system components such as CAI's and chondrules. Presolar grains where formed from material created from various stellar sources (Hoppe et al., 2010; Hoppe et al., 2009; Zinner et al., 2005). In order to assess the influence of adding such exotic material on isotope compositions in the Solar System, the contribution to all isotopes needs to be examined. In the following, such calculations, following the approach presented by Steele et al. (2012) for Ni isotope data, are performed for Ti isotopes. This will allow us to identify plausible nucleosynthetic components that can generate correlated Ti isotope anomalies in solar system materials.

An important consideration in the approach is accounting for variations on the normalising isotope ratio, in our case the ⁴⁹Ti/⁴⁷Ti. Solar system samples are corrected for natural and instrumental fractionation using the exponential law (equation 3.4).

$$R_{frac}^{49/47} = R_{ref}^{49/47} \left(\frac{m_{49}}{m_{47}}\right)^{\beta}$$
(3.4)

 $R_{ref}^{49/47}$ and $R_{frac}^{49/47}$ are the ratios of the natural reference material and a sample fractionated from that reference material respectively. Both the natural reference material and fractionated reference utilise the normalising ratios of ${}^{49}\text{Ti}/{}^{47}\text{Ti}=0.749766}$ (Niederer et al., 1981) and β is the exponential fractionation factor. In order to make the slope compatible with the relative data presented in nucleosynthetic models, the isotope ratios are normalised to their respective terrestrial ratios such that (equation 3.5),

$$\Delta S_{49/47}^{i/47} = S_{mix} - S_{frac} = \left(\frac{\left(R_{nuc}^{i/47}/R_{ref}^{i/47}\right) - 1}{\left(R_{nuc}^{49/47}/R_{ref}^{49/47}\right) - 1}\right) - \left(\frac{\ln(m_i/m_{47})}{\ln(m_{49}/m_{47})}\right) \quad (3.5)$$

Where S_{mix} , represents the mixing of a particular nucleosynthetic source $(R_{nuc}^{i/47})$ into solar system material ($R_{ref}^{i/47}$) where I can be ⁴⁶Ti, ⁴⁸Ti and ⁵⁰Ti. The input of the nucleosynthetic material is normalised by utilising the ratio ⁴⁹Ti/⁴⁷Ti of the nucleosynthetic source divided by the solar system material normalised ratio of ⁴⁹Ti/⁴⁷Ti = 0.749766 (Niederer et al., 1981). The second term, S_{frac} relates to the slope of fractionation given by the exponential law. In order to create an equation were the slope produced by a system of four, or more isotopes can be directly compared to that of the addition of different nucleosynthetic sources to the solar system, we divide $\Delta s_{49/47}^{i/47}$ by $\Delta s_{49/47}^{j/47}$ (equation 3.6) as given by Steele et al (2012).

$$\frac{\varepsilon_{49/47}^{i/47}}{\varepsilon_{49/47}^{j/47}} = \frac{\Delta s_{49/47}^{i/47}}{\Delta s_{49/47}^{j/47}}$$
(3.6)

In the case of Ti, *i* and *j* are the isotopes under examination ⁴⁶Ti, ⁴⁸Ti and ⁵⁰Ti respectively, while ⁴⁹Ti and ⁴⁷Ti are the normalising isotopes. Therefore the slope line of 5.34 \pm 0.34 from the $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} correlation discussed earlier can be compared to various nucleosynthetic environments in order to identify possible source regions responsible for Ti variations in bulk meteorites.

The isotopic composition of different astrophysical environments has been modelled by many studies. For the modelling we have used data for SNIa from Maeda et al. (2010) and Travaglio et al. (2011). Dynamic models of Type Ia supernova undergo Rayleigh-Taylor instabilities that likely cause large scale mixing of the stellar material (Maeda et al., 2010). The isotopic composition of a SN Ia is largely determined by the e-process or NSE and QSE where production of iron-group elements dominates at extreme densities (Meyer et al., 1996). This suggests that SN Ia are likely to give homogenised isotope ratios for iron group elements, implying a bulk treatment of its composition is warranted.

For SN II we have used data from Rauscher et al. (2002a). Supernovae II core collapse explosions are from much larger stars in the range of 8 - $70M_{\odot}$ where homogenization of the internal composition is less likely. As a consequence the modelling reflects the lack of homogenization of its internal composition and the model investigates the isotope anomalies found in individual shells of the SN II. Utilising the data of Rauscher et al (2002a) from the nucastro.org/nucleosynthesis, we were able to investigate the effects of varying the key reaction 22 Ne (α , n) 25 Mg (Table 3.3). Rauscher et al. (2002) computed isotopic abundances of $2x10^{31}$ g spherical shells of a range of SN II models (a28-a39), see http://nucastro.org. The models differ in that the value for the important reaction rate ²²Ne (α , *n*) ²⁵Mg is varied as its value at energy levels found within the astrophysical environment is still only inferred (Table 3.3). These shells can be treated in the same way as the bulk supernova models and the slope in mass-independent isotope space can be determined for variable mixing of a small amount of each shell into the Solar System. Full convection within the zones was assumed as the mass fractions within each zone were integrated to give the zonal yields. For the same reason as discussed in Meyer et al. (1995), namely a balance between galactic occurrence and mass ejected, we examine in detail a 25Mo supernova model. The stellar interior is divided into zones of primary nucleosynthetic reactions as defined by Meyer et al. (1995). A schematic illustration of the different zones within a 25 solar mass type II core collapse supernova is shown in figure 3.1 as described by Meyer et al. (1995) including illustration of the size of the zones given in solar mass units. The AGB data are presented as final isotopic composition for the bulk environment, using models from Cristallo et al. (2011).

Internal name	Reaction rate set
S25a27	RATH + suggested rate for 22 Ne(α ,n) 25 Mg from KAE
S25a28	RATH + KAE lower limit for ${}^{22}Ne(\alpha,n){}^{25}Mg$ rate (HWW)
S25a29	RATH + 88 CF 22 Ne(α ,n) 25 Mg rate
S25a30	RATH + NACRE
S25a31	RATH + NACRE with high 22 Ne(α ,n) 25 Mg
S25a32	HWW coprocessing ("490" isotope network,bdat921)
S25a33	RATH + JAE 22 Ne(α ,n) 25 Mg rate
S25a34	RATH+JAE ²² Ne(α ,n) ²⁵ Mg high rate
S25a35	RATH+JAE ²² Ne(α ,n) ²⁵ Mg low rate
S25a36	NACRE + improved fit for high 22 Ne(α ,n) 25 Mg rate
S25a37	NACRE + KAE lower limit 22 Ne(α ,n) 25 Mg rate (HWW)
S25a38	NACRE + JAE ²² Ne(α ,n) ²⁵ Mg rate but no (α , γ)
S25a39	RATH +no 22 Ne(α ,n) 25 Mg rate but KAE low "standard" (α , γ)
S25a40	RATH + no $^{16}O(n,\gamma)$ (modified bdat file)
S25a41	RATH + 59Fe(n, γ) rate reduced by 2 (modified bdat file)

Table 3.3: List of different nucleosynthetic models used from Rauscher et al. (2002).

Note:	
RATH=	T. Rauscher & FK. Thielemann, 2000, At. Data Nucl. Data Tables, 75, 1
NACRE=	C. Angulo et al., Nucl. Phys. A, 656, 3
HWW=	R. D. Hoffman, S. E. Woosley, & T. A. Weaver, 2001, ApJ, 549, 185; rate data
KAE=	F. Käppeler et al., 1994, ApJ, 437, 396
JAE=	M. Jaeger et al., 2001, Phys. Rev. Lett. 87, 202501

3.5.2.1. Models for SN type II

The production of Ti isotopes through a 25 M₀ SN II according to Rauscher et al. (2002) is shown in Figure 3.7, whereas the slopes of the correlation in $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} produced by mixing this material in to the Solar System is displayed in Figure 3.8 The addition of a mixture of material from the O/Ne and O/C zone from a SN II produces the same correlation slope in $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} as is found for bulk solar system meteorite samples (Fig. 3.3, 3.8). Utilising similar modelling techniques Qin et al. (2011) had proposed that the O/Ne and O/C match the ε^{54} Cr composition found for spinel in the CI chondrite Orgueil. Although the Ti isotope variations appear to be created in the same source region, the difference in condensation temperature between Ti (T_c=1634) and Cr (T_c=1301) could create separate phases in which these elements condensate. Steele et al. (2012) suggested for the source of Ni isotope heterogeneity in solar system material that the Si/S zone could reproduce the correlation found for $\varepsilon^{64/61}$ Ni_{58/61} versus $\varepsilon^{62/61}$ Ni_{58/61}. Taken at face value this suggests that the production of heterogeneities in the Ti and Ni isotope composition of solar system material are decoupled and not produced in the same zone of a supernova. However, models show that

different supernova shells could produce condensates with varying chemical and physical properties. These phases could then be processed during transport to the interstellar medium and subsequently thermally altered by the formation of the protostellar disk (Cassen and Moosman, 1981) and a consequence of this is that only the most refractory of phases would retain the cosmic chemical memory of the source, as less refractory phases would be thermally vaporised.



Figure 3.7. Mass fractions of a supernova type II S25a27 shown against interior mass. Illustrates the production sites of Ti. From Rauscher et al. (2002).



Figure 3.8. Plot of the slope of $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} produced in a 25M $_{\odot}$ supernova type II for various models of Rauscher et al (2002), plotted against interior mass. The Internal structure is displayed as defined by Meyer et al. (1995). Correlation line for solar system whole rock $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} data is shown as dashed dotted line for comparison.

A key uncertainty within the proposed model is how the material from the core region of the supernovae could penetrate the outer layers and then form dust grains, before being delivered to the ISM prior to incorporation within solar system material. Observational investigations of the astrophysical event SN1987A, one of the most extensively studied supernova type II explosions yet, has revealed that from the evolution of the light curves of iron group elements that material from deep within the core move through the outer region. Spyromilio et al. (1990) and Li et al. (1993) inferred that these elements were concentrated in high velocity 'bullets' that formed deep within the star and punctured the outer regions. 3-D dynamical simulations of supernova explosions show 'fingers' of material from deep within the supernova moving out forming clumps that pass through the outer zones (Hammer et al., 2010). These 'fingers' could create a pathway for the material from the O/Si, O/Ne and O/C zones to escape to the ISM and later be incorporated into nebula material.

3.5.2.2. Models for SN type Ia

The data for nucleosynthetic modelling of bulk SNIa are displayed in figure 3.9 and shows that it creates a negative $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} correlation for solar system material as well as large positive results, whereas the Ti isotope data of meteorites gives a positive correlation slope of 5.34 ± 0.34 (Fig. 3.3). SNIa produce large quantities of neutron rich iron peak isotopes such as ⁵⁰Ti and ⁵⁴Cr through NSE at the core boundaries at high densities (Meyer et al., 1996). However, by creating large amounts of ⁵⁰Ti they utilise the seed nuclei of ⁴⁶Ti, ⁴⁷Ti, ⁴⁸Ti and ⁴⁹Ti which causes a large deficit in the neutron poor isotopes of Ti. A SNIa supernova would be capable of producing large quantities of ⁵⁰Ti for injection into the ISM component but would leave large deficits in the neutron poor Ti isotopes. Hence, these types of supernovae cannot explain the Ti isotope data well.



Figure 3.9 Plot of slope of $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} produced in a various bulk models of SNIa supernova explosions,

3.5.2.3. Models for AGB stars

The modelled AGB data show the variability in the Ti isotope composition due to altering initial mass and metallicity of the star (Fig. 3.10). From this data the slope in $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} can be reproduced in the special case of a 3 solar mass low metallicity AGB star. The 3 solar mass AGB star is a good candidate for the production of the Ti isotopic signature of solar system material for two reasons. The lifetime of the star is short enough to occur in the time period prior to the formation of the molecular cloud, and periodic dredge up

of material from near the He shell by thermal pulsing would bring *s*-process material to the surface of the star to be lost to the ISM by stellar winds.



Figure 3.10 Modelled $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} (y-axis) values from 1 -3 solar mass AGB stars for various metallicities (x-axis) using models from Cristallo et al. (2011)

3.6. Summary and Conclusions

Titanium isotopic compositions have been determined for a range of chondritic groups and planetary bodies and display a strong correlation between $\epsilon^{50/47}$ Ti_{49/47} and $\epsilon^{46/47}$ Ti_{49/47}. The slope of 5.34 ± 0.34 for the correlation in $\epsilon^{50/47}$ Ti_{49/47} versus $\epsilon^{46/47}$ Ti_{49/47} is in good agreement with previous work (Trinquier et al., (2009) and Zhang et al., (2010)). Carbonaceous chondrites show the largest positive anomalies of the bulk meteorites on the neutron rich $\epsilon^{50/47}$ Ti_{49/47}, enstatite chondrites and the moon show terrestrial ratios within uncertainty, as is observed for other iron group elements such as Ni on $\epsilon^{64/61}$ Ni_{58/61} (Steele et al., 2012), Cr on $\epsilon^{54/52}$ Cr_{50/52} (Trinquier et al., 2007) and Zr on $\epsilon^{96/90}$ Zr_{94/90} (Schönbächler et al., 2003; Akram et al., 2011).

A correlation is also observed between $\varepsilon^{96/90}$ Zr_{94/90} and $\varepsilon^{50/47}$ Ti_{49/47} where admixing of variable amounts of CAI's into Earth materials can explain part of the Ti and Zr isotopic anomalies within the carbonaceous chondrite groups, where the anomalies scale with CV>CM>CR>CI. This indicates that CAI's are a main carrier phase of anomalous Ti and Zr. Chromium and Ni isotope data for CI carbonaceous chondrites indicate that Ti and Zr anomalies are held within different components to Cr and Ni (Steele et al., 2012; Trinquier et

al., 2007). An additional carrier phase is also required as is evident from the different results found for Murchison when utilising two different digestion techniques. The Murchison aliquot digested using the microwave technique did not fall on the $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} solar system correlation line of 5.34 ± 0.34 unlike the Murchison aliquot utilising the Parr Bomb technique. This indicates that the microwave technique was unable to dissolve all presolar refractory phases.

We have investigated the effects of mixing small fractions of the average compositions of various nucleosynthetic environments such as SNIa, SNII and AGB stars into the solar system. The results were compared with the slope line of 5.34 ± 0.34 found for $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} defining the large scale heterogeneity in the solar system. Addition of material from SNIa could not reproduce the correct slope in $\varepsilon^{50/47}$ Ti_{49/47} v $\varepsilon^{46/47}$ Ti_{49/47} isotope space. However bulk addition of a 3 solar mass low metallicity AGB star would produce the correct Ti composition. The investigation of individual shells and zonal yields of SNII by utilising various nucleosynthesis models provided by Rauscher et al. (2002) enabled the examination of the isotopic products of a range of hydrostatic and explosive burning phases. The O/Ne, O/C and He/C zones of a 25 solar mass SNII can reproduce the Ti isotope signature observed in the solar system. However, as there is an array of presolar components found within solar system materials, input from multiple stellar sources must be considered. Thermal processing of material in the protoplanetary disk cannot solely explain the observed Ti isotope variations as suggested by Trinquier et al. (2009).

The X-wind model is a likely process that radially redistributes the isotopically anomalous CAI grains relative to others could explain the variation of isotopic anomalies in the Ti and Zr isotope systems observed in meteorites.

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3.8 . References

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Chapter 4:

Titanium isotope variations in leachates of ordinary and carbonaceous chondrites and their implications

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4.1. Abstract

Stepwise dissolutions were performed on the ordinary chondrite (OC) QUE 97008 and the carbonaceous chondrites (CC) Allende, Murchison and Orgueil in order to determine the carriers of isotopically anomalous material. The results of the different leach steps reveal different patterns of Ti isotope variations. The OC, QUE 97008 displays negative $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{46/47}$ Ti_{49/47} variations relative to the terrestrial standard for all leachate steps. Murchison displays variations between leachate steps: In detail, for $\varepsilon^{50/47}$ Ti_{49/47} the first two leachate steps display negative anomalies whilst the third and residue display positive anomalies. For $\epsilon^{46/47}$ Ti_{49/47} the first leachate step displays negative anomalies whilst the other two leachate and residue steps display positive anomalies. Comparison of the leachate data with the whole rock correlation line of 5.34 \pm 0.34 between $\epsilon^{50/47}$ Ti_{49/47} and $\epsilon^{46/47}$ Ti_{49/47} for a suite of solar system material indicates there are at least two separate carrier phases of Ti and show that $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{46/47}$ Ti_{49/47} variation are not situated in the same carrier phase. Comparison of the Ti leachate data with the Zr isotope data from Schönbächler et al. (2005) that were obtained on the same leach fractions displays an anti-correlation. The acetic acid fraction for Murchison displays the largest positive anomalies of 48 for ϵ^{96} Zr and the largest negative values of -4 for ϵ^{50} Ti. In contrast, the refractory residue step displays both the largest positive value for Ti $(\varepsilon^{50/47}\text{Ti}_{49/47} = 5)$ and Zr of -12.5.

4.2. Introduction

Whole rock analysis of solar system materials has revealed they carry a chemical memory of the nucleosynthetic process, which formed the material (Clayton, 1982). For Ti, previous work on meteorite components showed that Calcium Aluminium rich Inclusions (CAIs), which were the first condensates\evaporation products of the protoplanetary disk display excesses more than 1 per mil on the neutron rich isotope ⁵⁰Ti compared to the terrestrial standard ((Leya et al., 2008; Niederer et al., 1981; Trinquier et al, 2009). The analysis of bulk solar system material showed that primitive solar system material such as CV carbonaceous chondrites display smaller ⁵⁰Ti excesses of 0.3 per mil (Leya et al., 2008; Trinquier et al., 2009; Zhang et al., 2011). Previous studies of Ti isotope compositions of refractory components within solar system material revealed that for Ti, at least four different nucleosynthetic components are required to create the observed Ti composition (Niemeyer and Lugmair. (1984)). Titanium is an appropriate element to test the mixing level of nucleosynthetic component in the initial solar nebula for two reasons; firstly it is highly refractory and

condensed in the earliest solids formed in the solar system and secondly it is immobile and its isotopic composition is not easily modified during secondary alteration processes. Further knowledge of the initial mixing of Ti isotopes therefore provides constraints on dynamical mixing models of the evolution of the solar system as well as revealing details regarding stellar nucleosynthesis. The iron group elements (Ca -Ni) reveal large isotopic anomalies for their corresponding neutron rich isotopes (⁴⁸Ca, ⁵⁰Ti, ⁵⁴Cr, ⁵⁸Fe and ⁶⁴Ni (Lee, T., 1988) in Fractionation and Unknown Nuclear effects inclusions (FUN) (Lee, T., 1988) and Hibonites (Ireland et al., 1985)). These compositions are a direct result of nucleosynthetic processes in the interior of massive stars by synthesis in a neutron rich nuclear statistical equilibrium ((Woosley, 1997); Clayton, D., 1968). In addition to FUN CAIs, normal CAIs and chondrules that are held within solar system materials, many carbonaceous chondrites host numerous presolar grains such as nano-diamonds, graphite, SiC, corundum and silicates, which contain large isotopic variations indicative of a particular stellar source ((Amari et al., 2000a; Ireland et al., 1991; Ott, 2001; Zinner, 1998). By utilising step wise acid digestion of meteorites, studies of Cr and Zr have been able to increase the magnitude of isotope variations found within certain meteorite phases on ⁵⁴Cr and ⁹⁶Zr respectively, likely due to the presence of presolar grains (Podosek et al., 1997; Rotaru et al., 1992; Trinquier et al., 2007). Schönbächler et al. (2005) reported that the ε^{96} Zr, ε^{91} Zr and ε^{92} Zr leachate results for carbonaceous chondrites Allende, Murchison and Orgueil correlate, and that SiC isotopic results fall on the extension of the correlation line. The Zr data revealed the presence of two nucleosynthetic components with SiC grains likely to be the source material. Osmium isotopic anomalies within leachates also point to SiC grains (AGB) as a source of the isotopic variations (Yokoyama et al., 2010). Dissolution studies of Murchison of W isotopes by Burkhardt et al. (2012) revealed that two or more distinct nucleosynthetic sources are required to produce the observed co variation between ε^{182} W and ε^{183} W.

In a previous investigation, Schönbächler et al. (2005) performed a step-wise acid digestion of the carbonaceous chondrites Allende (CV3.2), Murchison (CM2) and Orgueil (CI1) for the investigation of Zr isotope variations. This study compliments the study of Schönbächler et al. (2005) by analysing the same aliquots for the Ti isotope composition. In addition to the complementary study of Schönbächler et al. (2005), sample aliquots from the work of Qin et al. (2011a) were also investigated for Ti. The latter study performed acid leaching experiments on the carbonaceous chondrite Murchison (CM2) and the ordinary chondrite QUE 97008 for the elements Cr, Sr, Ba, Sm, Nd and Hf. This study compliments the

work of Qin et al. (2011a) by investigating Ti isotope compositions of the same leachate aliquots. By investigating the isotope compositions of a range of carbonaceous chondrites and the unequilibrated OC QUE 97008 we aim to constrain the source and carrier phases responsible for the nucleosynthetic bulk rock variation within primitive solar system materials.

4.3. Analytical Method

4.3.1. Nu 1700 Ti isotope analysis

The following method was carried out by Ingo Leya and the results of the analysis were kindly passed to the author in order to contrast and compare with other leachate data. Titanium was separated from the sample matrix following the two stage anion exchange procedure described in Schönbächler et al. (2004) and Leya et al. (2007). A short summary is given in the following. The first column, using 0.7 ml of Bio-Rad AG1-X8 resin (200-400 mesh, chloride form), is preconditioned with 6 ml 4 M HF. After loading the sample in 4 M HF, the matrix is eluted with 8 ml 4 M HF, while Ti, Zr, Hf, Mo, Te and W remain on the column. Titanium is eluted using 2 ml 6 M HCl -1 M HF. Following the first column the Ti fraction is dried down and taken up in 1.5 ml of 0.25 M H₂SO₄ - 1% H₂O₂. This solution is loaded onto the second column (0.7ml AG1-X8 resin), which has been preconditioned with 6ml of 0.25 M H₂SO₄ - 1% H₂O₂.

The isotope measurements were performed using a NU-1700 High Resolution Multi Collector- Inductively Coupled Plasma Mass Spectrometer (HR MC-ICPMS) at ETH Zurich following the protocol of Leya et al. (2007). Every sample measurement comprised two cycles each consisting of 40 analysis with 15 second integration, in 2 blocks of twenty with results beyond 2sigma being discarded. On-peak baselines were measured for 30s before each block by deflecting the ion beam with the electrostatic analyser. Two data collection protocols were necessary to measure all Ti isotopes and that of interfering isotopes from Ca, V and Cr. The first cycle measures from mass 44 to 49, while the second cycle includes mass 47 to 53 (Leya et al., 2007)

Isobaric interferences on stable Ti isotopes from single charged atomic ions are possible from ⁴⁶Ca+ (0.004% relative abundance) and ⁴⁸Ca (0.187%), ⁵⁰V(0.2497%) and ⁵⁰Cr (4.3452%)(Table 2.1). These Interferences were corrected using signals on mass ⁴⁴Ca, 2.086%, mass ⁵¹V, 99.7503%, and mass ⁵³Cr, 9.5006%, respectively. Measurements of ⁴⁴Ca were sensitive to baseline variations caused by the large ⁴⁰Ar beam. The ⁵⁰Cr interferences on ⁵⁰Ti were corrected using ⁵³Cr instead of ⁵²Cr to avoid the ⁴⁰Ar¹²C interference on ⁵²Cr, which are two orders of magnitude larger than the interferences on ⁵³Cr by ⁴⁰Ar¹³Ar.

4.3.2. Neptune Finnigan MC-ICPMS Ti analysis

The chemical separation of Ti from the samples matrix for the high precision Ti analyses utilised a three stage ion exchange chromatographic procedure in order to achieve a cleaner separation of Ti from the sample matrix and in particular the isobaric interfering elements Ca, V and Cr. The exact procedure is described in Chapter 2.3.2. The exceptions are samples, which were obtained from the study of Qin et al. (2011). The analytical procedure of these samples also included a three stage ion exchange chemistry. The first and second columns differ and are described in detail elsewhere (Qin et., 2011). The procedure included a first column with AG-50W-X8 cation exchange resin in order to elute Hf, Sr, Ba, Sm and Nd. This was followed by a second column in which Ti was eluted from LN spec resin in 0.09 M citric acid – 0.45 M HNO₃ – 1 wt% H₂O₂ (Carlson et al., 2006). The samples were then dried down and dissolved in 4 M HF before being loaded onto a third column with 0.7 ml pre cleaned AG1-X8 anion exchange resin (third column, chapter 2.3.2). Subsequently, 5.5 ml 4 M HF was added for matrix elution before switching to 5 ml 0.5 M HCl + 1 M HF. Titanium was eluted from the resin using 3 ml 6 M HCl + 1 M HF. Prior to analysis an aliquot was checked for other interfering elements such as Ca and Zr as well as checking the yields by comparing with abundance data for Ti in Qin et al. (2011a). The Ti chemical separation procedures employed here ensured total yields in excess of 90%. Full procedural blanks averaging at 3 ng with a range of between 0.6 and 16 ng.

The high precision Ti isotope analyses were performed on a Thermo-Fischer Neptune MC-ICPMS at the Open University, Milton Keynes. The details were discussed in chapter 2.3.2 and chapter 3.3.1. The samples were bracketed with a Ti Alfa Aesar single element standard solution and were introduced using Aridus II desolvating nebuliser. Measurements on the Neptune were carried out over two cycles. In the first cycle ⁴⁴Ca, ⁴⁵Sc, ⁴⁶Ti, ⁴⁷Ti (axial), ⁴⁸Ti, ⁴⁹Ti and ⁵⁰Ti were measured with an integration time of 8.4 s comprising of 40 blocks of measurements. The second cycle measured ⁵⁰Ti (axial), ⁵¹V and ⁵³Cr with an integration time of 4.2s comprising of 40 blocks of measurements. Measurements were conducted in medium resolution (MR) were MR was defined as M/ Δ M <10000 and HR as M/ Δ M>10000 were between 5% and 95% of full height across a single peak edge are measured. Acid blanks were

measured prior and after every standard and sample measurement in 0.5 M HNO₃ - 0.005 M HF and subtracted from the analyte beam intensities during data processing.

For analyses utilising both the Neptune and Nu 1700, the Ti isotope ratios were internally normalised to $Ti_{49/47}=0.749766$ (Niederer et al., 1981) and the values are reported in the ε notation relative to the Alfa Aesar standard solution (equation 4.1)

$$\epsilon^{i/47} \mathrm{Ti}_{49/47} = \left(\left(\frac{i/47}{(i/47} \mathrm{Ti}_{49/47} \mathrm{Sample}(B) + i/47} \mathrm{Ti}_{49/47} \mathrm{Sample}(A) \right) - 1 \right) * 10,000$$
(4.1)

The ε notation is defined as the difference in parts per ten thousand between the sample and the standards. The average of the standards measured before (B) and after (A) are used to correct for potential drift during the samples measurement. *i*, can be ⁴⁶Ti, ⁴⁸Ti and ⁵⁰Ti. Uncertainties are reported as 2SE(Standard Error), were the 2σ standard deviation from multiple analyses over several measurement sessions are divided by the square root of the number of analysis.

4.3.3. Leaching Procedure

4.3.3.1. Allende- a and-b, Murchison-a and-b and Orgueil leachates (Nu 1700 analysis)

Powdered whole rock samples of Allende (samples a, b), Murchison (Samples a, b) and Orgueil were sequentially digested with reagents of increasing strength (Table 4.1). The details of the leaching procedure including data for Zr and Te isotopes are reported elsewhere (Schönbächler et al. 2005 and Fehr et al., 2006).

4.3.3.2. Leachates of the Ordinary chondrites QUE97008 and the carbonaceous chondrite Murchison (for Neptune Finnigan analysis)

Leachates of the ordinary chondrites QUE97008 and the carbonaceous chondrite Murchison were also obtained from the study of Qin et al. (2011) (Table 4.1). The details are described in Qin et al. (2011) and summarized in Table 4.1. For these samples, 5.14g of Murchison and 5.05 g of QUE 97008 were crushed to less than 60µm grain size in a steel mortar. The powdered sample was then leached with three different acids resulting in fraction Q1-Q3 (Table 4.1). The final residue (QR) after leaching was dried, weighing 2.10 g for Murchison and 3.165 g for QUE 97008. Around 1 g of each residue was dissolved in a Parr

Bomb using a mixture of HF-HNO₃ in a 2:1 ratio at a temperature of 170°C for 1 week (Qin et al., (2011) to obtain fraction QR (Table 4.2). The Ti content of each fraction (Q1-3 and QR) was determined using an Axiom high resolution ICP-MS by measuring a 10% aliquot of each leach and residue step and the results are reported in Qin et al 2011.

Step	Reagent	Procedure	Phase dissolved			
	Allende	(a,b) - Murchison (a, b) - O	rgueil*			
1a	0.4 M CH ₃ COOH	30 min - RT	Carbonates, sulfates, sulfides			
1b	8.5 M CH ₃ COOH	1 day - RT	metal			
2	4 M HNO ₃	5 days - RT	Silicates			
3a	6 M HCl	5 days - RT	Silicates			
3b	6 M HCl	1 day - 36°C	Silicates			
3c	6 M HCl	1day - 80°C	Silicates			
4	13.5 M HF - 3 M HCl	4 days - 100°C	Silicates			
5a	conc aqua regia	3 hours - 220°C HPA	Silicates			
5b	Conc HF-HNO ₃	3 days, 170°C Parr Bomb	Refractory minerals			
		Murchison - QUE97008 [^]				
Q1	8.5 M CH ₃ COOH	24h, RT	metal			
Q2	6 M HNO ₃	5 days, RT	Silicates			
Q3	6 M HCl	24h - 75°C	Silicates			
QR	HF-HNO ₃ (2:1 ratio)	1 week, Parr Bomb - 170°C	Refractory minerals			
		Orgueil [#]				
T - 1	0.4 M CH ₃ COOH	30 min - 20 °C	Carbonates, sulfates, sulfides			
Т-2	8.5 M CH ₃ COOH	1 day - 20°C	metal			
Т - За	0.5 M HNO ₃	10 min - 20°C	Silicates			
T - 3b	1 M HNO ₃	1 hour - 20°C	Silicates			
T - 3c	4 M HNO ₃	1 day - 20 °C	Silicates			
T - 3d	8 M HNO ₃	1 day - 20°C	Silicates			
T - 3e	6 M HCl	1 day - 35°C	Silicates			
T - 3f	6 M HCl	1 day - 80°C	Silicates			
T-4	3 M HCI-14 M HF	4 days - 100°C	Silicates			
T - 5	8 M HNO ₃ -14 M HF	10 days - 150°C	Refractory minerals			

Table 4.1. Leaching procedures

* From Schönbächler et al., (2005)

^ From Qin et al., (2011a)

From Trinquier et al., (2009). Trinquier et al., (2009) utilised a different leaching procedure complicating a direct comparison with Schönbächler et al., (2005). The main difference between the two leaching procedures is the additional HNO3 steps 3a, 3b and 3d, which are not utilised by Schönbächler et al., (2005)

4.4. Results

4.4.1. Allende (a, b), Orgueil, and Murchison (a, b)

4.4.1.1. Interference corrections for Nu 1700 isotope data

Due to a mixture of problems encountered during analysis, additional corrections were

applied to interfering elements. For the leachate experiment Allende-a, some of the $\epsilon^{50/47} Ti_{49/47}$

data suffered from moderate interference corrections. Leachate steps 1b and 4 were corrected for Cr interferences by about 23 ε and 8 ε , respectively. The latter leachate step had an additional correction of 16 ε - for ⁵⁰V interferences. Also the 3a and 3c steps had to be corrected for 50 V of around 16 ϵ . Due to technical problems the percentage of Ti released in each step was unable to be measured. Therefore we were unable to determine the mass balance whole rock value and the Ti isotope composition for the final leachate step with aqua regia. Due to these limitations it is impossible to perform detailed mass balance calculations on these samples. For the leachate set-up of Allende-b, the $\varepsilon^{48/47}$ Ti_{49/47} and $\varepsilon^{46/47}$ Ti_{49/47} data obtained for the step 5b had to be corrected by about 92 ϵ - and 48 ϵ -units for interfering Ca isotopes, respectively. Due to large Cr interferences we were unable to provide results for the $\varepsilon^{50/47}$ Ti_{49/47} for the 1b and 5b steps. For Murchison-a most of 1a and 1b leachate data was compromised by Ca, V, and/or Cr interferences; only the $\varepsilon^{50/47}$ Ti_{49/47} of step 1a is within the reliable range and we can therefore give a ratio with the correction of about 70 ε -units. The data for step 2, 3c, and 5b steps had to be corrected by about 15 ε -, 17 ε -, and 215 ε -units for ⁵⁰Cr interferences, respectively. The latter step also needed an additional correction due to 50 V of about 50 ϵ . Note that the missing data for the 1a and 1b steps do not really compromise detailed mass balance calculations as only small amounts of Ti are released in this first leachate steps (see, e.g., Allende and Orgueil data). For Murchison-b a correction for the $\varepsilon^{50/47}$ Ti_{49/47} data from steps 2, 3a-3c, and 4 steps by about 113 ε -, 185 ε -, and 60 ε for ⁵⁰Cr interference respectively had to be made; step 4 had to be corrected by about 120 ε for ⁵⁰V. The data for the first step cannot be given because of unreliable high interference corrections on all isotopes.

For *Orgueil*, the Ti isotope ratios for the steps 1a and 1b were unable to be recorded due to unreliably high Cr and Ca corrections. Also some of the other leachate steps suffered from high interference corrections; the $\varepsilon^{50/47}$ Ti_{49/47} ratio of step 4 had to be corrected for about 120 ε - and 60 ε -units for ⁵⁰V and ⁵⁰Cr, respectively. The $\varepsilon^{50/47}$ Ti_{49/47} data of the 3a-3c and 4 steps had to be corrected by about 35 ε - and 60 ε -units for interference of ⁵⁰Cr. Due to technical problems we were unable to measure Ti isotope data for step 5b, which again compromised detailed mass balance calculations.

4.4.1.2. Allende data

The leachate fractions 2 and 4 of Allende-a were analysed using the Nu 1700 and the Neptune Finnigan. The results of both techniques (Table 4.2, Fig. 4.1a) overlap within uncertainty and demonstrate the accuracy of both data sets in addition to the increased precision

gained from the combination of the additional chemistry and utilisation of the Neptune MC-ICPMS. The exception is the $\varepsilon^{48/47}$ Ti_{49/47} data, where the data differs and this most likely reflects underestimated uncertainties for the Nu 1700 $\varepsilon^{48/47}$ Ti_{49/47} data. The cause might be a background problem, which affected the Ca correction. The more reliable repeated analysis of step 2 (2*) and 4 (4*) from Allende-a (Neptune Finnigan data with improved chemical separation of Ca) yield a value of -0.03 ± 0.05 and 0.01 ± 0.09, respectively. This suggests that there are no $\varepsilon^{48/47}$ Ti_{49/47} variations compared to the bulk rock data and the terrestrial standard. Therefore, potential anomalies in the Nu 1700 isotope data for $\varepsilon^{48/47}$ Ti_{49/47} (Table 4.2) need to be considered with caution.

The leachate data for Allende - a in general displays $\varepsilon^{46/47}$ Ti_{49/47} ratios that are more variable than those for Murchison (Tables 4.2). Leachate steps 2, 2*, 3a, 4 and 4* fall close to the bulk rock measurement if the associated uncertainties are considered. Leachate 1b, however, shows a small excess in $\varepsilon^{46/47}$ Ti_{49/47} (3.7 ± 2.0).

Table 4.2. Titanium and $\epsilon^{96/90}$ Zr_{94/90} isotope data for Allende-a,-b, Murchison-a, –b and Orgueil-a. Also shown are whole rock data from various sources.

Sample	raction (%	á Step	Reagent	Procedure	$\epsilon^{46/47} Ti_{49/47}$	2σ	ε ^{48/47} Τi _{49/47}	2σ	ε ^{50/47} Τί _{49/47}	2σ	ε ^{96/90} Zr _{94/90}	ο 2σ
Allende - a	N.D	1a	0.4 M CH ₃ COOH	RT for 30 min	43/4/		- 43/47		- 43/47	-	- 54/50	5 -
Allende - a	N.D	1b	8.5 M CH ₃ COOH	RT for 1 day	3.70	2.00	2.30	0.30	-1.20	8.1 ²	10.00	1.50
Allende - a	N.D	2	4 M HNO ₃	RT for 5 days	0.90	1.40	0.50	0.20	1.40	2.10		
Allende - a *	N.D	2	5 M HNO ₃	RT for 5 days	0.32	0.05	-0.03	0.05	1.58	0.08		
Allende - a	N.D	3a	6 M HCI	RT for 5 days	0.80	1.90	-0.20	0.20	3.30	1.4 ³		
Allende - a	N.D	3b	6 M HCI	36°C for 1 day								
Allende - a	N.D	3c	6 M HCI	80°C for 1 day							2.6	1.5
Allende - a	N.D	4	13.5 M HF- 3 M HCl	100°C for 4 days	0.50	1.50	-0.60	0.20	3.30	1.2 2,5	0.50	1.50
Allende - a *	N.D	4	13.5 M HF- 3 M HCI	100°C for 4 days	0.52	0.07	0.01	0.09	3.40	0.11	0.50	1.50
Allende - a	N.D	5a	conc aqua regia	220°C for 3 hours							-0.1	1.5
Allende - a	N.D	56	conc HF-HNO ₃	Microwave							-0.2	1.4
Allende - b	N.D	18		RT for 1 day							7	1.4
Allende - b	10.4	2010		PT for 5 days	0.50	0.60	0.10	0.20	1 90	1.00	1 20	1.4
Allende - b	23.2	2 3a	6 M HCl	BT for 5 days	0.00	1 50	-0.10	0.20	2.20	1.00	4.80	1.40
Allende - b	N.D	3b	6 M HCI	36°C for 1 day	0.00	1.50	0.10	0.50	2.20	1.00		
Allende - b	N.D	3c	6 M HCI	80°C for 1 day							0	1.4
Allende - b	64.3	4	13.5 M HF- 3 M HCl	100°C for 4 days	0.60	0.60	1.10	0.40	2.80	1.40	-0.10	1.30
Allende - b	N.D	5a	conc aqua regia	220°C for 3 hours								
Allende - b	N.D	5b	conc HF-HNO ₃	Microwave							-3	1.4
Allende	-	WR	conc HF-HNO ₃ (3:1)	Parr Bomb 170°C for 5 days	1.00	0.40	-1.20	0.60	3.40	0.50	1.00	1.20
Allende '	-	WR	conc HF-HNO ₃ (3:1)	Teflon beaker on hot plate 170°C for 5 days	0.94	0.11	0.12	0.12	5.01	0.29		
Allende ^z	-	WR	conc HF-HNO ₃ (3:1)	Parr Bomb 170°C for 5 days	0.72	0.02	0.02	0.08	3.49	0.04		
Allende ^w	-	WR	conc HF-HNO ₃ (3:1)	Parr Bomb 170°C for 5 days	0.62	0.05	0.03	0.11	3.39	0.18	1.00	1.20
Allende ^w	-	WR	conc HF-HNO ₃ (3:1)	Parr Bomb 170°C for 5 days	0.57	0.17	-0.05	0.14	3.26	0.10	1.00	1.20
Murchison - a	N.D	1a	0.4 M CH ₃ COOH	RT for 30 min								
Murchison - a	N.D	1b	8.5 M CH ₃ COOH	RT for 1 day	0.00	2.50	0.70	0.30	-15.70	12.40	48.60	1.40
Murchison - a	N.D	2	4 M HNO ₃	RT for 5 days	-0.20	1.40	-15.20	0.40	-0.60	2.4 ^{2,3}	28.40	1.40
Murchison - a	N.D	3a	6 M HCl	RT for 5 days								
Murchison - a	N.D	3b	6 M HCI	36°C for 1 day						2		
Murchison - a	N.D	3c	6 M HCl	80°C for 1 day	0.50	1.40	-0.40	0.30	3.20	3.2 -	19.00	1.40
Murchison - a	N.D	4	13.5 M HF- 3 M HCI	100°C for 4 days	-0.30	1.90	0.20	0.30	5.20	2.60	-4.30	1.30
Murchison - a	N.D	5b	conc HF-HNO ₂	Microwave							-12.5	1.4
Murchison - h	0.02	1a	0.4 M CH_COOH	BT for 30 min							12.05	1.1
Murchison - b	0.45	1b	8.5 M CH ₃ COOH	RT for 1 day							44.9	1.4
Murchison - b	24.50	2	4 M HNO ₂	RT for 5 days	1.20	1.00	0.40	0.40	-2.60	3.9 ²	30.80	1.40
Murchison - b	22.10	3a	6 M HCI	RT for 5 days	0.60	0.90	0.30	0.50	1.20	3.40	24.10	1.40
Murchison - b	10.50	3b	6 M HCI	36°C for 1 day	0.20	2.10	0.70	0.40	1.80	2.00	20.30	1.40
Murchison - b	6.20	3c	6 M HCI	80°C for 1 day	0.70	2.00	0.70	0.40	4.70	1.5 2	13.40	1.90
Murchison - b	33.80	4	13.5 M HF- 3 M HCl	100°C for 4 days	0.40	0.80	-0.10	0.40	4.10	1.30	-1.70	1.40
Murchison - b	ND	5a	conc aqua regia	220°C for 3 hours								
Murchison - b	2.30	5b	conc HF-HNO ₃	Microwave	1.80	1.30	-4.80	5.00	7.00	1.6	-8.00	1.40
Murchison	-	WR	conc HF-HNO ₃ (3:1)	Teflon beaker on hot plate 170°C for 5 days	0.35	0.12	0.01	0.11	3.06	0.33		
Murchison ²	-	WR	conc HF-HNO ₃ (3:1)	Parr Bomb 170°C for 5 days	0.47	0.15	-0.06	0.09	2.83	0.19		
Murchison "	-	WR	conc HF-HNO ₃ (3:1)	Parr Bomb 170°C for 5 days	0.32	0.11	-0.03	0.08	2.94	0.10	0.90	1.60
Murchison "	-	WR	conc HF-HNO ₃ (3:1)	Microwave 170°C for 5 days	0.50	0.17	-0.06	0.12	5.12	0.14	0.90	1.60
Orgueil - a	0.02	1a	0.4 M CH ₃ COOH	RT for 30 min								
Orgueil - a	0.56	1b	8.5 M CH ₃ COOH	RT for 1 day								
Orgueil - a	45.9	2	4 M HNO ₃	RT for 5 days	1.20	0.90	-0.40	0.60	1.00	0.7	20.80	1.40
Orgueil - a *	(45.9)*	2	5 M HNO ₃	RT for 5 days	0.35	0.05	0.02	0.03	0.04	0.16	20.80	1.40
Orgueil - a	32.7	3a	6 M HCl	RT for 5 days	0.60	1.30	0.70	0.30	-0.60	1.4 2		
Orgueil - a Orgueil - a		3b 3c	6 M HCI	36°C for 1 day							19.6	14
Orgueil - a	20.7	ر ار	13.5 M HE- 3 M HC	100°C for 4 days	0.30	0.70	0 10	0 20	3 00	1 00 2	-1 20	1 20
Orgueil - a	20.7 N.D	-+ 5a	conc aqua regia	220°C for 3 hours	0.30	5.70	0.10	0.50	3.00	1.00	-1.00	1.50
Orgueil - a	N.D	5b	conc HF-HNO ₃	Microwave							-377.5	3.3
Orgueil	-	WR	conc HF-HNO ₃ (3:1)	Parr Bomb 170°C for 5 days	3.40	1.90	1.80	0.50	-0.10	1.60	-0.10	1.50
Orgueil ^T	-	WR	conc HF-HNO ₃ (3:1)	Teflon beaker on hot plate 170°C for 5 days	0.38	0.07	0.01	0.04	1.87	0.04		
Orgueil ^z	-	WR	conc HF-HNO ₂ (3:1)	Parr Bomb 170°C for 5 days	0.35	0.04	0,00	0.15	1.74	0.05		
Orgueil ^W	-	WR	conc HF-HNO ₃ (3:1)	Parr Bomb 170°C for 5 days	0.21	0.09	-0.10	0.10	1.79	0.12	-0 10	1.50
* Fraction was reprocessed an	nd re-measured	lutilisin	g high precision meth	iod	0.21	5.05	0.10	0.10	2.7.5	0.12	0.10	1.55

N.D - not determined

^L Data From Leya et al., (2008)

^T Data from Trinquier et al.,(2009)

^z Data from Zhang et al., (2012)

W Data from Chaper 3.4

 $\epsilon^{96/90} Zr_{94/90}\,data$ from Schönbächler et al., (2005)

² Data are comprimised by large Cr corrections

³ Data are comprimised by large V corrections

⁴ Data are comprimised by large Ca corrections

The $\varepsilon^{50/47}$ Ti_{49/47} data show a similar trend as that of Murchison - a in displaying a larger range compared to $\varepsilon^{46/47}$ Ti_{49/47} and $\varepsilon^{48/47}$ Ti_{49/47}. Also like Murchison the anomalies within the first leachate steps display depletions relative to the terrestrial standard whilst the latter steps display enrichments.



Figure 4.1. (A) The Ti isotope data for the leachate steps of Allende-a. *i* (x-axis) denotes the isotope used in the numerator of $\varepsilon^{i/47}Ti_{49/47}$. (B) The Ti isotope data for the leachate steps of Allende-b. WR^W result from chapter 3.4. * Fraction analysed with high precision methods. Uncertainties shown are the 2 S.D values of the measurement.

The leachate data for Allende-b (Table 4.2, Fig. 4.1b) is only available for three fractions due to the encountered limitations associated with the purification and measurement procedure. The data overlap with the results from Allende-a and demonstrate the reproducibility of the experiment. The only exception is fraction 4 with an $\varepsilon^{48/47}$ Ti_{49/47} of -0.6 ± 0.2 for Allende-a and 1.1 ± 0.4 for Allende-b. As discussed above, this difference might be due to an analytical problem.

4.4.1.3. Murchison data

The $\varepsilon^{46/47}$ Ti_{49/47} ratios for all leachate steps of the experiment Murchison-a overlap with the bulk rock measurements (Table 4.1, Fig.4.2 A). The $\varepsilon^{48/47}$ Ti_{49/47} data are more variable, although most ratios fall close to the bulk rock data, step 2 shows a large depletion in $\varepsilon^{48/47}$ Ti_{49/47} of -15.2 ± 0.40 ε relative to the laboratory standards and is considered unreliable whereas step 3c only displays a slight depletion of -0.40 ± 0.30 ε . The $\varepsilon^{50/47}$ Ti_{49/47} data displays a larger range of results compared to $\varepsilon^{46/47}$ Ti_{49/47} and $\varepsilon^{48/47}$ Ti_{49/47}. Step 1b displays a large deficit of -15.70 ± 12.40 ε , while step 2 plots with a slight deficit around the origin at -0.60 ± 2.40 ε . Step 3c and 4 both display enrichments in $\varepsilon^{50/47}$ Ti_{49/47} of 3.20 ± 3.20 ε and 5.20 ± 2.60 ε respectively, both overlapping with the bulk rock value of Murchison (Table 4.2).



Figure 4.2. A) The Ti isotope data for the leachate steps of Murchison-a. *i* (x-axis) denotes the isotope used in the numerator of $\varepsilon^{i/47}$ Ti_{49/47}. (B) The Ti isotope data for the leachate steps of Murchison-b. WR^W result from chapter 3.4. Uncertainties shown are the 2 S.D values of the measurement.

The leachate data of Murchison-b (Table 4.2, Fig. 4.2 B) shows $\epsilon^{46/47}Ti_{49/47}$ ratios identical to the bulk rock data except steps 5b and 2. These steps both display slight enrichments of $1.80 \pm 1.30 \epsilon$ and $1.20 \pm 1.00 \epsilon$ respectively. The $\epsilon^{48/47}Ti_{49/47}$ for steps 2, 3a, 4 and 5b all plot within uncertainty, while steps 3b and 3c both display slight enrichments of 0.70

 \pm 0.4 ε. The ε^{50/47}Ti_{49/47} data matches that of Murchison-a in displaying a larger range of results compared to ε^{46/47}Ti_{49/47} and ε^{48/47}Ti_{49/47}. Step 3a and 3b both display ε^{50/47}Ti_{49/47} values of 1.20 \pm 3.40 ε and 1.80 \pm 2.00 ε respectively, both plotting within uncertainty of the origin. Leachates 3c and 4 both overlap within uncertainty of each other with enrichments in ε^{50/47}Ti_{49/47} of 4.70 \pm 1.50 ε and 4.10 \pm 1.30 ε respectively, while steps 3c and 4 overlap with the whole rock (WR) value.

4.4.1.4. Orgueil data

The Ti isotope data for Orgueil (Table 4.2; Fig. 4.3) displays $\varepsilon^{46/47}$ Ti_{49/47} and $\varepsilon^{48/47}$ Ti_{49/47} data for the Nu 1700 Neptune Finnigan data of step 2 (2*) that overlap with each other within uncertainties. However, for $\varepsilon^{50/47}$ Ti_{49/47} the data of 2 and 2* only almost overlap within uncertainty. This is most likely due to underestimated uncertainties for the Nu 1700 data. Considering the uncertainties of the data in general, most Ti isotope ratios of Orgueil leachates are similar to the bulk rock data. The most expressed difference is in step 4, which seems to have an excess in $\varepsilon^{50/47}$ Ti_{49/47} of $3.00 \pm 1.0 \varepsilon$.



Figure 4.3. The Ti isotope data for the leachates of Orgueil-a. Fraction * analysed with high precision methods. WR^W result from chapter 3.4. I (x-axis) denotes the isotope used in the numerator of $\epsilon^{i/47}$ Ti49/47.



Figure 4.4. The Ti isotope data for all leachate steps of Allende-a, b, Murchison-a, b and Orgueil are displayed for the $\varepsilon^{46/47}$ Ti_{49/47}, $\varepsilon^{48/47}$ Ti_{49/47} and $\varepsilon^{50/47}$ Ti_{49/47} isotope ratios (x-axis). Whole rock results for Allende, Murchison and Orgueil from chapter 3.3 are displayed for comparison.

A compilation of all Nu 1700 Ti isotope data of the leachate steps of Allende-a, b, Murchison-a, b and Orgueil is displayed in figure 4.4. The results demonstrate that carbonaceous chondrites display positive variations in $\epsilon^{46/47}$ Ti_{49/47} and $\epsilon^{50/47}$ Ti_{49/47}.

4.4.2.QUE 97008 and Murchison (Q) data Table 4.3. Neptune MC-ICPMS Ti and Cr isotope data for leachates and whole rock fractions of QUE 97008 (OC) and Murchison (CM2).

	-			_ ·	46/47-1	-	48/47	-	50/47	-	53/50 -	-	54/50 -	-
Sample	Туре	Fraction	Reagent	Procedure	ε ^{40/4} /Ti _{49/47}	2σ	ε ^{48/47} Ti _{49/47}	2σ	ε ^{30/4} Ti _{49/47}	2σ	ε ^{33/30} Cr _{52/50}	2σ	ε ^{54/30} Cr _{52/50}	2σ
QUE 97008 ^Q	oc	Q1	8.5 M CH ₃ COOH	RT for 1 day	-0.58	0.11	0.07	0.19	-5.57	0.10	0.95	0.08	-9.89	0.29
		Q2	6 M HNO ₃	RT for 5 days	-0.14	0.11	0.11	0.32	-2.45	0.19	0.52	0.04	-3.47	0.20
		Q3	6 M HCI	75°C for 1 day	-0.10	0.06	-0.04	0.16	-0.08	0.11	0.16	0.05	-2.37	0.21
		QR	conc HF-HNO ₃ (2:1)	Parr Bomb 170°C for 7 days	-0.18	0.09	-0.26	0.28	-0.49	0.05	-0.19	0.32	-4.40	2.30
		Calc WR	-	-	-0.17		-0.21		-0.67		-0.03		-4.17	
Murchison ^Q	CM2	Q1	8.5 M CH ₃ COOH	RT for 24 h	-0.09	0.10	0.14	0.13	-3.79	0.17	0.40	0.07	-13.40	0.70
		Q2	6 M HNO ₃	RT for 5 days	0.24	0.09	0.20	0.14	-2.11	0.11	0.40	0.10	-9.63	0.19
		Q3	6 M HCI	75°C for 24 h	0.47	0.07	-0.03	0.18	2.98	0.07	0.17	0.08	17.94	0.22
		QR	conc HF-HNO ₃ (2:1)	Parr Bomb 170°C for 7 days	0.00	0.13	-0.28	0.14	4.97	0.12	-0.15	0.04	11.75	0.10
		Calc WR	-	-	0.17		0.03		3.15		0.15		1.55	
Murchison ^W	CM2	WR	conc HF-HNO ₃ (3:1)	Parr Bomb 170°C for 5 days	0.32	0.11	-0.03	0.08	2.94	0.10				
Murchison ^W	CM2	WR	conc HF-HNO ₃ (3:1)	Microwave 170°C for 5 days	0.50	0.17	-0.06	0.12	5.12	0.14				
^Q Cr isotone data from Qin et al. (2011a)														

W Data from chapter 3.4

QUE 97008: The $\varepsilon^{48/47}$ Ti_{49/47} values obtained are consistent for all steps and plot within uncertainty of each other at the origin (Table 4.3 and Fig. 4.5 A). The $\varepsilon^{46/47}$ Ti_{49/47} values for QUE 97008 shows that the first leachate step displays a clear deficit relative to the Ti Alfa Aesar laboratory standard with a value of -0.58 ± 0.11 ε . The scale of deficit decreases in leachate steps 2, 3 and R with values of -0.14 ± 0.11 ε , -0.10 ± 0.06 ε and -0.18 ±0.09 ε respectively. The $\varepsilon^{50/47}$ Ti_{49/47} data displays a larger range of variations than $\varepsilon^{46/47}$ Ti_{49/47} and $\varepsilon^{48/47}$ Ti_{49/47}. Leachate fraction 1 displays the largest deficit with a value of -5.57 ± 0.10 ε , before decreasing to -2.45 ± 0.19 ε for leachate fraction 2 and decreasing again to -0.08 ± 0.11 for leachate 3. The final residue fraction displays an $\varepsilon^{50/47}$ Ti_{49/47} value of -0.49 ± 0.05 ε . Contrary to the Ti isotope data for QUE 97008 the $\varepsilon^{53/50}$ Cr_{52/50} displays clear and resolvable excesses for leachate fractions 1, 2 and 3 that decrease to lower values in the later steps. The $\varepsilon^{54/50}$ Cr_{52/50} variation (leachate 1, -9.89 ± 0.29) is almost twice as large as that for $\varepsilon^{50/47}$ Ti_{49/47} (leachate 1, -5.57 ± 0.10).



Figure 4.5. (A) Titanium and Cr isotope data for all leachate steps of QUE 97008 (Q). i (x-axis) denotes the isotope used in the numerator of $\epsilon^{i/47}Ti_{49/47}$ while j denotes the numerator of $\epsilon^{i/50}Cr_{52/50}$. MB: bulk values calculated by mass balance. (B)Titanium and Cr isotope data for all leachate steps of Murchison (Q). i (x-axis) denotes the isotope used in the numerator of $\epsilon^{i/47}Ti_{49/47}$ while j denotes the numerator of $\epsilon^{i/50}Cr_{52/50}$. MB: bulk values calculated by mass balance.

Murchison (Q): The $\varepsilon^{48/47}$ Ti_{49/47} values overlap with each other for all three of the leaching steps except for the final residue step, which displays a slight deficit of -0.28 ± 0.14 ε . The $\varepsilon^{46/47}$ Ti_{49/47} data shows that the first leachate step displays a slight deficit relative to the Ti Alfa Aesar laboratory standard with a value of -0.09 ± 0.10 ε . In fraction 2 and 3 the variations turn from an initial deficit in fraction 1 into a clear enrichment 0.24 ± 0.09 ε and 0.47 ± 0.07 ε respectively. The value of the final residue decreases to 0.00 ± 0.13 ε . The $\varepsilon^{50/47}$ Ti_{49/47} data for Murchison define a trend from negative to positive values across the range of leachate fractions. Fraction 1 displays the largest deficit with a value of -3.79 ± 0.17 ε , before increasing to -2.11 ± 0.11 ε for fraction 2 and turning into an enrichment of 2.98 ± 0.07 for leachate 3. The final residue fraction displays the most positive $\varepsilon^{50/47}$ Ti_{49/47} value (4.97 ± 0.12). The $\varepsilon^{54/50}$ Cr_{52/50} data display a similar trend as $\varepsilon^{50/47}$ Ti_{49/47} with the exception of the final residue. The latter exhibit lower $\varepsilon^{54/50}$ Cr_{52/50} than fraction 3. The scale of the variations on $\varepsilon^{54/50}$ Cr_{52/50} are almost four times as large as for $\varepsilon^{50/47}$ Ti_{49/47} for leachate 1 with a value of -13.40 ± 0.70 ε compared to -3.79 ± 0.17 ε .

4.4.3. Comparison with earlier data

Previous Ti leachate data are available from Trinquier et al. (2009) (table 4.4 and Fig. 4.6). Trinquier et al. (2009) utilised a different dissolution procedure, (Table 4.3) and the data was used here to compare with Nu 1700 isotope data for Orgueil-a. The pattern observed for Orgueil is similar to that found in the Orgueil leach experiment (Fig. 4.3), although the uncertainties are larger in our study (Nu 1700 data except for leach step 2*). The $\varepsilon^{50/47}$ Ti_{49/47} data also bear similarities to the Murchison-a, Murchison-b and Murchison (Q) leach experiments. They show an overall trend from negative to positive $\varepsilon^{50/47}$ Ti_{49/47} values from the weak acetic acid leachates to progressively stronger dissolutions. The $\varepsilon^{46/47}$ Ti_{49/47} and the $\varepsilon^{48/47}$ Ti_{49/47} ratios for Orgueil also display a similar pattern to Murchison. The $\varepsilon^{48/47}$ Ti_{49/47} only display very small variations (<0.3, if only the high precision data is considered) for both Murchison and Orgueil. For $\varepsilon^{46/47}$ Ti_{49/47} the first leachate fraction yields a deficit, while the remaining fractions display excesses of similar magnitude. This overall similarity demonstrates a good reproducibility and accuracy of our leaching experiments.

Table 4.4. The Ti isotope compositions of leach fractions from Orgueil from Trinquier etal. (2009).

Sample	Туре	Fraction	Reagent	Procedure	ε ^{46/47} Τi _{49/47}	2σ	$\epsilon^{48/47}$ Ti _{49/47}	2σ	ε ^{50/47} Ti _{49/47}	2σ
Orgueil	CI	1	0.4 M CH ₃ COOH	20°C for 30 minutes						
		2	8.5 M CH₃COOH	20°C for 1 day						
		3a	$0.5M HNO_3$	20°C for 10 minutes	-0.2	0.06	0.03	0.2	-0.46	0.39
		3b	1 M HNO ₃	20°C for 1 hour	0.21	0.11	0.01	0.14	-0.48	0.04
		3c	4 M HNO ₃	20°C for 1 day	0.44	0.03	-0.05	0.03	0.52	0.08
		3d	8 M HNO ₃	20°C for 1 day	0.67	0.01	-0.13	0.34	2.15	0.14
		3e	6 M HCl	35°C for 1 day	0.46	0.07	0.02	0.07	4.28	0.04
		3f	6 M HCl	80°C for 1 day	0.24	0.15	0.1	0.05	2.37	0.06
		4	3 M HCI-14 M HF	100°C for 4 days	0.46	0.13	-0.34	0.15	10.38	0.28
		5	8 M HNO ₃ -14 M HF	150°C for 10 days						
		Calc WR			0.31		-0.02		1.87	

Calc Wr: mass balanced calculated value of the whole rock.



Figure 4.6. The Ti isotope data for leachate steps of Orgueil from Trinquier et al. (2009). i (x-axis) denotes the isotope used in the numerator of $\epsilon^{i/47}Ti_{49/47}$.

4.5. Discussion

Pristine solar system materials such as carbonaceous chondrites contain several different components such as CAIs, and chondrules (Hezel et al., 2008, Rubin et al., 2011). Titanium and Zr isotope data for three CAI's seperated from Allende which are reported in chapter 3.4 display positive variations for $\varepsilon^{46/47}$ Ti_{49/47}, $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{96/90}$ Zr_{94/90}. Modelling of CAI content within different carbonaceous chondrites groups for $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{96/90}$ Zr_{94/90} demonstrates that isotopic anomalies scale with CAI content. Also held within carbonaceous chondrites are presolar grains which display the exotic signature of their stellar birthplace (Ott, 2001). It is therefore important to calculate the effect of leaching some of the important presolar phases:

4.5.1. SiC grains

The majority of SiC grains (>90%), are termed mainstream grains and originate from low to intermediate mass AGB stars (Hoppe et al., 2009). These types of SiC grains are likely to release most of the Ti from SiC grains. In this work, the effect of these grains on the bulk rock Ti isotope composition of Murchison and Orgueil was estimated using mass balance calculations. For these calculations we utilised the Ti concentrations of SiC grains from Amari et al., (1995)(24.4 ppm) and the average Ti isotope compositions of SiC grains reported by Amari et al. (2000b) for Murchison and from Huss and Smith. (2007) for Orgueil. This information together with the Ti concentration and Ti isotope compositions of the whole rock meteorites (Chapter 3.4) as well as the concentration of SiC in individual samples (Huss, 2003) was utilised to calculate the total contribution of Ti within the whole rock sample from mainstream SiC grains. From the detailed mass balance equations a negligible (<0.01 ε) effect on the whole rock Ti isotopic composition would be expected from the mainstream SiC grains. The largest effect was calculated to be 0.002 ε on Orgueil as it contains the largest abundance of SiC grains.

4.5.2. Hibonite grains

Hibonite (Ca(Al,Mg,Ti)₁₂0₁₉) is one of the most refractory phases within solar system material and were shown to display large ⁵⁰Ti effects in the range of -7% to 10% (Ireland et al., 1985). Although hibonites contain abundant Ti concentrations of around 2500ppm (Liu et al., 2009) and display large isotopic variations they occur in low abundances within meteorites. Utilising the data Liu et al., (2009) detailed mass balance equations were used to calculate the

effects of hibonite on the whole rock Ti isotopic contribution. Again it was found that this single presolar phase had and negligible effect on the bulk rock scale ($<0.01\varepsilon$).

4.5.3. The carrier phases of $\epsilon^{50/47}$ Ti_{49/47} and $\epsilon^{46/47}$ Ti_{49/47} variations

Previous studies have shown that there is a correlation of 5.34 \pm 0.34 for $\epsilon^{50/47}Ti_{49/47}$ versus $\epsilon^{46/47}$ Ti_{49/47} between different meteorite groups at the bulk meteorite scale (Trinquier et al., (2009); Leya et al., (2008) and Chapter 3.4)). In our earlier work (Section 3.4), we interpreted that the $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} solar system correlation could be produced by input of material from a Type II supernova or AGB star. An interesting difference between the carbonaceous chondrites and the ordinary chondrites is the lack of enrichments in $\epsilon^{50/47}$ Ti_{49/47} and $\epsilon^{46/47}$ Ti_{49/47} for QUE 97008. This indicates that anomalous Ti in these meteorites is located in different carrier phases. It is conceivable that the carrier phase(s) enriched in $\epsilon^{50/47}$ Ti_{49/47} and $\epsilon^{46/47}$ Ti_{49/47} were thermally vaporised during the formation of the parent body of QUE97008, whilst the carbonaceous chondrites didn't reach a critical temperature to destroy the phases. In contrast to the bulk rock samples, which define a linear correlation with a slope of 5.34 \pm 0.34 in the $\epsilon^{50/47}$ Ti_{49/47} versus $\epsilon^{46/47}$ Ti_{49/47} diagram, the $\epsilon^{50/47}$ Ti_{49/47} and $\epsilon^{46/47}$ Ti_{49/47} of the leach fractions are not correlated (Fig 4.7). This indicates that the $\epsilon^{46/47}$ Ti_{49/47} and $\epsilon^{50/47}$ Ti_{49/47} anomalies are hosted in different phases and are thus decoupled. Trinquier et al. (2009) came to the same conclusion based on the data for Orgueil and we can extent it here to the carbonaceous chondrites Murchison and the Ordinary chondrite QUE 97008.



Figure 4.7. High precision $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} data for Murchison (Q) and QUE 97008 (Q) and Orgueil (this study and Orgueil (Trinquier et al., 2009). The dashed line shows the whole rock correlation line of 5.34 ± 0.34 for comparison.

4.5.4. The relationship between $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{96/90}$ Zr_{94/90}

Previous studies have shown that there is a correlation between $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{96/90}$ Zr_{94/90} between different meteorite groups at the bulk meteorite scale (Harper et al., 1991; Harper et al., 1990; Leya et al., 2009). In our earlier work (Section 3.4), we argued that the $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{96/90}$ Zr_{94/90} correlation in carbonaceous chondrites was produced by input of CAI material and that the achondrites contained a different composition to that the carbonaceous chondrites. Figure 4.8 plots the $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{96/90}$ Zr_{94/90} data of the CM2 carbonaceous chondrite Murchison (a and b) from the Nu 1700 data alongside the leachate data of Schönbächler et al., (2005). The whole rock data of Murchison and the data for CAI 1NV has been overlaid for comparison. An interesting difference between the Murchison carbonaceous chondrite leachate data is the anti-correlation between $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{96/90}$ Zr_{94/90} compared to the whole rock data. This possibly indicates that the carrier phases of the enrichments in $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{96/90}$ Zr_{94/90} are coupled. One interpretation is that the SiC mainstream grains which display negative $\varepsilon^{96/90}$ Zr_{94/90} anomalies whilst having positive $\varepsilon^{50/47}$ Ti_{49/47} anomalies compared to the terrestrial standard are responsible.


Figure 4.8. The $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{96/90}$ Zr_{94/90} data for Murchison-a,-b. Zr isotope data are from Schönbächler et al. (2005). The Ti and Zr isotope data were obtained in the same leach fractions, such that sample heterogeneities can be excluded. The numbers denote the leach steps. WR: whole rock.

4.5.5. The relationship between $\epsilon^{50/47}$ Ti_{49/47} and $\epsilon^{54/50}$ Cr_{52/50}

By combining the data for Cr from Qin et al., (2011) with the Ti data from this study, which was obtained on the same leach fractions, it is possible to investigate the carrier phases of the neutron rich isotopes in the region of the iron group elements. The isotopes ⁵⁰Ti, ⁵⁴Cr, ⁵⁸Fe and ⁶⁴Ni have been shown to be correlated for some solar system components such as FUN CAI's (Meyer and Zinner, 2006). Figure 4.9 illustrates a similar pattern as in $\varepsilon^{50/47}$ Ti_{49/47} - $\varepsilon^{46/47}$ Ti_{49/47} diagram between QUE 97008 and Murchison, where the refractory phases show no enrichments for the ordinary chondrite but clear enrichments for the refractory phases of Murchison. It is also evident that the carrier phases of $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{54/50}$ Cr_{52/50} are decoupled in the same way as $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{46/47}$ Ti_{49/47}.

Qin et al. (2001) discussed the variability of ^{54/50}Cr between the different meteorite groups being caused by a presolar component responsible for the enriched Cr isotope compositions observed in the refractory signature being heterogeneously mixed into the solar nebula at the time of planetesimal formation. In this case, the magnitude of ^{54/50}Cr isotope variations between different meteorite groups samples the initial nebular heterogeneity within the areas that their parent planetesimals formed. Qin et al. (2011) discussed the contribution of an s-process signature by comparing the Cr data with the Sr data obtained on the same leachate fractions. Qin et al. (2011) stated that if the ^{54/50}Cr_{52/50} variability truly reflected a variable contribution to the solar nebula of the s-process Cr produced in the O/Ne and O/C zones of a Type II supernova then one would expect to see ⁵⁴Cr variations correlate with Sr isotope variations because this stellar setting very efficiently produces Sr, but not elements above Z =40 (Woosley and Heger, 2007). Both ⁸⁶Sr and ⁸⁷Sr are produced in abundance through the weak s-process in high mass stars that become Type II supernova (Woosley and Heger, 2007). However the variations in ⁸⁶Sr do not correlate with those of ⁵⁴Cr. This, along with the similarity in Sr and Ba leaching behaviours suggest that the main carrier of s-process Sr in Murchison is presolar SiC produced in AGB stars and is not related to the carrier of the ⁵⁴Cr excesses.



Figure 4.9. The $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{54/50}$ Cr_{52/50} data for the leachates of Murchison (Q) and QUE 97008 (Q), Cr data from Qin et al. (2011).

4.6. Conclusion

The effects of mainstream SiC and Hibonite grains on the bulk whole rock Ti isotopic composition were investigated with mass balance equations, and found to have a negligible effect. Previous work (chapter 3.4) demonstrated that bulk rock isotopic anomalies within carbonaceous chondrites scale with CAI content for $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{96/90}$ Zr_{94/90} however the $\varepsilon^{50/47}$ Ti_{49/47}versus $\varepsilon^{96/90}$ Zr_{94/90} leachate data display an anti-correlation.

The $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} data of the leachate fractions of the un-equilibrated ordinary chondrite QUE 97008 (Q), the CM2 carbonaceous chondrite Murchison (Q) and Orgueil from Trinquier et al. (2009) demonstrated that the isotopic anomalies are held within different phases and are decoupled. The $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{96/90}$ Zr_{94/90} anti-correlation found for Murchison carbonaceous chondrite leachate data compared to the whole rock data indicates that the carrier phases of the enrichments in $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{96/90}$ Zr_{94/90} are also decoupled. One interpretation is that the SiC mainstream grains which display negative $\varepsilon^{96/90}$ Zr_{94/90} anomalies whilst having positive $\varepsilon^{50/47}$ Ti_{49/47} anomalies compared to the earth determine the observed pattern.

4.7. Acknowledgements

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Chapter 5:

Absolute titanium isotope compositions of solar system materials: mass dependent stable isotope fractionation and stellar sources

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5.1. Abstract

Mass independent studies utilise internal normalization for mass bias correction. The analysis limits the full interpretation of the true location of nucleosynthetic anomalies within solar system material, because it requires utilising a known ratio for the internal normalization procedure to correct for the mass bias introduced in the instrument. Various Ti studies (Leva et al., 2008; Trinquier et al., 2009; Zhang et al., 2012, Chapter 3) used the ⁴⁹Ti/⁴⁷Ti ratio of 0.749766 for internal normalization and reported correlated ^{50/47}Ti_{49/47} - ^{46/47}Ti_{49/47} variations, while ^{48/47}Ti_{49/47} remained constant. The determination of the exact isotope(s) that display nucleosynthetic anomalies is vital for the identification of the stellar source(s) that contributed material to our solar system and generated the nucleosynthetic variation. In this study a ⁴⁷Ti-⁴⁹Ti double spike procedure is utilized to correct for instrumental mass fractionation. The Ti isotope compositions of an un-spiked and a spiked aliquot were measured and used to obtain the absolute Ti isotope compositions. The results demonstrate that ⁴⁸Ti and ⁴⁹Ti do not suffer from nucleosynthetic anomalies in contrast to the other Ti isotopes. Based on the invariant ⁴⁸Ti/⁴⁹Ti ratio in solar system material, the Ti isotope data was corrected for natural mass dependent isotope fractionation utilising a kinetic fractionation equation ((Wombacher and Rehkämper, 2004). The data reveals correlated variations for $\epsilon^{46/48}$ Ti and $\epsilon^{50/48}$ Ti in good agreement with previous Ti studies that assumed an invariant ⁴⁹Ti/⁴⁷Ti ratio. The result confirms that modelling of the nucleosynthetic sources of Ti isotopes carried out in chapter 3 holds true for the new data, implying that SNII and AGB stellar sources are viable sources for Ti within solar system materials. In addition $\epsilon^{47/48}$ Ti and $\epsilon^{50/48}$ Ti display a liner correlation for bulk rock meteorite samples, while an Allende chondrule separate and CAI 1 NV fall off the correlation line. This suggests that a third nucleosynthetic component with varying ⁴⁷Ti abundances exists in the latter samples. The nucleosynthetic origin of this component is unknown.

5.2. Introduction

The isotopic composition of solar system materials reflects the mixing of multiple components delivered to the solar nebula from specific nucleosynthetic sources (Burbidge et al., 1957; Cameron, 1957). Previous mass independent studies examining isotopic heterogeneity within solar system materials has been carried out for a variety of elements, including Ti (Leya et al., 2008; Trinquier et al., 2009; Zhang et al., 2011), Cr (Trinquier et al., 2007; Qin et al., 2010), Ni (e.g. Steele et al., 2011), Zr (e.g. Akram et al., 2013) and Sm (e.g. Carlson et al., 2007). These mass independent results indicate that nucleosynthetic variations

exist on the neutron rich isotope for carbonaceous chondrites and their components. Mass independent results are however compromised by the requirement to fix one isotope ratio for the internal normalisation procedure to correct for mass bias. Utilising the high precision of multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) in combination with the double spike method has allowed the investigation of stable isotope systems of Zn (Arnold et al., 2010) and Ni (Steele et al., 2012), which has enabled the examination of biological and planetary and nebular processes respectively. Titanium stable isotope variations have been observed in terrestrial magmatic rocks (Millet and Dauphas, 2014; Chapter 2 of this study) and in Calcium Aluminium rich Inclusions (CAIs) (Niederer et al., 1985). By analysing the stable isotope system of Ti within various solar system materials we aim to investigate both the Ti stable isotope fractionation and also the nucleosynthetic anomalies inherited in the solar nebula and held within solar system material.

Titanium is a refractory lithophile element which has a high condensation temperature of 1600 K which would have made it condense very early in the solar nebula and make it minimally affected by evaporation. The refractory nature of Ti also allows the preservation of the isotopic compositions of presolar grains which are direct condensates of particular stellar regions. Presolar grains display large isotopic signatures for all Ti isotopes (Amari et al., 2001; Nittler et al., 1995; Zinner, 1998) and are found as components within carbonaceous chondrites. Previous studies report correlated enrichment and depletions in $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{46/47}$ Ti_{49/47} when utilising ^{47/49}Ti =0.79766 as internal normalization for bulk solar system materials and their components, indicating spatial and/or temporal heterogeneity within the protoplanetary disk (Trinquier et al., 2009; Zhang et al., 2011).

To investigate nucleosynthetic variations of Ti on all stable isotopes a ⁴⁷Ti-⁴⁹Ti double spike procedure was used in conjunction with mass independent data for a wide range of bulk solar system materials and their components. The new results also allow the investigation of mass dependent fractionation that occurred to the samples and provide constraints on the nebular processes effecting Ti. The new absolute Ti data is important as it will enable the scrutiny of how well mixed the proto-solar environment was.

5.3. Samples and analytical techniques

The employed experimental techniques are described in detail in chapter 2 and a brief description is included here:

5.3.1. Samples

Meteorite samples were chosen to encompass a wide range of bulk solar system material and their components. Carbonaceous chondrites from a variety of groups were analysed including Orgueil (CI), GRA 06100 (CR), Allende (CV) and Murchison (CM) ; the ordinary chondrites Allegan (H5) and Richardton (H5); R-chondrites NWA 755 (3.7) and NWA 753 (3.9); various achondrites including the eucrites Pasamonte (P-eucrite)and Juvinas (M-eucrite), Dhofar 125 (Acapulcoite), EET 96042 (Ureilite) and the unknown achondrite NWA 7325. Three CAIs (CAI_NV_1, CAI_NV_2, and CAI_NV_3; Akram et al., 2013) as well as a chondrule sample consisting of several chondrules (Allende chondrule; Akram et al, 2013) were separated from Allende (CV3).

5.3.2. Sample digestion and purification

Meteorite samples were crushed in a boron carbide mortar under a laminar flow of filtered air to avoid contamination. Whole rock meteorite samples of up to 100 mg were digested following the modified procedure of Schönbächler et al. (2004) utilising the Parr Bomb® technique.

Meteorite sample aliquots containing 25 µg of Ti were processed through a three stage ion-exchange chromatographic procedure to isolate Ti from matrix elements. The first aliquot was put through an anion exchange chromatography procedure to purify Ti and was subsequently analysed using the mass independent method before being spiked and analysed again using the double spike method. The second aliquot was spiked prior to column chemistry in order to compare with the spiked after column chemistry data to evaluate any mass dependent fractionation that could occur during chemical processing of the samples. Several samples previously analysed utilising the mass independent method in Chapter 3 of this study were also spiked in order to enlarge the range of samples within the investigation. Two groups of data are shown; samples designated with * are samples that have had the double spike added to the sample aliquot after column chemistry, and samples without a * are those that have had the double spike added prior to column chemistry. The procedure of adding the spike prior to and after column chemistry was necessary in order to evaluate possible mass dependent fractionation effects caused by the ion chromatography technique. The separation of Ti utilised a 3 stage ion-exchange chromatographic procedure described in chapter 2 of this study, utilising the procedure developed by Schönbächler et al. (2004).

The Ti fraction was then dried down and re dissolved in 60 μ l conc. HNO₃ + 10 μ l 1 M HF. The solution was then dried down to approximately 0.04 ml of solution before adding 0.96 ml of H₂O. The solutions were then ready for dilution prior to analysis with a Neptune Finnigan MC-ICP-MS at the Open University.

5.3.3. Ti isotope data

In order to obtain absolute Ti isotope data, the applied technique combines results from spiked samples obtained using the 47 Ti 49 Ti double spike method (Chapter 2; Millet and Dauphas, 2014) with mass independent data measured on unspiked aliquots of the same samples. A brief description of the approach is included here, whereas a full description of the analytical methods is given in chapter 2. The mass independent Ti isotope results of the investigated samples (normalised to ${}^{49/47}$ Ti = 0.79766; Niederer et al., 1981) are presented in Chapters 2 and 3.

The double spike data reduction was performed off line, using a procedure previously described by Siebert et al. (2001). This procedure applies a geometric approach to solve the double spike equations in three dimensional isotope spaces. The three axes are defined by isotope ratios with a common denominator, necessitating the use of four isotopes in the inversion process (Russell, 1971). For the inversion process ⁴⁶Ti, ⁴⁸Ti and ⁴⁹Ti with ⁴⁷Ti as the denominator were utilised.

The Ti isotope data are reported relative to the Ti wire standard using the ε notation:

$$\epsilon^{i/48} Ti = \left(\frac{R_{sample}}{R_{standard}} - 1\right) x 10^4 \tag{5.1}$$

Where *i* denotes the isotope masses 46 Ti, 47 Ti, 49 Ti and 50 Ti.

In order to evaluate the absolute nucleosynthetic anomalies that are carried within the Ti composition of solar system materials the fractionation line defined by the following equation (equation 5.2) by Wombacher and Rehkämper. (2003) was applied to the mass dependent fractionated and nucleosynthetic anomalies combined values.

$$\in^{i/48} Ti = \left[\left(\frac{\varepsilon^{48/49}}{10^4} + 1 \right)^{\beta} - 1 \right] x 10^4$$
(5.2)

Where, *i* represent the isotope of mass m_i , and β is given by $[\ln (m_i/m_{48})]/ [\ln (m_{48}/m_{49})]$. Where two of the same samples have been measured the weighted mean has been calculated by:

Weighted mean:
$$= \frac{\sum e^{i/48} Ti x \frac{1}{2 S.E^2}}{\sum 2 S.E}$$
(5.3)

Associated error:
$$\frac{1}{\sqrt{\Sigma \frac{1}{(2 \ S.E)^2}}}$$
 (5.4)

Section 5.4.1 discusses the rational of utilising the ⁴⁸Ti and ⁴⁹Ti data to separate the mass dependent and the nucleosynthetic anomaly data from the combined results of mass dependent fractionation and nucleosynthetic anomalies data. Section 5.4.3 describes the procedure of how the absolute nucleosynthetic anomalies data is separated from the combined mass dependent fractionation and nucleosynthetic anomalies data.

5.4. Results and Discussion

5.4.1. Absolute Ti isotope data: Mass dependent fractionation and nucleosynthetic anomalies data

The Ti mass dependent fractionation and nucleosynthetic anomaly data of terrestrial and solar system materials is presented in table 5.1 and plotted in figures 5.1 and 5.2. A suite of solar system materials including CM and CV carbonaceous chondrites, ordinary chondrites, Achondrites and components of meteorites such as CAI's and chondrules were analysed. For comparison, data for three terrestrial reference samples, two basalts (BHVO-2 and BCR-2) and one andesite (AGV-2) as well as two laboratory standard (Ti AA and Ti wire) are also displayed. For terrestrial samples and laboratory standards these data record mass dependent Ti isotope fractionation (Panels A and B Fig. 5.1), whereas for meteorite samples the absolute Ti isotope data represent a combination of mass dependent fractionation and nucleosynthetic anomalies.

			16/19		47/49		40/49		E0/49	
Sample	Туре	Number	ε ^{™/™} Ti	2 SE	ε ^{τ//†°} Τi	2 SE	ε ^{-s/+} °Ti	2 SE	ε ^{σσγτο} Τί	2 SE
Terrestrial and la	boratory standards									
BHVO-2	Basalt	6	2.12	0.04	1.16	0.04	-1.07	0.01	-2.07	0.12
BHVO-2 *	Basalt	2	2.00	0.04	0.99	0.03	-1.02	0.23	-2.07	0.04
000.0	Prost	<i>c</i>	2.22	0.10	1 21	0.00	1.01	0.05	2 1 2	0.05
BCR-2	Basalt	0	2.32	0.10	1.21	0.06	-1.01	0.05	-2.13	0.05
DCR-2	Basalt	2	2.56	0.01	1.25	0.02	-1.55	0.15	-2.00	0.06
	Andosito	-	1 20	0.15	0.79	0.19	0.77	0.22	1 60	0.04
AGV-2	Andesite	5	1.50	0.15	0.78	0.10	-0.77	0.25	-1.00	0.04
AGV-2	Andesite	2	0.88	0.25	0.47	0.07	-0.45	0.54	-0.91	0.42
Ti wire	Laboratory standard	2	0.49	0.35	0.29	0.35	-0.13	0.28	-0.40	0.37
Τί ΔΔ	Laboratory standard	2	0.15	0.49	0.16	0.35	0.10	0.13	0.06	0.03
Τί ΔΔ #	Laboratory standard	2	0.68	0.45	0.10	0.55	-0.16	0.23	-0.45	0.03
11 00 #		-	0.00	0.20	0.42	0.25	0.10	0.25	0.45	0.25
Carbonaceous ch	ondrites									
Murchison	Carbonaceous chondrite CM2	3	2.03	0.15	0.82	0.11	-0.70	0.05	1.77	0.06
Murchison *	Carbonaceous chondrite CM2	2	2.39	0.05	1.08	0.11	-0.99	0.10	1.15	0.26
Allende	Carbonaceous chondrite CV3	4	2.04	0.31	0.72	0.11	-0.66	0.16	2.12	0.09
Allende *	Carbonaceous chondrite CV3	2	1.33	0.31	0.37	0.14	-0.28	0.15	2.73	0.30
Allende *	Carbonaceous chondrite CV3	2	0.61	0.02	0.04	0.13	-0.06	0.02	3.40	0.11
Ordinary chondri	tes									
Allegan	Ordinary chondrite H5	4	1.36	0.04	0.79	0.05	-0.70	0.07	-1.82	0.10
Allegan*	Ordinary chondrite H5	2	1.59	0.15	0.89	0.06	-0.76	0.11	-1.97	0.08
Richardton	Ordinary chondrite H5	4	2.06	0.11	1.21	0.10	-0.92	0.05	-2.36	0.21
Richardton *	Ordinary chondrite H5	2	-0.08	0.14	0.03	0.07	-0.05	0.10	-0.59	0.15
R-chondrites										
NWA 755	R-chondrite 3.7	2	2.27	0.04	1.13	0.08	-1.10	0.09	-2.54	0.09
NWA 753	R-chondrite 3.9	2	2.18	0.24	1.14	0.16	-0.90	0.20	-2.33	0.34
Achondrites										
Pasamonte	Eucrite-P	2	1.98	0.09	1.15	0.18	-1.13	0.19	-3.47	0.40
Pasamonte *	Eucrite-P	2	2.03	0.39	1.23	0.19	-1.09	0.15	-3.48	0.33
Juvinas	Eucrite-M	2	2.06	0.33	1.21	0.32	-1.18	0.03	-3.64	0.08
Dhofar 125	Acapulcoite	2	1.10	0.14	0.61	0.06	-0.70	0.10	-2.71	0.14
EET 96042 *	Ureilite	2	4.83	0.04	2.49	0.01	-2.57	0.08	-7.04	0.04
NWA 7325	Unknown	3	-5.46	0.18	-2.47	0.09	2.42	0.08	2.98	0.17
CAI's and chondre	ules									
CAI NV 1		3	3.49	0.19	0.63	0.10	-1.47	0.08	7.05	0.11
CAI NV 1*		2	4.80	0.00	1.22	0.06	-2.15	0.09	5.83	0.03
CAI NV 2*		3	0.62	0.20	-0.73	0.11	-0.27	0.14	9.36	0.32
CAI NV 3 *		2	0.55	0.24	-0.08	0.10	0.54	0.21	5.98	0.23
Allende chondrul	es*	2	1.64	0.12	0.30	0.10	-0.60	0.06	3.67	0.13

Table 5.1. Titanium mass dependent fractionation and nucleosynthetic anomaly data for terrestrial and solar system materials. Uncertainties are reported as 2SE.

* Denotes samples spiked after column chemistry

 $\epsilon^{49/48}$ Ti data correspond to mass dependent isotope fractionation data

Ti AA measured relative to Ti AA

Ti AA # measured relative to Ti wire

The employed ion-exchange separation procedure can fractionate Ti stable isotopes, as has been shown in chapter 2. This effect can be further evaluated using data for samples spiked before and after column chemistry presented in table 5.1 and figure 5.1, which indicate that mass dependent fractionation does occur during column chemistry as is shown by the difference in ε ^{49/48}Ti values between the same samples for the two different procedures. The

amount of mass dependent fractionation caused by the column chemistry technique varies and is not constant as is shown by the large fractionation observed for the ordinary chondrite Richardton, whereas other samples (e.g. Allegan and Pasamonte) show no resolvable difference in the Ti isotope data between samples spiked before and after column chemistry. The Richardton data for samples spiked before column chemistry gives a value of -0.92 ± 0.05 for $\varepsilon^{49/48}$ Ti while the data for Richardton spiked after column chemistry gives a value of -0.05 ± 0.10 for $\varepsilon^{49/48}$ Ti. It is therefore necessary to only consider the samples spiked before column chemistry when discussing mass dependent fractionation as the amount of fractionation caused by the column chemistry technique cannot be quantified for the samples that were spiked after column chemistry.

Igneous processes can cause Ti stable isotope fractionation, as has been shown in chapter 2 by analyses of the terrestrial basalts BHVO-2 and BCR-2 that display relative to the Ti wire standard slightly more Ti stable isotope fractionation compared to the andesite AGV-2 (Fig. 5.1(A)). The absolute Ti isotope data of meteorite samples contain both Ti stable isotope fractionation and nucleosynthetic Ti isotope anomalies (Fig. 5.1). Hence, the effects of nucleosynthetic anomalies must be separated from the effects of mass dependent fractionation in order to evaluate both effects independently.



Figure 5.1. Titanium mass dependent fractionation and absolute nucleosynthetic anomalies displayed as $\epsilon^{i/48}$ Ti (y-axis) per isotope *i* for: (A) Terrestrial reference samples, (B) Laboratory standards, (C) CM and CV carbonaceous chondrites, (D) CI and CR carbonaceous chondrites, (E) Ordinary chondrites, achondrites and R chondrites spiked before column chemistry. (F) Ureilite and NWA 7325 (potentially from Mercury). Black line indicates a mass dependent fractionation line of 1 ϵ unit per amu. All uncertainties are displayed as 2 SE.

All investigated bulk samples lie on the mass dependent fractionation line $\varepsilon^{48/47}$ Ti versus $\varepsilon^{49/47}$ Ti (Fig 5.2 A + B). Hence, this suggests that for bulk meteorite samples ⁴⁹Ti and ⁴⁸Ti display no nucleosynthetic anomalies. Based on this observation it was decided to use the ^{48/49}Ti ratio to determine the Ti mass dependent stable isotope fractionation of samples and use the ^{48/49}Ti ratio within the kinetic fractionation equation in order to deduce the mass dependent and nucleosynthetic components of the absolute Ti isotope data. Hence, it was chosen to report the newly obtained Ti isotope data as $\varepsilon^{i/48}$ Ti and not as $\varepsilon^{i/47}$ Ti, which has been used in several recent studies (Leya et al., 2007; 2009; Trinquier et al., 2009 and Zhang et al., 2011). The absolute Ti isotope data suggest though that CAI's and Allende chondrules display small nucleosynthetic anomalies for ⁴⁸Ti and/or ⁴⁹Ti. Therefore, this will impact on the determination of the mass dependent fractionation and nucleosynthetic Ti isotope components of CAI's and Allende chondrules utilising the ^{49/48}Ti ratio.



Figure 5.2. Titanium mass dependent isotope fractionation and absolute nucleosynthetic isotope anomalies displayed as (A) ^{49/47}Ti (x-axis) against ^{48/47}Ti (y-axis) for all samples spiked before chemistry. (B) ^{49/47}Ti (x-axis) against ^{48/47}Ti (y-axis) for all samples spiked before (black) and after chemistry (grey, ACC).

The data presented in figure 5.3 enables the investigation of where the Ti isotopic anomalies reside within solar system materials. Figure 5.3 (A) demonstrates that nucleosynthetic isotoep anomalies reside on both ⁴⁶Ti within bulk samples and also within ⁴⁷Ti for components such as CAIs and chondrules. Figure 5.3 (B) confirms that 46Ti displays nucleosynthetic anomalies within solar system materials. Figure 5.3 (C) again confirms anomalies reside on ⁴⁷Ti within solar system materials.



Figure 5.3. Titanium mass dependent isotope fractionation and absolute nucleosynthetic isotope anomalies data for meteorite samples displayed as (A) ^{46/48}Ti (x-axis) against ^{47/48}Ti (y-axis). (B) ^{46/48}Ti (x-axis) against ^{49/48}Ti (y-axis). (C) ^{47/48}Ti (x-axis) against ^{49/48}Ti (y-axis).

5.4.2. Titanium stable isotope composition solar system materials

In order to compare the stable isotope composition with stable isotope composition data of other elements such a Cu and Zn (Luck et al., 2003; 2005) the data has been displayed in the δ notation as $\delta^{49/48}$ Ti ($\delta^{49/48}$ Ti= $\epsilon^{49/48}$ Ti/10). As shown in the previous section ⁴⁹Ti and ⁴⁸Ti display no nucleosynthetic anomalies and can be utilised to display stable isotope compositions of terrestrial and meteorite samples. All samples except NWA 7325 display a light Ti stable isotope composition relative to the Ti wire standard while NWA 7325 displays an extreme heavy stable isotope composition (Fig. 5.4). This indicates that NWA 7325 experienced extreme parent body fractionation processes likely from igneous activity that affected its Ti stable isotope signature.



Figure 5.4. Titanium mass dependent only data for samples spiked prior to column chemistry. Data is displayed in the delta notation as $\delta^{49/48}$ Ti relative to Ti wire.

The carbonaceous chondrites Murchison (CM) and Allende (CV) display within uncertainty of each other identical Ti stable isotope compositions with -0.07 ± 0.01 and -0.07 ± 0.02 for $\delta^{49/48}$ Ti, respectively (Fig. 5.5). This indicates similar nebular processing during the formation of CM and CV carbonaceous chondrites. NWA 755 and NWA 753 also have within uncertainties the same Ti stable isotope signature of $\delta^{49/48}$ Ti = at -0.11 ± 0.01 and -0.09 ± 0.02

respectively. The ordinary chondrites Allegan and Richardton display a slight difference in their $\delta^{49/48}$ Ti values of -0.07±0.01 and -0.09±0.01 respectively. The achondrites Pasamonte and Juvinas display the lightest Ti stable isotope composition of the investigated bulk meteorite samples with values of -0.11±0.02 and -0.12±0.01 for $\delta^{49/48}$ Ti respectively.



Figure 5.5. Titanium mass dependent only data for samples spiked prior to column chemistry with NWA 7325 data removed. Data is displayed in the delta notation as $\delta^{49/48}$ Ti

5.4.3. Absolute nucleosynthetic Ti isotope anomalies:

After applying the kinetic fractionation equation of Wombacher and Rehkämper, (2004) the mass dependent fractionation can be separated from the absolute nucleosynthetic anomalies within solar system materials. Applying equation 5.2 to the mass dependent plus nucleosynthetic anomaly data allows the calculation of the mass dependent only data. As described in section 5.4.1 the ⁴⁸Ti and ⁴⁹Ti data display no nucleosynthetic variations for bulk solar system materials and were utilised in the kinetic fractionation equation (equation 5.2). The $\varepsilon^{48/49}$ Ti values of the initially of mass dependent fractionation plus nucleosynthetic anomalies data was utilised as they only display mass dependent fractionation. In order to

calculate the absolute nucleosynthetic anomaly data, the mass dependent data was subtracted from the initially calculated mass dependent plus nucleosynthetic anomaly data. Absolute Ti nucleosynthetic anomalies results for samples spiked before and after column chemistry are listed in table 5.2.

Tab	le 5.2	. Absolute	e nucleo	osyntheti	ic Ti	i isotope	variations	data	for	terrestrial	and	solar
syst	em ma	aterials for	r sampl	les spike	d be	fore and	after colu	mn ch	emi	stry.		

Sample Type Number e T 2.5e t T 2.5e t T 2.5e E T
Carbonaceous chondrites 0.42 0.17 0.09 0.03 0.00 1.79 0.13 Murchison Carbonaceous chondrite CM2 3 0.58 0.05 0.11 0.07 0.00 0.00 3.16 0.05 Murchison * Carbonaceous chondrite CM2 2 0.58 0.05 0.11 0.07 0.00 0.00 3.16 0.05 Murchison * Carbonaceous chondrite CM2 2 0.35 0.22 0.08 0.21 0.00 0.00 3.10 0.17 Murchison weighted mean Carbonaceous chondrite CV3 4 0.68 0.29 0.05 0.13 0.00 0.00 3.44 0.36 Allende * Carbonaceous chondrite CV3 2 0.75 0.29 0.09 0.10 0.00 3.28 0.01 Allende * Carbonaceous chondrite CV3 2 0.49 0.02 -0.02 0.11 0.00 0.00 3.28 0.01 Allende weighted mean Carbonaceous chondrite CV3 2
Orguell* Carbonaceous chondrite CI1 2 0.42 0.17 0.09 0.00 0.00 1.79 0.13 Murchison * Carbonaceous chondrite CM2 3 0.58 0.05 0.11 0.00 0.00 3.16 0.05 Murchison * Carbonaceous chondrite CM2 2 0.35 0.22 0.08 0.21 0.00 0.00 3.16 0.05 Murchison weighted mean Carbonaceous chondrite CM2 2 0.57 0.05 0.11 0.00 0.00 3.10 0.17 Allende Carbonaceous chondrite CV3 2 0.57 0.05 0.11 0.00 0.00 3.44 0.36 Allende * Carbonaceous chondrite CV3 2 0.75 0.29 0.09 0.10 0.00 3.28 0.01 Allende * Carbonaceous chondrite CV3 2 0.75 0.29 0.09 0.10 0.00 3.52 0.15 Allende weighted mean Carbonaceous chondrite CV3 2 0.70 0.42 0.21 0.18 0.00 0.00 3.28 0.01 GRA
Murchison Carbonaceous chondrite CM2 3 0.58 0.05 0.11 0.07 0.00 0.00 3.16 0.05 Murchison * Carbonaceous chondrite CM2 2 2 0.08 0.21 0.00 0.00 3.10 0.17 Murchison weighted mean Carbonaceous chondrite CM2 2 0.05 0.11 0.06 0.00 0.00 3.10 0.17 Allende Carbonaceous chondrite CV3 4 0.68 0.29 0.05 0.13 0.00 0.00 3.44 0.36 Allende * Carbonaceous chondrite CV3 2 0.75 0.29 0.09 0.10 0.00 0.00 3.28 0.01 Allende * Carbonaceous chondrite CV3 2 0.75 0.29 0.09 0.10 0.00 0.00 3.28 0.01 Allende * Carbonaceous chondrite CV3 2 0.49 0.02 -0.02 0.11 0.00 0.00 3.28 0.01 GRA 06100 * Carbonaceous chondrite CR2 2 0.70 0.42 0.21 0.18 0.00 0.00
Murchison * Carbonaceous chondrite CM2 3 0.35 0.02 0.00 0.00 3.10 0.01 Murchison weighted mean Carbonaceous chondrite CM2 2 0.08 0.11 0.07 0.00 0.00 3.10 0.17 Allende Carbonaceous chondrite CV3 4 0.68 0.29 0.05 0.13 0.00 0.00 3.44 0.36 Allende * Carbonaceous chondrite CV3 2 0.75 0.29 0.09 0.10 0.00 3.28 0.01 Allende * Carbonaceous chondrite CV3 2 0.75 0.29 0.09 0.10 0.00 3.28 0.01 Allende * Carbonaceous chondrite CV3 2 0.75 0.29 0.09 0.10 0.00 3.28 0.01 Allende weighted mean Carbonaceous chondrite CV3 2 0.49 0.02 -0.02 0.11 0.00 3.28 0.01 GRA 06100 * Carbonaceous chondrite CR2 2 0.70 0.42 0.21 0.18 0.00 2.08 0.41
Murchison weighted mean Carbonaceous chondrite CV3 2 0.33 0.22 0.06 0.21 0.00 3.10 0.17 Allende Carbonaceous chondrite CV3 4 0.68 0.29 0.05 0.13 0.00 0.00 3.44 0.36 Allende * Carbonaceous chondrite CV3 2 0.75 0.29 0.09 0.10 0.00 3.28 0.01 Allende * Carbonaceous chondrite CV3 2 0.75 0.29 0.09 0.10 0.00 3.28 0.01 Allende * Carbonaceous chondrite CV3 2 0.49 0.02 -0.02 0.11 0.00 0.00 3.28 0.01 Allende weighted mean Carbonaceous chondrite CV3 2 0.70 0.42 0.21 0.18 0.00 0.00 3.28 0.01 GRA 06100 * Carbonaceous chondrite CR2 2 0.70 0.42 0.21 0.18 0.00 0.00 2.08 0.41
Allende Carbonaceous chondrite CV3 4 0.68 0.29 0.05 0.13 0.00 0.00 3.44 0.36 Allende * Carbonaceous chondrite CV3 2 0.75 0.29 0.09 0.10 0.00 3.44 0.36 Allende * Carbonaceous chondrite CV3 2 0.75 0.29 0.09 0.10 0.00 3.28 0.01 Allende weighted mean Carbonaceous chondrite CV3 2 0.49 0.02 -0.02 0.11 0.00 0.00 3.28 0.01 GRA 06100 * Carbonaceous chondrite CR2 2 0.70 0.42 0.21 0.18 0.00 2.08 0.41
Allende Carbonaceous chondrite CV3 4 0.68 0.29 0.05 0.13 0.00 0.00 3.44 0.36 Allende * Carbonaceous chondrite CV3 2 0.75 0.29 0.09 0.10 0.00 3.24 0.36 Allende * Carbonaceous chondrite CV3 2 0.75 0.29 0.09 0.10 0.00 3.28 0.01 Allende weighted mean Carbonaceous chondrite CV3 2 0.49 0.02 -0.02 0.11 0.00 0.00 3.28 0.01 GRA 06100 * Carbonaceous chondrite CR2 2 0.70 0.42 0.21 0.18 0.00 0.00 3.28 0.01
Allende * Carbonaceous chondrite CV3 2 0.75 0.29 0.09 0.10 0.00 3.28 0.01 Allende * Carbonaceous chondrite CV3 2 0.49 0.02 -0.02 0.11 0.00 0.00 3.28 0.01 Allende * Carbonaceous chondrite CV3 2 0.49 0.02 -0.02 0.11 0.00 0.00 3.28 0.01 GRA 06100 * Carbonaceous chondrite CR2 2 0.70 0.42 0.21 0.18 0.00 0.00 2.08 0.41
Allende * Carbonaceous chondrite CV3 2 0.49 0.02 -0.02 0.11 0.00 0.00 3.52 0.15 Allende weighted mean Carbonaceous chondrite CV3 2 0.49 0.02 -0.02 0.11 0.00 0.00 3.52 0.15 GRA 06100 * Carbonaceous chondrite CR2 2 0.70 0.42 0.21 0.18 0.00 0.00 2.08 0.41
Allende weighted mean 0.49 0.02 0.04 0.06 0.00 3.28 0.01 GRA 06100 * Carbonaceous chondrite CR2 2 0.70 0.42 0.21 0.18 0.00 2.08 0.41
GRA 06100 * Carbonaceous chondrite CR2 2 0.70 0.42 0.21 0.18 0.00 0.00 2.08 0.41
Ordinary chondrites
Allegan Ordinary chondrite H5 4 0.04 0.02 0.11 0.05 0.00 0.00 -0.52 0.09
Allegan* Ordinary chondrite H5 2 0.03 0.34 0.12 0.17 0.00 0.00 -0.47 0.25
Allegan weighted mean 0.04 0.02 0.12 0.05 0.00 0.00 -0.52 0.08
Richardton Ordinary chondrite H5 4 0.15 0.01 0.27 0.12 0.00 0.00 -0.53 0.13
Bithardton * Ordinary chandrics HS 2 -0.18 0.21 0.00 0.00 0.05 0.19
Richardton weighted mean 0.15 0.01 0.09 0.00 0.00 0.00 0.00 0.02 0.12
R-chondrites
NWA 755 R-chondrite 3.7 2 0.01 0.21 0.02 0.17 0.00 0.00 -0.37 0.26
NWA 753 R-chondrite 3.9 2 0.32 0.34 0.22 0.32 0.00 -0.55 0.16
Achondrites
Pasamonte Eucrite-P 2 -0.34 0.35 0.01 0.35 0.00 0.00 -1.24 0.12
Pasamonte * Eucrite-P 2 -0.21 0.09 0.12 0.04 0.00 0.00 -1.34 0.04
Pasamonte weighted mean -0.22 0.09 0.12 0.04 0.00 -1.33 0.04
Juvinas Eucrite-M 2 -0.37 0.01 0.34 0.00 0.00 -1.31 0.02
Dhotar 125 Acapulcoite 2 -0.33 0.10 -0.11 0.00 0.00 -1.33 0.24
EET 96042* Ureilite 2 -0.48 0.15 -0.12 0.09 0.00 -0.00 -1.95 0.13
NWA 7325 Unknown 3 -0.48 0.02 -0.01 0.02 0.00 0.00 -1.80 0.15
CAI's and chondrules
CAI NV 1 3 0.47 0.29 -0.86 0.18 0.00 0.00 9.95 0.18
CAINV1* 2 0.38 0.18 -0.96 0.15 0.00 0.00 10.07 0.14
CAI NV 1 weighted mean 0.41 0.15 -0.92 0.11 0.00 0.00 10.03 0.11
CAINV 2* 3 0.08 0.18 -1.00 0.15 0.00 0.00 9.88 0.09
CAINV3* 2 1.67 0.65 0.47 0.31 0.00 0.00 3.60 0.00
Allende chondrules* 2 0.40 0.04 -0.31 0.10 0.00 0.00 4.86 0.03

The absolute Ti nucleosynthetic anomaly data clearly displays positive enrichment in the isotopes ⁴⁶Ti and ⁵⁰Ti within carbonaceous chondrites (Fig. 5.6 (A, B)). The $\varepsilon^{50/48}$ Ti results for Murchison and Allende display very similar values of 3.15 ± 0.05 and 3.28 ± 0.01 (Table 5.2), whereas Orgueil (CI) and GRA 06100 (CR) display slightly smaller excesses in ⁵⁰Ti with $\varepsilon^{50/48}$ Ti of 1.79 ± 0.13 and 2.08 ± 0.41 . The data furthermore indicates that small positive anomalies are also present on ⁴⁷Ti for Orgueil (CI), GRA 06100 (CR) and potentially also for

Murchison (CM) (Fig. 5.6 B). The ordinary chondrites, achondrites and R chondrites display enrichments and depletions on ⁴⁶Ti, however they all display clear depletions on ⁵⁰Ti (Fig. 5.6 C). The ureilite EET 96042 and the unknown achondrite NWA 7325 display identical depletions on ⁴⁶Ti as well as identical larger depletions on ⁵⁰Ti (Fig. 5.6 D). This indicates that the ungrouped achondrite NWA 7325 and the ureilites EET 96042 may have formed within similar regions within the early solar system or have accreted from material with similar compositions. Oxygen isotope data of mineral separates from NWA 7325 also indicate similarities with the ureilites (Jabeen et al., 2014). However the stable isotope composition data for NWA 7325 displays heavy isotope fractionation, which is contrary to all other samples measured (Fig. 5.4), indicating that it experienced extreme parent body fractionation potentially by igneous activity.

CAI NV 1 and NV2 display identical enrichment on ⁴⁶Ti of 0.41 ± 0.15 and 0.08 ± 0.18 for $\varepsilon^{46/48}$ Ti, respectively and 10.03 ± 0.11 and 9.88 ± 0.09 for $\varepsilon^{50/48}$ Ti, with identical depletions on $\varepsilon^{47/48}$ Ti of -0.92 ± 0.11 and -1.00 ± 0.15 (Table 5.2, Fig 5.6. E). CAI NV 3 displays the largest enrichment on ⁴⁶Ti of 1.67 ± 0.65 for $\varepsilon^{46/48}$ Ti with a small enrichment on $\varepsilon^{47/48}$ Ti of 0.47 ± 0.31. However, the enrichment displayed on ⁵⁰Ti is 4.90 ± 0.19 for $\varepsilon^{50/48}$ Ti which compared to the large enrichments displayed for CAI NV 1 and 2 is only half.



Figure 5.6. Titanium absolute nucleosynthetic isotope anomalies displayed as $\epsilon^{i/48}$ Ti (y-axis) per isotope *i* for: (A) CM and CV carbonaceous chondrites. (B) CI and CR chondrites. (C) Ordinary chondrites, achondrites and R- chondrites. (D) Ureilite and NWAA 7325 (potentially from Mercury). (E) CAI's and chondrules. All uncertainties are displayed as 2 SE.

The nucleosynthetic only Ti data suggest that correlated enrichments and depletions are present for ⁴⁶Ti and ⁴⁷Ti as is indicated by the main correlation line in the $\varepsilon^{47/48}$ Ti v $\varepsilon^{46/48}$ Ti plot that displays a slope of 0.233 (Fig. 5.7 A). However, two CAI's (CAI NV 1 and CAI NV 2) as well as Allende chondrules plot off this main correlation line on a different ⁴⁷Ti composition, hence implying the presence of an additional nucleosynthetic component. Type B and Type A CAIs sample two compositionally different reservoirs as is suggested by Hf (Sprung et al., 2010) and Zr (Akram et al., 2013) data for the same CAIs as investigated in the present study. Akram et al. (2013) attributed that the nucleosynthetic compositions of CAI NV 1 and NV 2 characterized by $\varepsilon^{96/90}$ Zr_{94/90} with average values of 1.9 ± 0.1 and depletions in ε^{177} Hf and ε^{179} Hf was distinct from other planetary bodies as is evident in Figure 5.7 (B and C) for Ti isotopes. While CAI NV 3 is characterized by smaller excesses in $\varepsilon^{96/90}$ Zr_{94/90} and enrichments in ε^{177} Hf and ε^{179} Hf pointing to a different composition containing *r*-process enrichment.

Correlated enrichments and depletions in ⁴⁶Ti and ⁵⁰Ti are present for different chondrite groups (Fig. 5.7 B), as was indicated from previous mass independent Ti work. Some CAIs plot as positive extreme values off the $\varepsilon^{50/48}$ Ti versus $\varepsilon^{46/48}$ Ti correlation line. CAI NV 3 plots along the mainstream solar system materials Ti isotope line (Fig. 5.7 C) indicating a different nucleosynthetic origin compared to CAI 1 NV and CAI 2 NV. The carbonaceous chondrites Orgueil (CI) and GRA 06100 (CR) represent normal solar system composition and plot along the correlation line of 2.52 ± 0.30 for $\varepsilon^{50/48}$ Ti versus $\varepsilon^{46/48}$ Ti (Fig. 5.7 C) A second correlation line appears to move off the mainstream solar system correlation line from the CI carbonaceous chondrite through CM and CV carbonaceous chondrite to the CAI composition of CAI NV 1 and NV2 (Fig. 5.7 C). This second trend line suggests that the absolute nucleosynthetic Ti isotope values of carbonaceous chondrites depends on the non-mainstream CAI's content within the whole rock.

The $\varepsilon^{50/48}$ Ti versus $\varepsilon^{46/48}$ Ti correlation (Fig. 5.7 C) is evidence for large-scale spatial and/or temporal isotopic heterogeneity in the solar protoplanetary disk. The mass independent correlation line of $\varepsilon^{46/47}$ Ti_{49/47} versus $\varepsilon^{50/47}$ Ti_{49/47} likely reflects mixing of material from the O/Ne and O/C zones of a Type II supernova. This based on the modelling of Rauscher et al. (2002) 25 solar mass Type II core collapse supernova data as is detailed in chapter 3. However, the absolute nucleosynthetic Ti isotope variations found utilising the double spike technique indicate that three different reservoirs of material existed at the beginning of the solar system with some CAI's exhibiting an independent signature



Figure 5.7. Absolute nucleosynthetic Ti isotope anomalies displayed as (A) $\epsilon^{46/48}$ Ti (x-axis) against $\epsilon^{47/48}$ Ti. (B) $\epsilon^{47/48}$ Ti (x-axis) against $\epsilon^{50/48}$ Ti. (C) $\epsilon^{46/48}$ Ti (x-axis) against $\epsilon^{50/48}$ Ti. Displayed are results for different classifications of meteorites and their components, samples spiked before and after chemistry.

5.5. Conclusion

New absolute Ti isotope data for various solar system materials determined via the double spike procedure for samples spiked before and after column chemistry are presented. From the double spike procedure of samples spiked before column chemistry, both absolute nucleosynthetic anomalies and stable isotope compositions were determined. Titanium stable isotope data of solar system materials demonstrate that all materials except NWA 7325 display isotopically light Ti stable isotope compositions compared to the Ti wire isotope standard. The stable isotope composition of the terrestrial basalts BHVO-2 and BCR-2 are distinct from the andesite AGV-2 demonstrating that different igneous processes induce stable isotope fractionation within terrestrial and solar system materials.

The absolute nucleosynthetic Ti isotope variations observed for solar system material demonstrate that the solar system is a mixture of at least two separate distinct compositions demonstrated by the differences observed within the CAI's examined. The Ti data of the CAIs compliments the study of the same CAI's for Zr and Hf by Akram et al. (2013) in confirming the existence of three distinct nucleosynthetic components within solar system materials.

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5.7. References

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6. Conclusion

Titanium isotopic compositions were determined for a range of chondritic groups and planetary bodies and display a strong correlation between $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{46/47}$ Ti_{49/47}. The slope of 5.34 ± 0.34 for the correlation in $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} is in good agreement with previous work by Trinquier et al. (2009) and Zhang et al. (2010). Carbonaceous chondrites show the largest positive anomalies on the neutron rich $\varepsilon^{50/47}$ Ti_{49/47}, enstatite chondrites and the moon show terrestrial ratios within uncertainty, as is observed for other iron group elements such as Ni on $\varepsilon^{64/61}$ Ni_{58/61} (Steele et al., 2012), Cr on $\varepsilon^{54/52}$ Cr_{50/52} (Trinquier et al., 2007) and Zr on $\varepsilon^{96/90}$ Zr_{94/90} (Schönbächler et al., 2003; Akram et al., 2011).

A strong correlation is observed between $\varepsilon^{96/90}$ Zr_{94/90} and $\varepsilon^{50/47}$ Ti_{49/47} where admixing of variable amounts of CAI's into Earth materials correlates the Ti and Zr isotopic anomalies with each carbonaceous chondrite group, where CV>CM>CR>CI indicating that CAI's are the main carrier phase of Ti and Zr. Chromium and Ni isotope data for CI carbonaceous chondrites indicate that Ti and Zr anomalies are held within different components to Cr and Ni (Steele et al., 2012; Trinquier et al, 2007). An additional carrier phase is also required as is evident from the different results found for Murchison when utilising two different digestion techniques. The Murchison aliquot digested using the microwave technique did not fall on the $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} solar system correlation line of 5.34 ± 0.34 unlike the Murchison aliquot utilising the Parr Bomb technique which indicates that the microwave technique was unable to dissolve all presolar refractory phases.

Various nucleosynthetic models of environments such as SNIa, SNII and AGB stars into the solar system were investigated. The results were compared with the slope line of 5.34 ± 0.34 found for $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} for different chondrite groups which span the large scale heterogeneity in the early solar system. Bulk addition of material from SNIa could not reproduce the correct slope in $\varepsilon^{50/47}$ Ti_{49/47} v $\varepsilon^{46/47}$ Ti_{49/47} isotope space. However bulk addition of a 3 solar mass low metallicity AGB star would produce the correct Ti composition. The investigation of individual shells and zonal yields of SNII by utilising various nucleosynthesis models provided by Rauscher et al. (2002) enabled the examination of the isotopic products of a range of hydrostatic and explosive burning phases. The O/Ne, O/C and He/C zones of a 25 solar mass SNII can reproduce the Ti isotope signature observed in the solar system. Therefore, there is no need for multiple stellar sources and thermal processing of material in the protoplanetary disk to explain the observed Ti isotope variations as was suggested by Trinquier et al. (2009). The double spike technique using ⁴⁹Ti-⁴⁷Ti spike combination was used to investigate mass dependent fractionation effects within terrestrial basalts BHVO-2 and BCR-2 as well as the andesite AGV-2. The results obtained for the terrestrial reference samples showed that mass dependent fractionation effects do exist between the two terrestrial basalts BHVO-2 and BCR-2 and the andesite AGV-2 indicating that the Ti double spike procedure is a valid technique to study igneous processes. Stable isotope compositions of a variety of solar system materials were also investigated which demonstrated that all materials except NWA 7325 displayed light stable isotope compositions compared to the Ti wire isotope standard.

The double spike technique was also utilised for the mass dependent analysis of Ti isotopes within solar system materials. The main aim of the study was to overcome the instrumental mass bias problems encountered during mass independent analysis and isolate the absolute nucleosynthetic variations that exist among solar system materials. The double spike methodology was combined with the kinetic fractionation equation of Wombacher and Rehkämper. (2004) in order to isolate absolute nucleosynthetic variations that exist among solar system materials. The two carbonaceous chondrites Allende and Murchison both display positive nucleosynthetic anomalies for $\varepsilon^{46/48}$ Ti and $\varepsilon^{50/48}$ Ti and correlates well with the previous mass independent Ti studies of Trinquier et al. (2009) and Zhang et al. (2012). The absolute nucleosynthetic variations observed for solar system material indicate that the solar system is a mixture of at least two separate distinct compositions as demonstrated by the differences observed within the CAI's examined. The Ti data of the CAIs compliments the study of the same CAI's for Zr and Hf by Akram et al. (2013) in confirming the two distinct nucleosynthetic components found within solar system materials.

The leachate study conducted on the Ordinary chondrite QUE 97008 and the carbonaceous chondrites Murchison (CM), Allende (CV) and Orgueil (CI) support the results of the absolute nucleosynthetic variations within the different meteorite samples. The $\varepsilon^{50/47}$ Ti_{49/47} versus $\varepsilon^{46/47}$ Ti_{49/47} data of the leachate fractions of the un-equilibrated ordinary chondrite QUE 97008 (Q), the CM2 carbonaceous chondrite Murchison (Q) and Orgueil from Trinquier et al. (2009) demonstrated that the isotopic anomalies are held within different phases and are decoupled. The refractory phase containing a positive ${}^{50/47}$ Ti_{49/47} was contained within the carbonaceous chondrites Murchison and Allende and absent from the Ordinary chondrite as the CAI's are the carriers of this phase, which are absent from ordinary chondrites. The $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{96/90}$ Zr_{94/90} anti-correlation found for Murchison carbonaceous chondrite leachate data compared to the whole rock data indicates that the carrier phases of the

enrichments in $\varepsilon^{50/47}$ Ti_{49/47} and $\varepsilon^{96/90}$ Zr_{94/90} are also coupled. One interpretation is that the SiC mainstream grains which display negative $\varepsilon^{96/90}$ Zr_{94/90} anomalies whilst having positive $\varepsilon^{50/47}$ Ti_{49/47} anomalies compared to the earth determine the observed pattern.

The timing by which inherited Ti nucleosynthetic components were delivered into the solar system before its formation remains unclear. However, it is shown that the protostellar disk was heterogeneous at the formation epoch of CAI's.

6.1. Future work

The absolute nucleosynthetic data indicates that CAI's display nucleosynthetic anomalies on ⁴⁶Ti, ⁴⁷Ti and ⁵⁰Ti, ⁹⁶Zr and deficits on ¹⁷⁷Hf and ¹⁷⁹Hf. It is therefore recommended that nucleosynthetic models be investigated to discover the stellar environment responsible for the production of this material.

Mass dependent fractionation has been shown to occur within terrestrial and solar system materials. Analysis of more solar system materials as well as lunar samples will provide a greater repository of information and hence enable greater scrutiny of the different processes at work.