Atomistic Scale Modelling of Phosphate Mineral Phases for Nuclear Waste Form Development

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by

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Abstract

Phosphate minerals such as β -tricalcium phosphate and fluorapatite are abundant, exhibit a large chemical variability and samples of both phases are often used for geochronometry; so their stability over thousands of years is known. This makes them attractive as nuclear waste forms as they are stable over extended periods of time and are able to accommodate a range of waste species. In particular, due to the difficulty of incorporating halides in conventional waste forms (in particular glass), fluorapatites are considered as potential hosts for radioactive waste streams containing both actinides and halides. β -tricalcium phosphate, a strucutre related to fluorapatite, is not only used as a precursor for preparing apatites, but could itself be used as a host for radioactive waste. To better understand the structure and stability of these phases, atomic scale computer simulation has been employed (both dynamic and static), using classical pair potentials .

One site in the β -tricalcium phosphate structure has previously been assigned a half occupancy from fitting to Rietveld power diffraction experimental data. The half occupancy gives rise to an ordering effect where the Ca²⁺ ions are arranged over the half occupied Ca(4) sites, in many different configurations. A comparison of different cell sizes (and increasing configuration number) is given and reported in terms of lattice energy and structural parameters. The largest cell size considered here generates the most stable structures, which have a symmetry group related to the experimentally derived average primitive unit cell. Simulated X-ray diffraction patterns indicate a difference in spectra for these low energy configurations. However, experimental X-ray diffraction patterns fail to differentiate between low energy structures. The results of the experiment and small difference in lattice energy for the most stable structures, indicate that domains containing different low energy structures are likely to exist. The configurations described here are also discussed in terms of statistical analysis.

Substitutions of a range of isovalent and trivalent cations have been carried out (and compared) at Ca²⁺ sites in both fluorapatite and β -tricalcium phosphate structures. The defect and solution energies were calculated for both structures and compared, in order to predict the partitioning across the two phases. For the isovalent defects investigated, the defects segregate to the β -tricalcium phosphate lattice. The trivalent defects present a different trend such that defects with a smaller ionic radii than Ca²⁺ have an energy preference for β -tricalcium phosphate, but for those with atomic radii closer to that of the host cation the preference for either structure is indistinguishable. The ramifications of cation partitioning are discussed.

Cation and anion migration in fluorapatite is considered, where the overriding feature of migration in this structure is that ionic transport (of either cations or anions) occurs preferably along the *c*-axis. Consideration of fluorine transport yields a more sophisticated migration mechanism than that reported previously. A "concerted mechanism" for fluorine ion transport in the lattice is discussed fully and described using fluorine density plots, over a range of temperatures.

Radiation damage effects in these minerals and their ability to recover and resist damage is a crucial consideration when designing a nuclear waste host. This thesis compares the Kinchin-Pease model of threshold displacement energies to full radiation cascades. Furthermore, the effect of radiation damage on the lattice is considered by virtue of incident damage, defect types, phosphate group response and recovery of the lattice. These results indicate that the fluorapatite lattice is "relatively tolerant" to radiation damage, especially with regard to the phosphate tetrahedra, but more cascades should be considered to obtain a more statistically reliable prediction.

Finally, loss of material from the waste form is most likely to occur at a surface and understanding the processes by which this occurs is important. Therefore, it is necessary to first model the surfaces, which involves static simulations of surfaces to predict surface formation energies. These energies are used as the basis for predictions of particle morphology and the effect of isovalent defect incorporation near the surface of fluorapatite.

Dedication

This thesis is dedicated to Momsville and Dadfordshire, the best parents a girl could ever wish for. Words simply cannot express my gratitude to you both.

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Acronyms

- β -TCP β -tricalcium phosphate
- **dpa** displacements per atom
- **FAp** fluorapatite
- **HEC** High Energy Configuration
- **IEC** Intermediate Energy Configuration
- **ILW** Intermediate Level Waste
- HLW High Level Waste
- **LEC** Low Energy Configuration
- **LLW** Low Level Waste
- **MD** Molecular Dynamics
- **NEB** Nudged Elastic Band
- **NFC** Nuclear Fuel Cycle
- **PKA** Primary Knock on Atom
- **QM** Quantum Mechanical
- **REE** rare earth element

SYNROC Synthetic Rock

- **TEC** Thermal Expansion Coefficient
- **E**_d Threshold Displacement Energy
- **UK** United Kingdom
- **UKAEA** United Kingdom Atomic Energy Authority
- **VLLW** Very Low Level Wastes
- **XRD** X-ray Diffraction
- **ZBL** Ziegler, Biersack and Littmark

"We do not inherit the earth from our ancestors, we borrow it from our children"

Native American Proverb

Introduction

1.1 Motivation

Today, one of the most important issues facing society is energy consumption and future energy supply. World energy demand is forecast to increase 53% by 2030, over two thirds of which will be in developing countries [1]. Today most of our energy comes from the fossil fuel trio of gas, coal and oil. However, security of supply is a crucial consideration and many countries receive interrupted deliveries of oil and gas due to local conflict [2], which has an effect on local economies, especially with the price of a barrel of oil currently being worth over £100 [1].

To secure supply, energy is also produced from a number of other sources, which include re-

newable sources such as wind, solar and biomass projects as well as nuclear power plants. An abundance of uranium (used as nuclear fuel) throughout the world in politically stable locations, provides greater security and reliability of supply compared to other energy generation mechanisms.

The civilian use of nuclear fission for electricity generation began nearly 60 years ago and has subsequently provided (and continues to provide) reliable energy base load capacity; nuclear generating capacity is set to increase by 14-19% in Europe by 2030 [3]. The first generation of nuclear power stations were justified by the need to reduce smog caused by coal fired power plants [3] as well as being an economical source of base load energy; nuclear plants reduced reliance on fossil fuel imports. Contemporary ideas have evolved somewhat. Heightened awareness of climate change has led to a push for low carbon energy programmes, such as nuclear energy, which has CO_2 emissions (per kWh generated) that are comparable to technologies such as on-shore wind power [4]. Furthermore, the cost of nuclear energy per MWh is said to be cheaper than offshore wind and coal plants by nearly £100/MWh [5].

Generally, the British public are becoming more receptive to the idea of nuclear power. Interestingly even after the recent events in Japan at the Fukushima-Daiichi plant [6], public opinion shows that 68% of the population are pro nuclear power [7], which is a reduction of only two points from the last poll in 2007 [8]. It follows that the nuclear industry in the United Kingdom (UK) is set to grow and international demand for nuclear energy has increased 13.5% in the last thirty five years and is currently forecast to continue to grow [9].

With the continued expansion of the nuclear industry, there are heightened concerns over the by-products of this industry; that is disposal of waste and possible proliferation, which is the diversion of nuclear materials for weapons purposes. The design and classification of nuclear waste packages requires an insight into the source, volume, composition and activity of the waste stream to be processed. This is because the precise type and radioactive constituents of waste attained from different nuclear power plants can vary greatly [10]. Furthermore, historical wastes such as legacy or orphan wastes (which are wastes with no long term disposal plan), often contain a range of species in different concentrations, which have low solubility levels (if any) in current proposed waste hosts [11]. Wastes like these include species such as halides that cannot be adequately encapsulated by traditional means; in borosilicate glasses, for example [12]. The solubility of actinides and chlorides in glass is low [13, 14]; for example 1-3% for Cl^- in silicate glasses [169] and alternative disposal methods must be developed.

While legacy and orphan wastes await disposal, the total waste stocks continue to increase. The issue of increasing nuclear waste stores is considered to be one of the most costly and pressing environmental problems for the 21st century [15], and is often cited as a negative by critics of nuclear power [13, 16, 17]. During the past fifty years the nuclear fuel cycle has produced what is estimated to be 1400 metric tons of plutonium and substantial quantities of actinides, such as Cm, Np and Am [18]; every year a further 200 kg of Pu is generated [19]. As a result, concerted research into radioactive waste management with various storage policies is of great importance.

The nuclear fuel cycle can be described as "Open", "Closed" or "Semi-Closed". In the Open Fuel Cycle all the spent nuclear fuel is disposed of without any chemical separation or recovery of fissionable material from the irradiated fuel, also known as reprocessing. In the Semi-Closed Fuel Cycle fuel is reprocessed to extract any remaining fissile Pu or U, then any remaining High Level Waste (HLW) waste is disposed. In a fully Closed Fuel Cycle Pu, U and many actinides and rare earth elements (REEs) are also reprocessed before disposal.

The nuclear fuel cycle, outlined in figure 1.1, includes reprocessing not just disposal of waste fuel. Immobilisation is defined as the conversion of a waste into a waste package by solidification, chemical incorporation into a matrix or encapsulation [10]. Encapsulation of waste is achieved by physically surrounding the waste in other materials, such as cement or bitumen [20]. Both chemical immobilisation and encapsulation processes are carried out on any higher activity waste to ensure maximum security and stability of the waste package itself.

It is generally proposed that, after immobilisation waste products will be stored permanently in borehole or underground geological repositories [21]. Such repositories are analogous to a Russian Matryoshka doll, with nested layers of protection between the biosphere and the nuclear waste. The rock into which the repository is built constitutes the outermost barrier, followed by the back fill and other engineered barriers. Within this multi-barrier scheme the immobilising material represents the innermost level of protection [10, 22].

Global pressure to immobilise or store a variety of legacy and orphan wastes, including those from reprocessing spent nuclear fuel, has led to increased interest in developing an alternative waste hosts (to those already on the market as discussed later) that supports halides. One collection of alternative materials are phosphates. Phosphate based materials have been proposed as a suitable waste host for Pu and halides, which have low solubilities in more traditional



Figure 1.1: An outline of the main stages of the nuclear fuel cycle, that includes reprocessing.

waste forms [22–24] (see section 1.3).

Interest in phosphate materials as potential waste forms stems from a natural phenomenon observed in Gabon, West Africa, where a deposit of uranium minerals of sufficient quantity and surrounding rocks of an appropriate porosity, gave rise to the formation of a natural nuclear reaction (see figure 1.2 [25]). This reactor was operational and produced hundreds of kilowatts of heat, for what could have been millions of years [25]. The area is remarkable not only for the presence of this natural nuclear reactor, but also the fact that the highly radioactive waste products have stayed within the vicinity of the reactor, without the elaborate containment systems of an engineered repository. Extraordinarily, after all this time, waste species have migrated only a few metres from their source. Further investigation into this area has revealed that the surrounding geology primarily comprises phosphate rich materials [23, 26].

Phosphate minerals are of great importance in a diverse range of fields; primarily due to their structure and chemistry, which allow a wide range of elements with different charge states to be incorporated into them. They are therefore of interest as long-term stable nuclear waste forms; they can incorporate a wide range of waste species, including those that have limited


Figure 1.2: Oklo mine in Gabon, West Africa, 1997. Photograph by Minesite Engineer, Andreas Mittler.

solubility in more conventional waste forms [27]. Thus, phosphate based materials may provide higher waste loadings and improved chemical stability for difficult waste species. To address the requirement for an alternative waste form that will encapsulate species such as halides and actinides in significant volumes, two phosphate structures will be investigated in this thesis. The two minerals are fluorapatite (FAp) and a related structure [28] β -tricalcium phosphate (β -TCP), which are often formed simultaneously.

1.2 Radioactivity and Types of Radioactive Waste

Radioactivity can originate from forced radiation events (e.g fission) or spontaneously where certain isotopes decay releasing energy and other particles, an example of this latter phenomenon is given in figure 1.3.

Decaying species only remain radioactive for a certain period of time. This time is governed by their half life, which is the amount of time taken for the radioactivity of a given species to diminish by half; thus, after a period of three half lives, the sample would have a radioactivity level $\frac{1}{8}$ of that when it started. Radioactive half lives can range from seconds, minutes through millions of years. As isotopes decay, either immediately or after further decay processes, they form more stable, non-radioactive isotopes [29].

As isotopes decay the subsequent radiation emitted transfers energy via two main mechanisms. The first mechanism is easy to imagine; ballistic collisions of the atomic nuclei. This energy is kinetic and shared between the particle hit and the recoil nucleus. This ballistic process is what disrupts and displaces ions in an otherwise perfect lattice. The recoil nuclei deposit large energies over short distances, which leads to the knock on effect of ion displacements, which further damages the matrix. This can also lead to a localised temperature spike in one particular



Figure 1.3: Spontaneous decay of $^{239}_{94}$ Pu, creating a helium ion (α particle) and $^{235}_{92}$ U which move off in opposite directions with energies specified.

area and retained energy in the matrix. The second mechanism is where energy is transferred to electrons by ionisation or electronic excitations.

In a nuclear reactor and in nature there are a number of different types of radiation that can affect surrounding materials, these are; alpha, beta, gamma and neutron. Each type of radiation interacts with materials in completely different ways and damage caused by radiation is dependent upon the type. Furthermore, heavy ion fragments from fission events can also cause displacement damage.

α radiation

Alpha radiation is the least penetrating form of radiation: it is a helium nucleus and as such has the largest mass of all the radiation types and consequently has a short radiation pathway; it can be stopped with relatively light shielding, as shown by figure 1.4. However, α radiation can be damaging to materials, especially nuclear fuel pellets or cladding materials, which are in the immediate vicinity of the decay event in a reactor. α radiation gives rise to high energy recoil nuclei, in the range of 70-100 keV, which dissipate energy via ionisation but also undergo many elastic collisions, leading to hundreds of atomic displacements. The α particle has a significant



Figure 1.4: Graphical representation of the type of shielding required to prevent the travel of various radiation types.

ionising effect and its associated recoil particles can cause large displacement cascades in the material via both elastic and inelastic collisions with other atoms in the material; as a result interaction with biological matter can have disastrous effects. Any material designed to store α emitters, such as uranium and plutonium will have to withstand constant damage. It is relatively straightforward to protect humans from α particles (given the relative stopping distance, figure 1.4), although inhalation or ingestion are considered to be high risk [30].

β radiation

 β particles are fast moving, high energy electrons or positrons. They are the result of a neutron decaying into a proton, a high energy electron and an anti-neutrino, as shown in equation 1.1.

$$n^0 \to p^+ + e^- + \bar{\nu}_e.$$
 (1.1)

This form of radiation is ionising and more penetrating than α but less so than γ rays or neutrons. β decay occurs most often in fission products from reactors that are neutron rich. β radiation can be stopped by a few millimetres of aluminium (figure 1.4), and β emitters are often used as medical tracers for cancers and other health conditions. β radiation often provides the source of positrons used in positron emission tomography scans [31].

X-ray and γ radiation

X-ray and γ radiation are highly penetrating and highly energetic forms of radiation and both are examples of electromagnetic radiation. They are produced by atomic interactions, for example electron-positron annihilation, radioactive decay, fission or fusion [30]. X-rays are different from γ -rays because they are emitted by electrons outside of the nucleus, while γ rays are only emitted by the nucleus. This type of radiation requires a thick shield of lead or concrete in order to stop it; γ rays are highly ionising; they can strip electrons off atoms, and the higher energy the radiation the thicker the shielding that is required. γ -rays can induce the alteration of deoxyribonucleic acid in biological materials and as such are the most biologically damaging forms of radiation.

Neutron radiation

Neutron radiation may be emitted during either fission or fusion and is highly penetrating, but less so than γ [32]. Neutrons can be captured by stable nuclei making them radioactive (creating an activated product) and so initiating further α or β decay processes. When a stable nucleus absorbs a neutron it is also possible for γ rays to be released as part of the absorption process, as the nucleus decays from an excited state to its ground state. Neutrons can also interact with atoms in solids to produce elastic collisions, if their energy is higher than the atomic displacement energy.

Neutron radiation is often used for scattering and diffraction experiments to determine the structural properties of materials. It is also used in medical fields to treat cancerous tumours and is the basis of a number of imaging techniques [33].

As discussed the various types of radioactivity interact differently with matter. Each type of radiation requires different shielding to prevent radiation from reaching the environment, figure 1.4 summarises these effects.

1.2.1 Waste Classifications

Radioactive waste can arise from the nuclear fuel cycle, or from decommissioning nuclear plants [34], it can also be a by-product from weapon production or testing, or in a material that simply becomes contaminated due to its proximity to other nuclear sources. This includes a wide variety of material, such as: used equipment, clothing and nuclear reactor components by volume. Nuclear waste can generally be described as something incorporating radionuclei which produce radioactivity above a threshold that is defined by legislation. Radioactive waste is classified by its activity and heat generating capacity. The classifications are aimed to enable proper treatment of waste, specialised handling and correct disposal. Non-nuclear industries also produce radioactive waste, for example hospitals, research establishments and oil and gas industries. In the medical industry radioisotopes are often used as tracers for imaging or for radiotherapy treatments [35]. The UK now classifies radioactive waste into four main groups as follows [35]:

Very Low Level Waste

Very Low Level Wastes (VLLW) contain such low levels of radioactivity that under current regulation they require no special protective measures. These wastes are generally sent to civil landfill sites, or are incinerated along with domestic refuse as they require no special handling.

Low Level Waste

Wastes that are considered to have an α content of no more than 4 GBq/tonne and a β/γ content of no more than 12 GBq/tonne [10] are said to be Low Level Waste (LLW). This includes waste arising from the use of radioactive materials in research, medicine and industry. LLW generally consists of discarded protective clothing, equipment and building rubble from nuclear host sites [10]. It requires containment to prevent any direct handling but does not normally require shielding. Since 1959, most of the UK's solid LLW has been disposed of at a United Kingdom Atomic Energy Authority (UKAEA) licensed sites in Drigg, Cumbria or at Dounreay, Scotland [35]. Interestingly large parts of Cornwall, England could be said to be LLW since the natural radioactivity of the topsoil and associated rock is within the limits defined for LLW!

Intermediate Level Waste

Intermediate Level Wastes (ILWs) are mainly made up of materials that have been irradiated in a nuclear reactor, or equipment from reprocessing radioactive materials and chemical residues. ILW are radioactive wastes whose activity exceeds the upper limits of LLW materials, but are not radioactive enough to be in the high level category. In particular the limit states that the waste must not exhibit any radiological self-heating [36]. As a by-product of both civil and military nuclear operations ILWs are often stored at the reactor sites where they arise, or at reprocessing and naval dockyards. ILWs can consist of reactor components, filters and chemical residues, pieces of irradiated fuel cladding and materials contaminated with plutonium [22].

High Level Waste

In the UK HLW is mostly the liquid waste produced from the reprocessing of nuclear fuels. The intensely radioactive fission products in HLW are created from the reprocessing of spent nuclear fuel (fuel that no-longer contains a sufficient proportion of fissionable material to make an economical fuel source) and weapons development. They are frequently left in the form of an acid liquor (an acidic liquid often containing dissolved metal salts or lanthanides), after the removal of U and Pu. The extent of α , β and γ activity is sufficiently high that these wastes are also referred to as 'heat generating' because their radioactive decay produces considerable heat, which needs special consideration [13, 21]. HLW requires sophisticated storage and disposal techniques which include substantial shielding; a balance of neutron absorbers is required in any host matrix [37].

Adding to the existing volume of waste, the UK annually produces about $16,000 \text{ m}^3$ of additional radioactive waste, as shown in figure 1.5. Most of this volume (about 86 % by volume) is LLW, and a much smaller fraction, around 0.1 % is HLW waste (see figure 1.5). Most of the radioactivity is in the HLW category, while the lower level wastes contributes most to the total volume. It is, however, the HLW and ILW that really need careful consideration when designing waste for long term storage.



Figure 1.5: Relative volumes of radioactive waste by category, data taken from the UKAEA [35].

1.2.2 Reactor Waste vs. Defence Wastes

Nuclear waste arises from three main sources: the nuclear fuel cycle used for civil energy and military considerations, non nuclear fuel cycle institutes (often medical or academic establishments) and from accidents. From these, the nuclear fuel cycle is the main contributor to nuclear waste stocks.

Civil waste from the nuclear fuel cycle comes from nuclear power reactors used to provide (at current statistics) 13-14 % of the world's electricity generating capacity [38]. The basis for this type of energy provision lies in starting a chain reaction in the main fuel elements and keeping the reaction critical (so that the stability of the reactor is maintained). This fission reaction is exothermic, providing thermal energy that is (typically) used to generate steam, which drives turbines that in turn generate electricity in the same way that a coal fired power plant would.

There are a number of different power plant types and each type of power plant produces wastes with different compositions. The waste comprises spent nuclear fuel (that which has reached the end of its useful life), impurities from the fuel cladding, transuranic elements formed by neutron capture and traces of separated Pu. Waste is subsequently stored to reduce its short term radioactivity and allow it to cool (decay heat). Sadly, during the early part of the nuclear era, considerations for nuclear waste were nowhere near as stringent as they are today, since disposal of waste with the whole nuclear fuel cycle in mind was not contemplated, now a requirement in the UK [39]. As a result many wastes from this time (also known as legacy wastes) have been poorly characterised and stored in conditions that are far from the ideal. The term "legacy wastes" covers a huge range of materials, from Pu contaminated materials, fuel cladding, corroded fuel elements, tools and equipment, all amalgamated together [10]. In many cases these wastes have been stored under water and have degraded to form sludges amongst other substances.

A good example of this is Building 38 in Sellafield [40], figure 1.6. During the 1972 miners' strike the nation's nuclear plants were run at full steam to fully supply the grid with energy. During this period there was not enough time to properly reprocess and store left over fuel and cladding so it was simply left in cooling ponds, in Building 38, to disintegrate. Building 38, is renowned as the most dangerous industrial building in Europe [40], where reactor fuel rods and reactor parts have been stored under water. For 50 years these parts have disintegrated and degraded into sludge that emits high doses of radiation [40].



Figure 1.6: Image of building 38 (centre) in Sellafield, UK taken by Robert Brook [40]

Defence wastes are produced mainly as a by-product from the processing of Pu and tritium for use in nuclear weapons. Defence wastes are inherently different from commercial types of waste; they are generally less radioactive and have far fewer fission products. However, they typically have high concentrations of sodium from treatment of initially acidic waste. There are also varying quantities of other ions present, such as: Fe, Al, Hg, Cl, F, Ni and Ce. The exact compositions depend upon the origin of the waste [41, 42].

To date there has been approximately 380,000 m³ or 960 million [23] Curies of waste produced from the reprocessing of waste for weapons production. About 99 % of the radioactivity will be related to non-actinide radionuclides (arising from reprocessing), whose half lives are generally less than 50 years. After 500 years the primary inventory of waste species in the stream is likely to be ²³⁸Pu, ¹³¹Sm and ²⁴¹Am. After 50,000 years the radioactivity levels will mainly be associated with species that have longer lived half lives, such as ²³⁹Pu and ²⁴⁰Pu, [23].

Under the Strategic Arms Reduction Treaties (START) I and II, [43, 44] as well as bilateral Russia-United States agreements, thousands of nuclear weapons are being dismantled. This results in a large volume of weapons grade plutonium that requires long-term disposal. The disposal path must ensure that the public and environment are protected from potentially harmful waste species. It is also crucial that any waste form must be proliferation resistant from its waste host, that is recovery of fissile material for use in weapons must be impractical.

The fate of nuclear wastes generated by the nuclear fuel cycle in both civilian and military operations is an extremely important issue; without global clear-up of waste there is no future for the nuclear industry. Military and civil wastes can both be handled in the same way; either the waste is reprocessed to remove any unused U or Pu for fuel, or stored directly. After reprocessing a mixed oxide fuel can be created, from the U and Pu removed, for use in a pressurised water reactor [10, 16]. As mentioned previously, generally fuel that cannot be reprocessed must be disposed of by dissolution of waste elements into a host lattice so the species are directly incorporated into the lattice as a solid solution (immobilisation), or alternatively, by encapsulation within an inert matrix, which forms a composite material. Both these strategies will be incorporated into an underground repository, leading to a multi-barrier system. Figure 1.7 shows an example of the Finnish waste repository, Onkalo, which is due to open in 2020 in accordance with the Finnish Nuclear Energy Act [45].

This thesis will specifically concentrate on immobilising a halide rich, legacy ILW waste stream arising from pyrochemical reprocessing of plutonium. This contains a large number of cations together with KCl and CaF₂. Conversion of these ILWs into a form acceptable for long-term temporary storage or permanent disposal requires the actinides and halides inherent in these wastes to be immobilised into a monolithic form [46].



Figure 1.7: Artist's impression of a typical geological store of the type being built in Onkalo, Finland (picture courtesy of Dr M.J.D.Rushton). Waste will be transported down vertical shafts and stored in chambers within the Earth's crust.

1.3 Waste Host Materials

Reprocessed legacy wastes can contain high levels of halides (specifically high concentrations of F^- and Cl^- ions) and actinides (which are highly toxic and radioactive). The solubility of these species within traditional glassy waste hosts is low [13, 47]. In addition to this, high leaching rates and chemical instability of glass while immobilising these cations [13] has led to a search for an alternative waste host for these particular waste streams.

The design of any waste form must comply with stringent rules and regulations, which aim to limit detrimental effects on the environment from a breach of the waste form. According to Ewing *et al.* [48] the most important properties to consider when choosing an ideal waste form

are:

- 1. Increased chemical durability as a function of waste loading.
- 2. Controlled radiation damage and radiation effects.
- 3. Consideration of the thermal and chemical nature of the disposal site.
- 4. Chemical tolerance to variation in waste stream composition.
- 5. Viable processing technologies that can be operated remotely.

1.3.1 Immobilisation of Radioactive Wastes in Glass

Glasses are amorphous in nature and do not exhibit any long range order and have a clear defined glass transition temperature [49]. Glasses were initially proposed as a waste form in the early 1950s in Canada using natural silicate minerals as a starting material, because the amorphous nature of glass provides protection against radiation damage and its effects [11, 14, 24].

Glasses are used in the nuclear industry as a waste immobilising matrix via vitrification (simply the transformation of a substance into a glass). Vitrification is attractive, not only because of the small volume of the resulting waste form, but also the large number of elements that can be incorporated into the open glass structure and the high durability of glasses [14, 49]. Interestingly, for an average person in a first world country all nuclear waste arising from creating the energy required for their life time can fit into a single borosilicate "puck" as shown in figure 1.8.

The type of glass selected for a nuclear waste host is a compromise between durability and processing ability. Ideally the glass needs to exhibit high solubility of waste species, low leaching rate, low processing temperatures and radiation tolerance and thermal stability [10, 13, 50]. The most durable silicate glass is pure SiO₂, however it has a processing temperature of 1773 K [51]. The most durable materials need processing temperatures of over 1500° C, however, radionuclides become volatile at much lower temperatures, generating secondary waste (and meaning the radionuclides to be immobilised do not actually enter the waste form) and decreasing the immobilising efficiency of the waste [10]. As a result borosilicate or phosphate glasses



Figure 1.8: A "puck" of borosilicate glass sufficient to hold all HLW waste arising from one person's lifetime, picture courtesy of BNFL.

are more commonly used as they have processing temperatures of 1000° C [10]. Glasses like these have typical waste loadings in the range of 10-30 wt % [24]. In principle the radionuclides are spread evenly throughout the glass, although some metal and crystalline oxide precipitates may be present.

When it comes to encapsulating wastes with high levels of actinides, lanthanides and halides, these glasses have limited loading; 0.5 wt% and 1 wt% for Ce and Hf respectively in borosilicate glasses [11, 22]. Furthermore, including these isotopes generates chemical instability, which increases leaching and devitrification in borosilicate glasses [13]. Thus, glasses cannot be considered as a suitable waste form for such legacy wastes, as poor stability can lead to unwanted crystal formation or enhanced leaching rates.

1.3.2 Encapsulation of Radioactive Wastes in Cement

Cements are often used as encapsulating materials for solid ILWs. An example of the use of cementitious materials is in the waste drums depicted in figure 1.9. These waste drums are then stacked in above ground repositories such as those at Dounreay and Drigg [35, 38], (see figure 1.10). Halides, however, are highly soluble in Portland cement and have the effect of reducing overall chemical durability to unacceptable levels, so excluding it as a suitable waste form candidate [16].



Figure 1.9: A waste drum containing solid waste from a light water reactor encapsulated in cementitious material. (Image courtesy of British Nuclear Fuels Limited.)



Figure 1.10: Stacking of barrels in a repository (picture courtesy of Dr M.J.D. Rushton).

1.3.3 Immobilisation of Radioactive Wastes in Crystalline Waste Forms

McCarthy *et al.* [52, 53] have previously assessed some of the problems associated with immobilisation in glass (devitrification and leaching problems under the action of water [12]) and proposed ceramic materials as an alternative. Many natural crystalline minerals have been seen to retain high concentrations of radionuclides whilst remaining thermodynamically stable for millions of years [25]. These minerals have also demonstrated long term chemical and physical durability in their indigenous environments. Similarly the first uranium was extracted from these same stable minerals that contain an appreciable proportion of U. There are a number of minerals that contain a range of elements that are of particular interest for waste encapsulation [10, 13, 48], these are: monazites, zircon, zirconolite, pyrochlores, zirconia, garnet, perovs-kites and apatites to name a few. Monazites, for example, have been found to contain up to $15 \text{ wt}\% \text{ UO}_2$ and $11 \text{ wt}\% \text{ ThO}_2$ [13]. Creating a waste form via a multi-component ceramic aims to achieve good waste loading of elements (specifically actinides and halides), mechanical strength, slow kinetics and thermodynamic stability over all geological time periods [17].

In both naturally occurring and synthetic crystalline hosts, radionuclides can be incorporated by occupying their usual sites in the mineral or substitution onto lattice sites that usually host other cations [54]. For crystalline minerals to incorporate such varied waste streams, an array of multi-phase minerals, incorporating polyhedra of varying size and chemistry are preferable. Interestingly, ceramic waste forms have also been shown to have higher waste loading for many elements compared with glasses [13]. One of the main problems with ceramics when compared to glasses, is that ceramics generally have a lower tolerance to radiation damage and readily amorphise during radiation damage, losing their structure and affecting the materials properties [14, 50]. However, geological samples from Gabon show that over long timescales surrounding ceramic matrices such as apatites and monazites appear to have withstood or recovered from radiation damage [55, 56].

Furthermore, ceramics have higher thermal conductivities leading to a more rapid decrease in waste form temperature allowing for easier handling. The natural analogues for waste immobilisation studied by Gauthier-Lafaye *et al.* [56] indicated that the most efficient matrix for actinide retention was the uranite mineral, but apatites, zirconium silicates and oxides came close behind [56]. These many advantages have paved the way for intensive research into crystalline and polycrystalline ceramics as potential waste hosts [54, 57].

1.3.3.1 Synroc

A good example of a multi-phase crystalline waste host is Synthetic Rock (SYNROC), first developed in Australia by Ringwood *et al.* [12, 58]. SYNROCs can be tailored to specific waste streams, to enable immobilisation of a wide range of waste species. Nevertheless, SYNROCs always consist of the same basic phases: zirconolite, hollandite and perovskite [54]. This offers a number of different structures and crystal chemistries into which a plethora of waste elements

can be incorporated [12, 58, 59]. For example, hollandite $(BaAl_2Ti_2O_6)$ can incorporate larger cations (Ba, Cs, Sr, K and Rb) into the 'large tunnels along the *c*-axis' [54], and smaller cations (Mo, Ru, Fe, Ni and Cr) in its octahedral sites [54]. Perovskite (CaTiO₃) is aimed at the containment of Sr and U on the Ca and Ti sublattice sites respectively, however a range of other elements can also be incorporated [54]. The final phase, zirconolite (CaZrTi₂O₇) is the proposed host for both U and actinides and shows solid solubility for rare earth elements.

The form of SYNROC preferred can accept up to 20% calcined HLW in the form of dilute solid solutions. The constituent materials of SYNROC have been seen in nature to maintain stability over geological time scales, whilst retaining elements that can also be found in nuclear wastes [60, 61]. Furthermore, SYNROC can survive 24 hour leaching tests with water or 10% NaCl solution at temperatures which would decompose borosilicate glasses.

SYNROCs are created via a hot pressing and recrystallisation process [13]. However, this requires temperatures of around 1200-1400 K [12] which can cause the radionuclides to become volatile and then generate further secondary waste; clearly this effect is undesirable [13].

1.3.3.2 Zircon

Zircon (ZrSiO₄) forms as a crystalline phase in glass ceramic waste forms and has been proposed for immobilisation and disposal of weapons-grade Pu [60] and actinides. Natural zircons, with an age of four billion years have been found and provide much evidence for their long-term durability, especially because of their widespread use in geochronology and fission track-dating [62]. An example of a zircon mineral can be seen in figure 1.11. Zircon has a relatively good resistance to radiation; it does not suffer crystalline - amorphous transition at high fluences [63].

These minerals have shown U and Pu retention over long time scales under a variety of natural geological conditions [15]. Pu readily substitutes for Zr in zircon and can even reach loading levels of 5-20 wt% [62], although of course these levels may have to be diminished to avoid criticality problems. Natural U and Th levels range from near zero to a few wt % [64]. However, enrichment of U and Th within the zircon structure often leads to a reduced ZrO_2 content and increased H₂O. It is assumed that REEs will substitute for Zr, but the limited presence of natural zircon with these elements reduces the knowledge of its stability over long time scales [64].



Figure 1.11: Example of zircon, sample is provided by the Natural History Museum, London.

1.3.4 Pyrochlores

The name pyrochlore originates from the Greek words for "fire" and "green" [65]; some pyrochlore samples become green after firing. Like the zirconolite phase used in SYNROC, pyrochlores share the same derivative crystallographic structure; fluorite. However, pyrochlores differ from the true fluorite structure in the ordering of their cation sublattices and a lower oxygen content [66].

U contents in samples of natural pyrochlores range from 0 to 22wt %. Species such as Na, Ca, Sr, Fe Nb, Ta, Ti can all be incorporated into pyrochlores to a similar level as U (~ 22wt %). These elements tend to cluster together in the matrix, creating zones with high concentrations of additional elements and zones with low or zero concentrations, which is undesirable [64]. Th on the other hand is rarely found in natural pyrochlores with the average natural loading being 1 wt% [64]. The age of natural pyrochlores tends to be lower than zirconolites or zircons, indicating that natural pyrochlores have a limited geological lifetime.

1.3.5 Phosphate Ceramics

Phosphate (PO_4) based structures have proved themselves to be promising candidates for hosting radioactive wastes. The main evidence for their suitability comes from one of nature's more curious events; fourteen natural nuclear fission reactors in three different ore deposits in the Franceville basin, Gabon, West Africa [67–69]. The large uranium deposits found here have been subsequently investigated to assess the effect of the fission products on the host rocks [55, 67, 70]. It is thought that around 2 billion years ago [67] fission reactions took place spontaneously (in uranium deposits of sufficient quality and quantity) and were sustained for some 100,000-500,000 years, moderated and cooled by rainwater, intermittently when heat dissipated allowing ingression of water. The remnants of the fission processes still lie close to the "reactors" where they were first created. Clearly, the long timescales over which these fission products have been retained in the surrounding rock, is of great interest to those seeking a new nuclear waste host with determinable longevity [55, 71]. Here sources of U have been found in monazite (Ce, La, U, Ca,REE)PO₄, and thorite (Th, U)SiO₄ [67], a sample of which can be seen in figure 1.12.



Figure 1.12: Sample of the monazite mineral. Sample provided by the Natural History Museum, London.

The word monazite is derived from the greek monazein and means "to be solitary" [72]. Even though monazites have high waste loadings of U, they can be slowly dissolved in leaching tests with HCl [10, 73]. The search at Franceville Basin showed that other minerals such as apatites, clays and zirconium oxides are instrumental in retention of fission products and actinides.

Apatites $(Ca_{10}(PO_4)_6X_2 X=F, Cl, OH)$ have also been discovered in close proximity to uranite (UO_2) in the mines at Franceville, see figure 1.13. Horie *et al.* [74] conclude that the apatite boundary (an example of which is shown in figure 1.13) has survived uranite dissolution for over 1.92 billion years. Furthermore, REEs and Pu have been seen in the apatite phases and are considered to be "selectively trapped" within them; these species segregate to the apatite phase over all others [74].

However, just like monazites, apatites can be slowly dissolved in HCl and other acidic solutions [10].



Figure 1.13: Enrichment of uraninite and apatite between clay and sandstone layers, taken from Oklo Mine, Gabon, West Africa. The image has been taken from the work of Horie *et al.* [74].

As mentioned previously radioactive wastes from pyrochemical reprocessing contain high concentrations of halides and actinides, so both must be incorporated into a waste host. However, as discussed while many minerals such as zircon, zirconolite, monazite and pyrochlores can incorporate actinides few minerals can also take on halides. Halide content can also be problematic at glass-ceramic interfaces (as they disrupt bonds), affecting the leaching properties [41]. Substantial Th and U contents combined with stability over geological timescales, apatites and monazites serve as natural analogues demonstrating the ability to encapsulate actinides. Furthermore, since Cl and F ions are constituent elements in the structure of apatite, incorporation of both Cl and F is intrinsic to the mineral itself.

A related phase, whitlockite (or β -TCP), is also found to exist alongside apatitic phases [25]. β -TCP (β -Ca₃(PO₄)₂), provides enormous compositional flexibility for a range of REEs and actinides. Previous study has shown that a range of lanthanides and actinides can be incorporated into the structure, by using X-ray phase analysis and scanning electron microscopy with an energy-dispersive X-ray system [75, 76]. Crucially for a waste form, Orlova *et al.* also suggest that β -TCP is resistant to radiation damage [73]. Furthermore, fission tracks in apatites disappear over geological timescales as the material can recover from such radiation damage in these timescales [77–80].

Both apatites and β -TCP are of interest as nuclear waste form [41, 46] because of their flexible chemistry in allowing a degree of compositional variation, stability over long time scales and the potential for radiation damage resistance. Thus, this thesis will concentrate on further understanding the ability of structures to accommodate waste species within the lattice and the local and long range effects of radiation damage. Understanding processes such as these is essential as part of wider ranging research for validating these waste hosts for use with waste streams with high actinide and chloride concentrations. Further discussion on the crystallography of the fluorine rich apatite (chemically the most durable of all apatites [10]) and β -TCP will now be given.

1.4 Fluorapatite

The apatite mineral, meaning "to deceive" in Greek [65], has been studied by numerous different sections of the scientific community for a variety of different reasons; for industrial and biological applications. Examples of natural apatites can be seen in figure 1.14.



Figure 1.14: Image of FAp crystals, where a), b), and c) exhibit prismatic crystals and d) exhibits a tabular FAp crystal. Mineral samples provided by the Natural History Museum, London.

Apatites are the most abundant phosphate based mineral in the Earth's crust [81], predominantly in igneous rocks where the prevailing class is FAp. Given their availability, apatites are used widely in the chemical industry as initial phosphorus supplies for fertilisers and phosphoric acid [82].

Apatites are also of profound interest for those looking at oxygen ion conductors for fuel cells [83–86], as well as those considering apatite for biological applications, such as prosthetic bones and teeth [87–90]. Apatites also have their use in biological applications; approximately 40 wt% of adult human bone is made up of hydroxyapatite ($Ca_{10}(PO_4)_6OH_2$) [91]. Apatites are, therefore, of great importance for bone replacement and therapy. Another biological use of apatites is in dentistry; the increased durability of FAps over other apatites [10] explains the use of fluorine in water and toothpastes, as F⁻ replaces OH⁻ via the tubules present in mammalian teeth (first reported by Leeuwenhoeck in 1677 [92]) preventing tooth decay. Lastly apatites are used as a metal sequestering agent in water treatment and contaminated soil remediation [93].

1.4.1 Crystallography of Fluorapatite

The apatite structure was first published almost simultaneously by both Naráy-Szabó and Mehmel in 1930 [91, 94]. Apatites consist of a complex arrangement of a large Ca site and phosphate (PO₄) tetrahedra surrounding a channel containing a large anion, such as Cl⁻, F⁻ or OH⁻, where the general chemical formula is $M_{10}(AO_4)_6X_2$. Where typically,

- 'M' represents, Sr²⁺, Ca²⁺, Ba²⁺, Pb²⁺ ...etc.
- 'AO₄' is a trivalent anionic group, PO_4^{3-} , VO_4^{3-} , AsO_4^{3-} ... etc.
- 'X' represents a Cl⁻, F⁻or OH⁻.

Although there are numerous different isomorphs possible, the most common are FAp ($Ca_{10}(PO_4)_6F_2$), chlorapatite ($Ca_{10}(PO_4)_6Cl_2$) and hydroxyapatite ($Ca_{10}(PO_4)_6'OH'_2$)[81]. As discussed in the previous section, this thesis will concentrate on the FAp isomorph.

After Naráy-Szabó [91] and Mehmel's [94] seminal papers on the structure of apatites, Beevers and McIntyre [95] followed with another more in depth description of apatite structures in 1945, after some gentle encouragement by the famous crystallographer Victor Goldschmidt



Figure 1.15: Apatite structure, with the two calcium sites as dark and light blue, Ca(1) and Ca(2) respectively. Phosphorus ions are purple, oxygen is red and the PO₄ tetrahedra are grey. The bounding polygon indicates one unit cell of FAp. The polyhedra surrounding the Ca(1) and Ca(2) sites are also shown explicitly.

[96]. In fact this work (the use of apatites for fertilisers) temporarily saved him from deportation to a Polish concentration camp in 1942 [97]. Beevers and McIntyre [95] crucially identified two key features of the apatite structure; firstly, the structure can be considered as a tunnel with CaO₆ and PO₄ polyhedra as corner connected units, secondly that these units come together to create tunnels in the *c*-axis direction. The channel's size and shape itself was deemed to be reliant on the positioning of the PO₄ tetrahedra [96]. Interestingly, they also discovered that unlike zeolites the central channel was not empty but can be filled with anions such as, OH⁻, Cl⁻ and F⁻. As the anion in the central channel changes the bond lengths change and the phosphate tetrahedra twist to accommodate the change [59, 96]. Therefore, lattice parameters for apatites change significantly depending on the type of anion occupying the central channel and also those in the rest of the lattice. The lattice parameters for pure FAp are measured as *a* = 9.375 Å and *c* = 6.887 Å [96, 98]. FAps from natural or synthetic sources exhibit a P6₃/m space group and are hexagonal [59, 96, 99, 100]. Neutron diffraction data was first published in 1964 by Kay *et al.* [101] for hydroxyapatite. They discovered that the structure exhibited two symmetrically distinct calcium sites with Wy-ckoff positions 4f and 6h or Ca(1) and Ca(2) sites respectively [102]; the ratio of these sites Ca(1)/Ca(2) is 2:3. The positions for all other sites in the structure are given in table 1.1.

Table 1.1: Wyckoff positions and fractional coordinates for the apatite structure [101, 103]. In calcium FAp variant M(1) and M(2) are the Ca sites, A=P and X=F.

Species	Wyckoff Site		Coordinates	
		X	У	Z
M(1)	4 <i>f</i>	0.6667	0.3333	0.0009
M(2)	6 <i>h</i>	0.7598	0.7518	$\frac{1}{4}$
А	6 <i>h</i>	0.3696	0.3986	$\frac{1}{4}$
0	6 <i>h</i>	0.8414	0.5155	$\frac{1}{4}$
0	6 <i>h</i>	0.4672	0.5884	$\frac{1}{4}$
0	12 <i>i</i>	0.6580	0.9150	0.0703
Х	2 <i>a</i> or 2 <i>b</i>	0	0	$\frac{1}{4}$ or 0

In FAp, the Ca(1) sites are nine fold coordinated by oxygen ions [81] (see figure 1.15); six of the Ca-O bonds are ≈ 2.4 Å and the other three ≈ 2.7 Å [59, 96, 104]. The Ca(2) site is seven fold coordinated, having six Ca-O bonds and one Ca-F bond [81]. The Ca(2) sites form around the central channel in triangular planes, with subsequent layers being arranged on a screw axis coinciding with columns of fluorine ions. In fact the major structural response to defect substitution into the lattice is from changes to this Ca(2) polyhedron [105]. Figure 1.16, shows the relative positions of possible anion end members in the *c*-axis, which corresponds to large shifts in the *z* coordinate in the central channel. Fluorine ions are small enough to lie in the same plane as the Ca(2) cations, but the larger anions (Cl and the OH complex) are displaced from the Ca(2) plane [105]. This displacement locally breaks the symmetry, allowing apatites with Cl or OH end members to crystallise in P2₁/*b* symmetry.

The rest of the structure contains phosphate, PO_4^{3-} , tetrahedra. The phosphate tetrahedron is said to be rigid [106] and does not alter as the anion changes. However, the group can exhibit isomorphic changes for the central P ion, such as Si, La and Ge.



Figure 1.16: Relative positions of different possible anions, F^- , Cl^- or OH^- , in the *c*-axis channel of apatite. The F^- interstitial site (F_i^*) in FAp is also indicated [106].

1.4.2 Cation Substitutions

As mentioned the two cation sites are very different from each other, with changes to the Ca(2) site having a greater effect on structural alterations than the Ca(1) site. However, in literature there is some confusion over defect partitioning between the two cation sites. Ca(1) is said to be more covalent than the other site and has a volume of 31.92 Å in FAp or 32.11 Å in chlorapatite, as reported by Luo *et al.* [107]. By contrast the Ca(2) is said to be more ionic, is under-bonded and has a smaller volume of 22.68 Å in FAp or 22.94 Å in chlorapatite [107].

As indicated by Pan and Fleet [108, 109], the major controls on defect site occupancy remain unclear and changes in bond valence could be an important factor, especially when predicting site occupancy (in their study they refined the structures of REE bearing apatites using single crystal X-ray measurements). They also hypothesise that the controlling factor for site occupancy could be the size of the defect species compared to that of the site in the structure. In their study Hughes *et al.* [110] used electron and ion microprobe analyses of the REE substituted apatites to assess the mean Ca-O bond lengths. Hughes *et al.* [110] agree with Pan and Fleet about the relative size of the Ca sites and that both radius constraints and bond valence requirements have a role in the substitution of defects into the apatite structure. Considering the volume of the cation sites given by their respective metaprisms, the conclusions of this work are that smaller defects could preferentially substitute into the larger Ca(1) site, while defects with a larger radius may substitute into the smaller Ca(2) sites, however, this is yet to be proven. This would seem to be contradictory to the effect expected from size alone. Khattech *et al.* [111] (who again used X-ray Diffraction (XRD) and infrared spectroscopy to analyse sites) suggest that the smaller of the two sites is near the central anion channel and as such, smaller defect structures will preferentially substitute into it and *vice versa*. It is of great interest to discover what effect is dominating the defect partitioning in apatites as this information will have ramifications for a range of disciplines.

1.4.3 Synthesis

The synthesis of FAps can be achieved in two ways; via a solid solution reaction or in aqueous solution via precipitation or hydrolysis. The type of apatite structure generated is a product of its preparation [42].

The solid state route involves taking powdered tricalcium phosphate, $Ca_3(PO_4)_2$, and calcium fluoride (CaF₂) and sintering at high temperatures, over 1000° C, which forms FAp [14, 112]. However, this route is not always desirable because of the high temperatures involved and the waste streams due for immobilisation. FAp phases can also be created via a two step process [113]. This involves taking powdered CaHPO₄ and adding radioactive waste, which has first been through pyrochemical and aqueous processing. This mixture is then calcined to produce a mixture of calcium phosphate phases: FAp, chlorapatite and β -TCP. A glass binder is then added to this and the waste form is cold pressed and sintered to produce a solid, as seen in figure 1.17. Although this is the process that has been selected for producing a solid phosphate waste form, there are still many questions about the effects of immobilising waste elements on the FAp structure.

1.5 β -Tricalcium Phosphate

Another phase found at Oklo [25], is tricalcium phosphate, also known as calcium orthophosphate. Similar to apatite this family of phases are observed in a wide range of circumstances, from biological systems such as dental calculi, to lunar materials and asteroids [114]. They



Multi phase microstructure

Figure 1.17: General process for immobilising radioactive wastes in FAp. Images courtesy of Dr S.K. Fong.

are also used in applications such as Ca-Ni phosphates in catalysis [115] and fertilisers [116]. As bioactive materials they can combine directly with hard tissues without fibrous connective tissues and are therefore used in applications such as bone fillers and artificial tooth roots [117]. Interestingly, cow bones (which contain tricalcium phosphate) are also used in the production of fine bone china (up to 50 wt%) [118]. In nature FAp and tricalcium phosphate are found together and during the synthesis of FAp, the tricalcium phosphate phase is also created and so is an important structure to consider.

1.5.1 Crystallography of β -Tricalcium Phosphate

The tricalcium phosphate structure provides considerable compositional flexibility and tolerates substantial non-stoichiometry, ideal for incorporating a range of waste species. Previous studies have investigated the incorporation of lanthanides including gadolinium and thorium [75, 76, 119]. It has also been suggested that β -TCP is resistant to radiation damage [73], which is obviously desirable for a waste form. This remarkable property could be due to an interesting feature of the lattice which is that one of the calcium sites is considered to be half occupied [119], which leads to inherent disorder and the presence of a number of differently coordinated CaO_n polyhedra, each with their own environment. A structure that is often confused with tricalcium phosphate, is whitlockite, figure 1.18. A sample of whitlockite taken from the United State's Palmero Quarry was investigated by Frondel in 1941 [120], who described the chemical formula as Ca₃(PO₄)₂. Later he concluded that whitlockite and synthetic β -Ca₃(PO₄)₂ were identical due to similar X-ray and optical constants [121]. Diffraction patterns give a space group for whitlockite that is consistent with space groups R3c and R $\overline{3}c$, although Frondel indicated no structural evidence for the lower space symmetry group. However, these diffraction patterns were limited due to poor resolution at low 2θ angles [122–125]. Subsequently a number of studies were performed on related structures of $Ca_3(VO_4)_2$ and $Ca_3(AsO_4)_2$ [125, 126] and magnesium containing tricalcium phosphate [127], and all these compositions show the same structure. Interestingly Gopal and Calvo [126] reported that whitlockite is distinguishable from synthetic tricalcium phosphate by careful assessment of diffraction patterns. There is general confusion over the nomenclature for whitlockite and synthetic tricalcium phosphate. Whitlockite incorporates not only Ca, but Mg and H and is therefore distinct from pure tricalcium phosphate [126]. More recently, a study by Yashima et al. [119] was carried out using high resolution, powder neutron diffraction and Rietveld refinement [128], in order to obtain more information with regards to the structure. The final fractional coordinates and Wyckoff numbers for the species in the structure can be seen in table 1.2.



Figure 1.18: An example of natural whitlockite. This sample is provided by the Natural History Museum, London.

Dickens *et al.* [127] reported that the synthetic β -TCP structure crystallises in the rhombohedral space group R3*c* with unit cell parameters given by Yashima *et al.* [119] where a = b = 10.439 Å and c = 37.375 Å. In a unit cell of β -TCP there are 21 formula units of β -Ca₃(PO₄)₂ and five symmetrically different calcium sites, three distinct phosphorus sites and ten types of oxygen sites. Three of the cation sites have Wyckoff positions 18*b* and the other two have positions 6*a*. The unit cell of the β -TCP structure is large, containing no less than 273 atoms. Thankfully, however, the structure can be broken down into two repeating columns, 'A' and 'B', each composed of CaO_n and PO_4 groups in chains down the *c* axis; see figure 1.19. In accordance to the positions given in table 1.2 and figure 1.19, the 'A' column is made up as follows: $Ca(5)O_6-Ca(4)O_3-P(1)O_4-Ca(5)O_6-Ca(4)O_3-P(1)O_4$. Therefore, column 'B' contains the following groups: $P(1)O_4-P(1)O_4-Ca(2)O_7-Ca(3)O_8-Ca(1)O_7-P(1)O_4-P(1)O_4-Ca(2)O_7-Ca(3)O_8-Ca(1)O_7$.

Species	Wyckoff Site	Occupancy		Coordinates	
		-	Х	У	Z
Ca(1)	18 <i>b</i>	1	-0.2741	-0.1382	0.1663
Ca(2)	18 <i>b</i>	1	-0.3812	-0.1745	-0.0332
Ca(3)	18 <i>b</i>	1	-0.2734	-0.1486	0.0611
Ca(4)	6 <i>a</i>	$\frac{1}{2}$	0.000	0.000	-0.0851
Ca(5)	6 <i>a</i>	1	0.000	0.000	-0.2664
P(1)	6 <i>a</i>	1	0.000	0.000	0.000
P(2)	18 <i>b</i>	1	-0.3128	-0.1394	-0.1315
P(3)	18 <i>b</i>	1	-0.3470	-0.1536	-0.2332
O(1)	18 <i>b</i>	1	-0.2744	-0.0944	-0.0917
O(2)	18 <i>b</i>	1	-0.2326	-0.2167	-0.1452
O(3)	18 <i>b</i>	1	-0.2702	0.0088	-0.1514
O(4)	18 <i>b</i>	1	-0.4779	-0.2392	-0.1373
O(5)	18 <i>b</i>	1	-0.4013	-0.0488	-0.2206
O(6)	18 <i>b</i>	1	-0.4262	-0.3070	-0.2150
O(7)	18 <i>b</i>	1	0.0803	-0.1010	-0.2229
O(8)	18 <i>b</i>	1	-0.3680	-0.1742	-0.2732
O(9)	18 <i>b</i>	1	0.0057	-0.1376	-0.0115
O(10)	6 <i>a</i>	1	0.000	0.000	0.0421

Table 1.2: Wyckoff positions and fractional coordinates for the β -TCP structure [119].



Figure 1.19: The β -TCP structure viewed down the *c*-axis. The 'A' and 'B' columns are also shown illustrating the configurations of CaO_n and PO₄ groups in the 'A' and 'B' columns.

1.5.2 Half Occupancy of β -Tricalcium Phosphate

The work by Yashima *et al.* [119] also concentrated on the occupancy of the Ca sites and coordination of the CaO_n polyhedra in the structure, see table 1.3. Yashima *et al.* [119] experimentally derived occupancies and isothermal parameters by fitting the β -TCP structure to Nuclear Magnetic Resonance data. Interestingly this work revealed that the Ca(4) site exhibits "half occupancy" [119, 127], which means that for every two Ca(4) sites there is only one calcium atom occupying the lattice. In one unit cell of β -TCP there are six Ca(4) sites with three calcium atoms split across them. Fully understanding the way in which these sites are spread across the cell is significant because the crystallography of β -TCP will impact upon waste loadings and the long term structural stability of the mineral as a waste form; if the structure is not fully understood then the consequences of loading with waste species cannot be predicted. Interestingly, the inherent disorder within the structure may be a contributory factor in the radiation tolerance of β -TCP [129].

To further understand the β -TCP structure, closer examination of experimental results will be made. The experimentally derived coordination numbers, occupancies of calcium sites and the isotropic thermal parameters (*B*, which give an idea of thermal vibrations within a structure) are displayed in table 1.3. Here, two refinements are presented (as previously reported [119]). The first of which is a preliminary refinement by Yashima *et al.* (a), where the occupancies of the five sites were allowed to vary freely whilst the isotropic thermal parameters were fixed to be equivalent for all sites and a final refinement (b), where the occupancies of Ca(1), Ca(2), Ca(3) and Ca(5) were set equal to 1 and the isotropic thermal parameters were allowed to vary along with the occupancy of the Ca(4) site. For refinement (b) the isotropic thermal parameters for the Ca(3) and Ca(5) sites were constrained to be equal. Both refinements reported in the Yashima *et al.* study [119] give rise to significantly non-stoichiometric compositions and the thermal parameters were allowed. Clearly though, the neutron diffraction data presented, show that the Ca(4) site is different from all others.

It is of interest and of great importance for the defect chemistry, to assess how the partial occupancy occurs. β -TCP is not a Ca ion conductor and therefore the disorder is unlikely to be formed by a dynamic mechanism in which the Ca(4) site is occupied by passing Ca ions. The remaining possibilities are therefore; (i) the Ca(4) sites are randomly occupied (i.e. the

Table 1.3: Occupancy of the different sites of β -TCP as reported by Yashima *et al.* [119]. (a) a preliminary refinement and (b) a final refinement - see text for details. B are the isotropic thermal parameters reported for each site.

Ion	Coordination	Site	Occupancy ^{<i>a</i>}	Occupancy ^b	B (Å ²)
Ca(1)	CaO ₇	18 <i>b</i>	0.96	1.0	0.38
Ca(2)	CaO _{6/8}	18 <i>b</i>	1.02	1.0	0.27
Ca(3)	CaO ₈	18 <i>b</i>	0.92	1.0	0.76*
Ca(4)	CaO ₃	6 <i>a</i>	0.36	0.43	2.0
Ca(5)	CaO ₆	6 <i>a</i>	1.11	1.0	0.76*

* thermal parameters were constrained to be equal.

probability of finding a Ca atom at a site is independent of the occupancy of adjacent sites) (ii) the observed partial occupancy is a symptom of a lower symmetry supercell structure, or (iii) there is local order, so that the probability of finding a Ca atom does depend upon the occupancy of adjacent sites but this does not extend to complete long range order. This issue will be considered later in this thesis.

Experimental data for β -TCP has been successfully replicated by Michie *et al.* [130] and Rabone *et al.* [131] through computational modelling, both studies confirming the experimental structure and exploring it further by using static modelling techniques. In this thesis, synthesised tricalcium phosphate (rather than the whitlockite structure) will be used as the basic structure, although the different natural minerals indicate just how flexible the structure is. Tricalcium phosphate has two distinct polymorphs depending on the operating temperature [123]; below 1120° C the low temperature phase exists which is known as β -tricalcium phosphate, this is followed by the α -tricalcium phosphate, which is stable between 1120° C -1470° C. α -tricalcium phosphate has a monoclinic unit cell with the space group P121, which differs from the rhombohedral (R3*c*) setting of β -TCP [132]. However, the exact transformation temperature is strongly dependent on the type and quantity of impurities present [133]. Some species, such as Mg have been found to stabilise the low temperature phase and increase the phase change temperature to above 1794 K [122].

1.5.3 Relationship Between the β-Tricalcium Phosphate and Fluorapatite Structures

Apatites can be found as a decomposition product of natural whitlockite and quartz minerals [134]. Sudarsanan *et al.* [135] also related the two structures via a twist through the Ca(1) site in FAp. They concluded that by twisting the Ca(1)'s surrounding PO₄ groups about one of the oxygen ions by 90° C, the metaprism surrounding the Ca(1) site would resemble the octahedral site of Ca(1) in β -TCP.

1.6 Lattice Defects and Notation

1.6.1 Point Defects

A perfect crystal lattice is just that; a lattice with no imperfections or defects or impurities. The most common imperfections in crystals are from chemical impurities or extra atoms that are not in the regular or 'perfect' lattice positions. Many important properties are controlled by imperfections in the crystal lattice. Furthermore, there is no such thing as a perfect crystal; thermal equilibrium guarantees that a certain concentration of lattice vacancies are always present (except at absolute zero temperature). This is especially important when considering materials for waste hosts; if the material cannot continue to perform, due to defects developed by damage events or indeed by secondary radioactive emissions generated by the incorporated waste, then its performance may be compromised. The following section contains a description of the types of point defects that can occur within a lattice and an explanation of the Kröger-Vink notation which will be used to describe defects throughout the rest of this thesis.

1.6.2 Kröger-Vink Notation

Kröger-Vink notation provides a compact and convenient way to describe defect processes in crystals. Originally proposed by Kröger and Vink [136] it has the general format outlined in figure 1.20 and some examples using an MO crystal given in table 1.4.



Figure 1.20: Kröger-Vink notation [136].

Type of defect	Nomenclature	Description
Lattice cation	M_M^{X}	A 'M' atom sitting on a 'M' lattice site
'M' Vacancy	$V_M^{''}$	A'M' ion has a charge of 2 ⁺ thus its ab-
		sence implies a net charge in the lattice
		of 2 ⁻
'M' Interstitial	$M_i^{ulletullet}$	A 'M' ion has a charge of 2^+ in the lat-
		tice and so, as an interstitial, creates an
		effective charge of 2 ⁺
B^{2+} substitutional on a	B_M^{X}	B^{2+} has the same charge as M^{2+} so the
M^{2+} site		lattice remains neutral.

Table 1.4: Types of defects and their associated Kröger-Vink notation for a hypothetical MO crystal.

1.6.2.1 Schottky Defects

The simplest imperfection is a lattice vacancy, which is simply a missing atom or ion; in a single element material, this is also known as a Schottky defect. Schottky defects or Schottky disorder [137, 138] can be created in inorganic compounds when oppositely charged ions leave their

lattice sites (creating vacancies), in a stoichiometric ratio, see figure 1.21. Schottky disorder is described in equation 1.2 for a material MO.

$$M_M^{\rm X} + O_O^{\rm X} \to V_M^{''} + V_O^{\bullet\bullet} + MO \tag{1.2}$$



Figure 1.21: Schottky disorder, where the spheres represent the MO lattice and the squares represent vacancies and arrows represent displacement.

1.6.2.2 Frenkel Defects

Frenkel disorder [139] occurs when an atom is displaced from its lattice site into an interstitial site, leaving a vacancy behind. Both anions and cations can undergo this type of disorder. Equation 1.3 describes the example of cation Frenkel disorder in MO (also see figure 1.22).

$$M_M^{\mathbf{X}} + V_i^{\mathbf{X}} \to M_i^{\bullet \bullet} + V_M^{''} \tag{1.3}$$



Figure 1.22: Frenkel disorder, where the spheres represent the MO lattice and the squares represent vacancies and arrows represent displacement.

1.7 Computational Modelling

Computational methods are used throughout this thesis in order to probe atomic structures. This is particularly important for nuclear materials' studies, where experimental work is particularly challenging. However, modelling results need to be compared to experimental data in order to validate the models.

Atomic scale computer simulation techniques, used here and implemented in GULP [140] and DL_POLY [141], have been used to predict the crystal structure and defect properties in a series of ceramic materials. In this work both static and molecular dynamic simulations are employed, both of which require a description of atomic forces. Here empirically derived pair potentials (which assume ionic bonding) are used for their description. However, in comparison to other, more physically rigorous techniques the Schrödinger equation [142] is not solved, thus, it follows that information about electronic structure or charge distribution is not provided by pair potential techniques. Therefore, any changes in electronic structure due to defects or variation in crystal structure are not explicitly described here. Furthermore, this method can be considered most reliable when applied to simple ionic materials.

Although, there are limitations to pair potentials, they have been useful in predicting structural trends and macroscopic properties and so represent a suitable method for simulating structures, even when using millions of atoms. For example, in radiation damage simulations electronic stopping effects cannot be calculated using pair potentials. However, the large supercells required to simulate high energy collision cascades such as radiation damage, are currently computationally intractable using Quantum Mechanical (QM) methods. This notwithstanding, some QM simulations on small cascades have been performed [143]. The successful implementation of classical force fields, relies on the development and application of appropriate potential parameters. A description of pair potential derivation is discussed in section 2.2.3.

1.8 Thesis Summary and Structure

The work in this thesis concentrates on further understanding the nature of phosphate minerals and their ability to contain radionuclides and other waste elements. The methodology section, which follows, will detail the main approaches that have been used to simulate the phosphate structures during this thesis.

The β -TCP structure, is described as half occupied [119] and further investigation of this phase will be carried out in order to more fully understand the effect of Ca(4) site ordering across the lattice.

As mentioned the ability of these minerals to effectively incorporate defect cations is an important consideration for a waste form and will be investigated for both divalent and trivalent cations across all lattice sites in each structure. Furthermore, the partitioning effect of these defects over both structures will be considered in an effort to ascertain, in a multi-phase waste form, which phase the defect ions prefer to reside within, if any.

Understanding transport and migration of defect (or lattice) species through the lattice is of particular importance for a waste form; the structure could become destabilised or species could build up at grain boundaries causing additional stress on the lattice leading to effects such as micro-cracking. The mechanism and pathways for cation and anion transport in FAp are examined and discussed.

Subsequently, the effect of radiation damage on the structures and their ability to recover from

such events, is considered in chapter 6. This chapter gives a brief overview of radiation damage effects and its interactions with the PO₄ structural unit in FAp.

Lastly, the surface morphologies for both FAp and β -TCP are considered with a view to preparing simulations for future interface calculations, which would be very beneficial for understanding radiation effects in a multiphase waste form. Finally, all issues and results will be summarised and suggestions for the continuation and development of the work presented in this thesis will be given.
"There is a theory which states that if ever anyone discovers exactly what the Universe is for and why it is here, it will instantly disappear and be replaced by something even more bizarre and inexplicable.

There is another theory which states that this has already happened."

Douglas Adams



Methodology

2.1 Introduction to Atomic Physics

Over the past fifty years there has been a considerable increase in the use of computing technology. The principal reason for this accelerated growth is the remarkable increase in processor power and the decrease in silicon chip size, as predicted by Moore's law [144]. In science, computational methods can be employed to probe the properties and behaviour of a range of systems and of significance here, provide insights at the atomic scale, which is often particularly challenging to experimental interrogation. This is particularly useful when contemplating materials for nuclear applications, where the materials of interest are often radioactive to the extent that physical investigation can only be carried out in restricted or specialised environments that are often extremely costly. Numerous approaches to atomistic simulations and modelling have been developed. However, atomistic simulations can be considered in two different groups: Quantum Mechanical (QM) simulations and classical simulations. QM simulations involve solving Schrödingers' equation [142] and yield information about electronic structure and charge transfer. Classical simulations generally treat ions as points with interactions between them obeying simple central force laws. However, due to the computational burden of QM methods the size of systems that can be studied is limited, as a result, due to the large unit cell of β -tricalcium phosphate (β -TCP) only classical simulations are reported in this thesis.

2.2 Classical Potential Simulations

In the early part of the 20th century Madelung [146], Born and Mayer [147] made great strides in the field of ionic crystal theory. This is of importance here as the calculations carried out in this work require an in-depth understanding of crystal structure. This can be achieved using classical simulation methods, which assume that it is possible to treat an ionic lattice with a Born-Mayer type model [147]. In this model the crystal is treated as a periodic array of charged points.

Using this model of a crystal, an adequate description of the lattice can be obtained by solely considering the interactions of pairs of atoms, *i* and *j*. It is convenient to consider pair interactions in terms of separate long-range, $\Omega_{LR}(r_{ij})$, electrostatic or Coulombic contributions and short range, $\Omega_{SR}(r_{ij})$, contributions. The short range contributions include terms for repulsion and attractive van der Waals forces. Therefore, the overall lattice energy (*U*) is given as a sum of these two terms;

$$U = \frac{1}{2} \sum_{i} \sum_{j \neq i} \Omega_{LR}(r_{ij}) + \Omega_{SR}(r_{ij})$$
(2.1)

where, the factor of $\frac{1}{2}$ is included to allow for double counting of interactions. Figure 2.1 shows a typical representation of the effect of interactions as a function of ion separation of two oppositely charged ions. This pair potential model only considers atom-atom interactions and does not include the ionization energy of the ions or the self energy of the atoms. Thus, direct comparison of energies produced by this method to experimental data, may be difficult. However, the comparison of relative energy trends should still be valid. Higher order interaction terms are sometimes used to augment pair potentials, for instance a three body angular dependence was used in this work to favour a tetrahedral O-P-O angle in PO₄ tetrahedra, see section 2.2.2.



Figure 2.1: An example of interaction energies between two oppositely charge ions. Long range Buckingham contribution is in blue, short range Coulombic contribution is in red and the sum of them both is shown in black.

2.2.1 Long Range Ionic Interactions

The interaction of charges within a lattice are modelled using a long range Coulombic expression (Ω_{LR}). In ionic systems interactions are dominated by electrostatic or Coulombic forces, as given by Coulomb's law:

$$\Omega_{LR}(r_{ij}) = \frac{q_i \, q_j}{4\pi\epsilon_0 r_{ij}} \tag{2.2}$$

where, q_i and q_j are the charges on the ions *i* and *j* respectively, and ϵ_0 is the permittivity of free space.

Energy contributions from long range interactions can be calculated via the Coulomb term (equation 2.2), which on first sight appears straightforward to calculate. However, its calculation requires the use of a more complicated algorithm than may be expected. This is because the Coulomb sum calculates the electrostatic potential experienced by one ion in the presence of all others. To understand the problem more fully, imagine a sphere projecting out from a central ion with radius (r), which includes all other ions whose interactions with the central ion must be calculated. As the radius increases the number of interacting ions increases and is proportional to r^3 . The Coulomb sum (equation 2.2) converges slowly (as $\frac{1}{r}$) with distance and convergence is conditional on the order in which the charges are summed [30], therefore a traditional calculation via this method is impractical. A method for fast convergence, to alleviate this problem, has been devised by Ewald [148] and is known as the Ewald Summation.

A brief discussion of the Ewald Summation method will be given here, as this is a basic method that the simulation codes used in this thesis rely upon. However, a full description of this technique is beyond the scope of this thesis, but can be located in Solid State Physics books by Kittel [30] and Tosi [149].

The Ewald technique sums the interactions between and ion, all other ions and their periodic images. The total potential (ϕ) at a particular ion is the sum of two sub-potentials (ϕ_1 and ϕ_2), which represent reciprocal and real space respectively and where $\phi = \phi_1 + \phi_2$. ϕ_1 represents a structure with a Gaussian distribution of charge situated at each ion site, with charge the same as the real lattice ions and ϕ_2 describes lattice point charges with an additional (and opposite) Gaussian distribution. The charge distribution on the reference ion is not considered to contribute to the overall potential, as described by Madelung [146].

Figure 2.2 provides a schematic of the charge distribution for an example ionic lattice. ϕ_1 is calculated as the difference between another two potentials ϕ_a and ϕ_b , where ϕ_a is the potential of a series of Gaussian distributions from the lattice, and ϕ_b is the distribution from the reference ion alone, (figure 2.2a). ϕ_2 is summed in real space and consists of lattice point charges with an additional Gaussian distribution in the opposite direction; see figure 2.2b. Splitting the two parts like this and choosing a suitable parameter to determine the width of the Gaussian distributions drop out completely on taking the sum of the separate charge distributions for ϕ_1 and ϕ_2 . Although the total potential of ϕ is independent of the initial width parameter, the rate of convergence is dependent.

The Ewald summation method described here is used as a basis for methods used in computational codes such as DLPOLY [141] (described later in this chapter), which use a smooth particle mesh Ewald summation method, a good description of which is given by Allen and Tildesley [150]. This type of method uses a fast Fourier transform to allow for computational efficiency while calculating long-range force terms.



Figure 2.2: Charge distributions in a lattice for the Ewald sum, with the reference ion marked 'X' and its Gaussian distribution shown as a dotted blue line. a) shows the charge distribution used for computing ϕ_1 . ϕ_a includes all distributions, while ϕ_b includes only the reference ion (dotted line). b) illustrates the charge distribution for the potential ϕ_2 .

2.2.2 Short Range Ionic Interactions

As previously mentioned the Ewald Summation [148] accounts for long range, attractive Coulombic interactions. However, since $\Omega_{LR} \to -\infty$ when $r_{ij} \to 0$ (from equation 2.2) this would mean that atoms would tend to occupy the same space and therefore overlap; this is un-physical. The Pauli Exclusion Principle [151] states that no two fermions may occupy the same quantum state. Thus, when electron clouds overlap, the ground state charge distribution must occupy a higher energy state (to increase the number of potential states available so electrons could occupy the same space) thereby increasing the electronic energy of the system. This leads to interatomic repulsion at small separation. For this reason, in addition to the Coulomb sum, short range pair potentials are required. Assuming a spherical charge distribution, the following expression is used to represent the repulsive short range interactions, where A_{ij} and ρ_{ij} are specific to the species *i*, *j*.

$$\Omega_{SR}(r_{ij}) = A_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right)$$
(2.3)

At slightly larger internuclear separations, there is an attractive component to the short range

interaction. This is known as the van der Waals force [152]. This represents a very small force and is generally only important for large polarisable ions such as oxygen. The van der Waals forces [152] can be derived from the potential energy of a dispersion interaction; the transient fluctuation in electron density and consequent induced electron dipole moment [154]. The van der Waals forces can be understood by considering two atoms (*i* and *j*), separated by a distance *r*. If in an atom, *i*, an instantaneous dipole occurs (P_i), then an electric field proportional to $\frac{P_i}{r^3}$ at a distance *r* from the atom exists. Thus, a dipole moment in atom *j* is induced, which is proportional to the electric field [155]:

$$P_j = \alpha E \sim \frac{\alpha P_i}{r^3} \tag{2.4}$$

where α is the polarisability of the atom and *E* is the electric field. It follows that two dipoles have an interaction energy which is proportional to their dipole moments and the distance between them [155]:

$$\frac{P_i P_j}{r^3} \sim \frac{\alpha P_i^2}{r^6} \tag{2.5}$$

Thus, this force (which is proportional to $\frac{1}{r_{ij}^6}$) falls quickly as distance increases and as such is weak, just as the van der Waals forces are [152, 155]. However, if atoms get too close to each other, this dipole approximation should no longer valid and core-core repulsions should dominate the atom-atom interaction [155].

Thus, the overall short range interaction can be given by combining the repulsive and attractive terms described above to give the two-body Buckingham potential [153], equation 2.6,

$$\Omega_{SR}(r_{ij}) = A_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$
(2.6)

where, A_{ij} , ρ_{ij} and C_{ij} are potential parameters. A known problem with this potential form is that when large C_{ij} parameters are used, the $\frac{C_{ij}}{r_{ij}^6}$ term can become very negative, causing the potentials to become attractive in an unphysical manner at small separations, this is discussed more fully in section 2.9.1.1.

Although A_{ij} , ρ_{ij} and C_{ij} parameter sets are often obtained through an entirely empirical fitting procedure (see section 2.2.3), a physical C_{ij} parameter can be calculated using the Slater-Kirkwood formula [156]. The C_{ij} term for identical interacting ions can be written as:

$$C_{ii} = \frac{3}{4} \alpha_i^{\frac{3}{2}} K_i^{\frac{1}{2}}$$
(2.7)

and for non-identical ions as:

$$C_{ij} = \frac{3\alpha_i \alpha_j}{2\left[\left(\frac{\alpha_i}{K_i}\right)^{\frac{1}{2}} + \left(\frac{\alpha_j}{K_j}\right)^{\frac{1}{2}}\right]}$$
(2.8)

where α represents the static dipole polarizability and K is the effective electron number (i.e. the number of electrons which contribute to the polarizability). Values for α and K can be found elsewhere [157].

The exponential (Born-Mayer [147]) term in equation 2.6, provides a good description of strong ionic repulsion due to overlap of the closed shell electron clouds as r_{ij} tends to 0. An exponential term is used, because (due to the Pauli exclusion principle [151]) the repulsion between two overlapping electron densities will take an exponential form at reasonable distances, assuming that the ions have spherical electron clouds [153].

In Buckingham's original paper [153], A_{ij} and ρ_{ij} only had a lose physical meaning, with the A_{ij} parameter relating to the hardness of an ion (how diffuse the electron cloud is) and ρ_{ij} describing the size of an ion. However, some success has been had in obtaining A_{ij} and ρ_{ij} from first principal methods, such as electron gas methods [159] or *ab initio* calculations using Hartree-Fock methodology [160, 161]. In these methods, the potential energy curve given by the interaction of an array or pair of atoms can be calculated and fitted to a suitable functional form [161].

A similar pair-wise potential, due to Morse [162], can also be used to describe effective interactions between atoms. The Morse potential has the form shown in equation 2.9, where D_e is the dissociation energy of the diatomic species and r_0 is the equilibrium bond length. The third term, *a*, is related to the force constant of vibrational frequency for the stretching mode [140].

$$U_{\text{Morse}}(r_{ij}) = D_e[(1 - \exp(-a(r_{ij} - r_0)))^2 - 1]$$
(2.9)

The phosphate (figure 2.3) minerals studied in this thesis contain a PO_4 group that is modelled by using a Morse term and by a potential known as a three-body potential [163]; see equation 2.10.

$$U_{\text{Three body}}(r_{ijk}) = \frac{1}{2}k_{ijk}(\theta_{ijk} - \theta_0)^2$$
(2.10)

Here, *i*, *j* and *k* are three different ions forming a dihedral angle within the structure, in this case O, P and O. Any deviation from the equilibrium bond angle is given by $(\theta_{ijk} - \theta_0)$. The k_{ijk} term is a force constant related to the typical oscillation frequency of the ions. A schematic of the phosphate tetrahedra can be seen in figure 2.3, where the bond angle θ_0 is 109.5°[164]. This type of model introduces rigidity into the PO₄ tetrahedra by imposing an energy penalty when the O-P-O angle deviates from 109.5°. For static simulations this model is able to reproduce

many of the experimentally observed properties (e.g. vibrational modes associated with the PO_4 species [131]). However, this rigid bonding is not expected to describe the lattice response well during radiation damage when oxygen ions may be removed from the tetrahedra.



Figure 2.3: The PO₄ group, where the O-P-O, angle is 109.5° [164]. Here oxygen atoms are red and the phosphorus is purple.

In order to better represent the crystal lattice, many different types of potential are used in conjunction with each other. In this thesis Morse [162], Buckingham [153] and three body potentials are all used together. The potential parameters are derived from the work of Rabone and de Leeuw in 2006 [131] through further improvement by Michie *et al.* [130].

2.2.3 Potential Derivation

As mentioned previously, this thesis will rely heavily on the use of pair potential calculations and it follows that these classical calculations rely on the quality of the short range potentials used to describe atomic interactions. There are two main methods for deriving the various parameters used in pair potentials, either empirically or by direct calculation.

Potential derivation by empirical methods often relies on a 'least squares fit', to a set of experimentally determined material properties;

$$F = \Sigma (f_{experiment} - f_{calculated})^2$$
(2.11)

Potential parameters are then chosen to minimise the squared difference (*F*), between experimental ($f_{experiment}$) and calculated properties ($f_{calculated}$). In this derivation process many material properties can be used, including lattice energy and parameters, elastic or dielectric constants and phonon data. A comparison of experimentally and computationally derived elastic constants and bulk modulus for both fluorapatite (FAp) and β -TCP can be seen in tables 2.1 and 2.2 respectively. The tables include values from the Voight, Reuss and Hill [165–167] approximations; whereby anisotropic single crystal elastic constants are converted into isotropic polycrystalline elastic moduli as discussed by Chung *et al.* [168]. The Reuss model [166] assumes uniform internal stress, and is calculated from the elastic coefficients (compliance), *S*, as seen in equation 2.12. The Voight model [165] assumes uniform strain from the elastic constants (stiffness), *C*, as described in equation 2.13. An average of both the Voight and Ruess model, as described by Hill [167], is often taken. The use of these approximations allow a more meaningful comparison between the simulated and experimentally obtained modulii.

$$K_{Reuss} = (S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{13} + S_{23}))^{-1}$$
(2.12)

$$K_{Voight} = \frac{1}{9}(C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}))$$
(2.13)

Previous studies by Rabone, de Leeuw and Michie *et al.* [130, 131, 174, 181, 182], have generated a set of interchangeable potentials that accurately reproduce the crystal structures, elastic constants and cell parameters of both FAp and β -TCP. These potentials have been produced via the least squares method (section 2.2.3) and were first published by Rabone and de Leeuw in 2006 [131] and have been improved by Michie *et al.* [130].

In the original work by Meis [77], Rabone and de Leeuw [131], potentials were fitted to experimentally known bulk properties of hydroxy-, chlor- and fluor-apatites: elastic constants, vibrational frequencies of PO₄ and bond dissociation energies. Pair potentials were altered until the the squared difference (as given in equation 2.11) was minimised. This model was then extended to produce parameters to describe the incorporation of a range of other species (e.g. actinides and lanthanides) often found in FAp and β -TCP (as given in their paper [131]). These additional potentials were generated from known structures (often monazites or xenotimes) and their elastic constants (where available). The potentials were then used to generate other known compounds (not used in the fitting process) and the cell parameters of these compounds were compared to experimental values. A full list of compound used to fit and compare the potentials cam be found in Rabone and de Leeuw's 2006 paper [131]. For example, the Sr²⁺-O²⁻ potential was fitted to the Sr₃(PO₄)₂ structure using elastic constants and then sub-

Elastic Constants (GPa)	Meis <i>et al.</i> [77]	Lee et al.[169]	Mkhonto and de Leeuw et al. [170]	Michie et al. [130]	Sha <i>et al.</i> [171]
			(Simulated)		(Experimental)
C ₁₁	162.77	150.12	148.95	152.83	152.00
C_{12}	55.17	56.74	64.16	61.13	49.67
C_{13}	61.08	59.97	75.98	75.50	63.15
C ₃₃	145.02	133.99	174.34	174.78	185.80
C_{44}	33.02	32.37	51.25	51.41	42.75
C ₆₆	53.80	46.69	42.40	ı	51.17
Bulk Modulus (GPa)					
K (Voigt)	91.70	87.51	100.50	101.19	93.50
K (Reuss)	91.58	87.35	99.30	100.26	92.00
K (Hill)	91.63	87.43	06.66	100.72	92.80

Table 2.1: Comparison of experimentally derived elastic constants and bulk moduli for FAp.

Elastic Constants (GPa)	Meis <i>et al.</i> [77]	Lee et al.[169]	Mkhonto and de Leeuw [170]
	(Simulated)		(Experimental)
C ₁₁	148.67	132.44	153.79
C ₁₂	56.56	69.53	67.24
C ₁₃	55.23	55.07	59.06
C ₃₃	71.53	62.94	145.44
C_{44}	23.74	24.31	43.34
C ₆₆	45.20	31.39	43.27
Bulk Modulus (GPa)			
K (Voigt)	76.52	76.34	91.53
K (Reuss)	65.16	61.79	91.42
K (Hill)	70.84	69.07	91.31
Shear Modulus (GPa)			
G (Voigt)	32.41	25.87	43.84
G (Reuss)	23.82	23.11	43.49
G (Hill)	28.12	24.49	43.66
Young's Modulus (GPa)			
E (Voigt)	91.47	78.35	114.73
E (Reuss)	86.17	78.33	114.73
E (Hill)	42.96	32.92	113.88

Table 2.2: Comparison of experimentally derived elastic constants and other constants for β -TCP.

sequently tested against known cell parameters for the $Sr_{10}(PO_4)_6F_2$ structure. Rabone and de Leeuw [131] found that the agreement between experimental and predicted lattice parameters was good, with almost all parameters "within 1%" of the experimental value [131]. The potentials used in this thesis are reported in table 2.3, and are used in conjunction with the partial charges described in section 2.5.

Table 2.3: The Buckingham, Morse and Three body potential parameters for FAp. Each has the same core potentials for the rest of the crystal.

Species	Parameter type	$A_{ij} (eV)$	$\rho_{ij}(\text{\AA}^{-1})$	$C_{ij} (eV Å^{-6})$
O _{shell} – O _{shell}	Buckingham	16372.00	0.213	3.47
Ca _{core} – O _{shell}	Buckingham	1550.00	0.297	0.00
F _{shell} – F _{shell}	Buckingham	1317.50	0.275	13.80
Cacore – F _{shell}	Buckingham	1550.00	0.297	0.00
O _{shell} – F _{shell}	Buckingham	583833.00	0.212	7.68
		D (eV)	$\alpha \left(\text{\AA}^{-1} \right)$	r_0 (Å)
P _{core} – O _{shell}	Morse	3.47	2.03	1.60
		$k \left(eV rad^{-2} \right)$	$ heta_0$ (°)	
O _{shell} – P _{core} – O _{shell}	Three body	1.323	109.47	

2.3 Potentials for β -Tricalcium Phosphate and Fluorapatite

In the present study, interest principally lies with various divalent cations, as well as rare earth elements (REEs), such as Ce, La, Pr, Sm, Nd and La. These potentials can be obtained either from the properties of natural FAp or β -TCP, which contain those species, or from an analogous structure known as monazite (*XPO*₄, where X can be almost any cation). Often more than one set of parameters can adequately reproduce the physical properties of a particular material [172].

There are limitations associated with this technique, namely that the potentials are calculated for the equilibrium position in the lattice. This can become problematic when assessing defective systems, as interionic separations shift away from equilibrium. To overcome this limitation, potentials are often fit to multiple structures and are considered transferable between those structures. The resulting potentials can be related to several different structures and are reported in table 2.5.

In this thesis all potentials have been fitted to both FAp and β -TCP with the aim of making them transferable between the two [170, 173, 174]. A range of cation potentials are used, which have been taken either from the literature or developed for this thesis (tables 2.5-2.6), using the method outlined in section 2.2.3. The Ba-O, Mg-O and Zn-O potentials were specifically developed for this work and were fitted to the monazite (X₃(PO₄)₂) structure (which, like FAp and β -TCP also contains oxygen in a phosphorus environment), where X represents either Ba [175], Mg [176] or Zn [177]. The potentials were fitted to the experimentally derived lattice parameters and atomic positions, given in the references [175], [176] and [177] for the Ba₃(PO₄)₂, Mg₃(PO₄)₂, Zn₃(PO₄)₂ monazites respectively. The potentials obtained from fitting reproduced the cell parameters as seen in table 2.4. These potentials were then validated against cell parameters for the mixed phosphate phases BaZn₂(PO₄)₂ [178] and MgBa₂(PO₄)₂ [179], which show good agreement as indicated in table 2.4.

	Expe	eriment	al (Å)	Pr	edicted	(Å)		% Error	
Formula	а	b	С	а	b	С	а	b	С
$Mg_3(PO_4)_2$	8.51	8.98	9.32	8.42	9.00	9.41	-1.04	0.20	1.00
$Zn_3(PO_4)_2$	9.39	9.17	8.67	9.31	9.24	8.76	-0.86	0.76	1.00
$Ba_3(PO_4)_2$	5.60	5.60	21.0	5.57	5.57	21.3	-0.60	-0.60	1.43
$BaZn_2(PO_4)_2$	8.58	9.74	9.14	8.43	9.90	9.04	-1.78	1.16	-1.06
$MgBa_2(PO_4)_2$	5.29	8.84	16.14	5.22	8.95	15.98	-1.34	1.23	-1.00

Table 2.4: Predicted and experimental cell parameters for Zn-O, Mg-O and Ba-O potentials.

Non-empirical fitting methods involve parametrisation by an energy surface fitting method, where *ab-initio* QM simulations are carried out to evaluate ion-ion interaction energies as a function of separation; this takes up much computational time. A set of variables is then changed until they reproduce energies predicted via the QM simulations [160]. This method is not used here.

Ion (A^{2+})	Atomic radius (Å)	A ²⁺ -0	D ²⁻	A ²⁺ -	F ⁻
		A (eV)	$ ho\left(\mathrm{\AA} ight)$	A (eV)	$ ho\left({ m \AA} ight)$
Mg	0.72	2295.15	0.250	1534.30	0.289
Zn	0.74	5599.98	0.228	2769.00	0.205
Mn	0.83	5536.55	0.234	4318.00	0.240
Fe	0.78	4972.08	0.230	3689.00	0.240
Sr	1.18	1654.44	0.312	1965.89	0.299
Ba	1.35	4023.23	0.300	4632.00	0.232

Table 2.5: Two body Buckingham [153] parameters for a range of divalent cations, derived for phosphate based structures. Here the C term is zero for each potential.

Table 2.6: Two body Buckingham [153] parameters for a range of trivalent cations, derived for phosphate based structures. Here the C term is zero for each potential.

Ion (B^{3+})	Atomic radius (Å)	B ³⁺ -O ²⁻		B ³⁺ -	F-
		A (eV)	$ ho\left(\mathrm{\AA} ight)$	A (eV)	ρ (Å)
Al	0.54	11583.00	0.206	1534.30	0.289
Ga	0.62	10687.02	0.215	1534.30	0.289
Yb	0.87	4782.28	0.258	2101.56	0.290
Er	0.89	3225.63	0.275	2576.18	0.283
Gd	0.94	2394.70	0.296	1683.11	0.306
Eu	0.95	2720.91	0.290	1807.77	0.303
Sm	0.96	2465.31	0.296	1486.38	0.314
Nd	0.98	2110.00	0.305	3117.59	0.290
Ce	1.01	1531.41	0.323	3806.17	0.286
La	1.03	1223.60	0.337	3182.74	0.295

2.4 Electronic Polarisabilty

Polarisation is one way in which lattice ions respond to changes in their surroundings and must be accounted for to ensure a good defect model representation. It reflects changes to an ion's charge density due to changes in the surrounding. As electrons in an ion respond to oppositely charged forces, a dipole is generated. The extent of the electron density shift is reliant on the size and charge of the ion and the field it is subjected to. Larger ions with more loosely bound electrons will polarise more easily, examples include F^- and O^{2-} .

The effect of polarisation can be described by splitting an ion into both a 'core' and a 'shell', as first suggested by Dick and Overhauser [180]. In this model ions consist of a charged massless shell, on which all short-range potentials will act. The core of the ion is then connected to the shell via an isotropic harmonic spring (see figure 2.4). The polarisability (α) can therefore be described as follows:

$$\alpha = \frac{1}{4\pi\varepsilon_0} \left(\frac{Y^2}{k}\right) \tag{2.14}$$

where k is a harmonic spring constant, the charge on the shell is given as Y, and ε_0 is the permittivity of free space. In this thesis, only the anions F⁻ and O²⁻ will be modelled as polarisable and the values given for those highly polar ions are reported in section 2.3. In general (and here) the shell is negatively charged and the core is positive, so that the shell represents the valence electrons and the core represents the nucleus and the core electrons, but this does not have to be the case.

2.5 Partial Charges

In full ionic models the sum of the core and shell of the ion should be equal to its formal charge. As mentioned previously, in this work the F⁻ and O²⁻ ions are represented by a core and shell model. With the ionic charge partitioned between the core and shell. The partition is carried out in order to better represent the polarity of the ion and a full discussion can be found in the literature [130, 131] and is reported here for O²⁻ and F⁻ ions in table 2.7. Regarding the oxygen model, the overall charge, *X* and *Y*, appears to equate incorrectly as it comes to -1.045 *e*, however, the addition of one P^{1.18+} to 4 O^{1.045-} ions generates the correct overall 3- charge for the PO₄ group. This partial charge oxygen and phosphorus model better describes



Figure 2.4: The shell model [180], where the core is represented by the smaller dark blue sphere and the shell is represented by the larger blue sphere. a) shows an unpolarised ion where both the core and shell are centred on the same point in space. In b) the effect of introducing a positively charged species (red sphere) near the original ion polarises the ion such that the core and shell are centred at a different points in space.

the covalent hybridised bonds in the PO₄ structural unit, where it is clear that the P ion is not ionised to 5+. Conversely the F⁻ ion is fully ionic as X + Y = -1 in this case; see table 2.7.

:		Char	ge (e)	
	Ion	Core	Shell	Core-Shell, k (eV $Å^{-2}$)
	0	0.587	-1.632	507.40
	F	0.3776	-1.3776	24.36
	Р	1.18		
	Ca	2.00		

Table 2.7: The potential charge model for the constitutent ions in FAp and β -TCP as discussed in [130, 131].

2.6 Static Energy Minimisation

Static energy minimisation is used to relax atom positions into a local energy minimum. To achieve this the potential energy surface is explored by an iterative process until a minimum has

been reached. This minimisation technique does not consider the thermal motion of atoms. As atomic velocity is not considered, energy minimisation is therefore referred to as a static technique. As discussed previously the overall potential energy of the system (U) can be calculated by summing over all pairs of ions using both long and short range interactions, equation;

$$U = \frac{1}{2} \sum_{i} \sum_{j \neq i} \Omega_{LR}(r_{ij}) + \Omega_{SR}(r_{ij})$$
(2.15)

$$U = \frac{1}{2} \sum_{i} \sum_{j \neq i} \frac{q_i q_j}{4\pi \epsilon r_{ij}} + A_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) - \frac{C_{g,ij}}{r_{ij}^6}$$
(2.16)

The internal energy of the system (U), can be described in terms of the atomic positions of all ions in the structure. U can also be related to the Helmholtz free energy (A) by,

$$A = U - TS \tag{2.17}$$

where T is temperature and S is entropy. The entropy term becomes zero when the temperature is 0 K and the free energy of the system is equivalent to the internal energy.

In the GULP program [140], the energy minimisation technique used is the conjugate gradient with a Broyden-Fletcher-Goldfarb-Shannon (BFGS) Hessian updating scheme [183]. In the conjugate gradient scheme, the direction and distance each atom is moved during each iteration are determined by the gradient of the energy hyper surface. Differentiating U (equation 2.15) in terms of the atomic position of each lattice ion gives a force vector along which the atom should be moved to reduce its energy. Simultaneously the second derivative of U gives the distance along the vector that the atom should move. At each step as the atoms move, the energy surface changes, thus the process must be done iteratively until the force on each atom approaches zero. Complete convergence between two steps is achieved when the change between two steps falls below a certain value. As each atomic position is relaxed, the lattice vectors can also be relaxed to zero stress. As a result, static energy minimisation can be used to predict lattice parameters for simulated structures. Within this thesis energy minimisation that allows lattice parameters to vary will be referred to as constant pressure whilst minimisation where they are held constant will be known as constant volume.

2.7 Mott-Littleton Method

An important part of this thesis involves an understanding of defective structures and incorporation of other species into the lattice. The model developed in the previous section is extended to provide a description of defective systems. Based on the work of Mott and Littleton [184], a method was developed which allows coupling of a region of defective lattice to the bulk material, to assess the response of a lattice to the defect. This can be achieved by decomposing the simulation into two regions, one containing the defect and one containing the rest of the lattice, see figure 2.5. In this approach the total energy of the defective lattice (U_{defLat}) can be written as:

$$U_{\text{defLat}}(\mathbf{x}, \mathbf{y}) = U_{11}(\mathbf{x}) + U_{12}(\mathbf{x}, \mathbf{y}) + U_{22}(\mathbf{y})$$
(2.18)

where (with reference to figure 2.5) U_{11} is the potential energy of ionic interactions in region I, U_{22} is the energy of ionic interactions in region II and U_{12} represents the interaction energy between regions I and II.

Region I is defined as a sphere centred on the defects and includes all atoms that fall within this sphere. Since relaxation of the lattice will be greatest in close proximity to the defects, the energy is minimised with respect to the positions of the ions in this region. Interactions within this region are calculated between all other atoms in region I and IIa.

Region II extends from the boundary of region I to infinity, and the response of the lattice in this region, arising from the defects, is relatively weak. As a result, the response of the lattice can be calculated using a continuum approach, considering the polarising effects of defects rather than explicit minimisation [184]. In a refinement to the original two region Mott-Littleton method, region II is split further, into regions IIa and IIb. Region IIa provides a transition between region I and the continuum region, IIb. Within region IIa, the ions are assumed to be situated in a harmonic well, where they respond to the effective charge on the defect and move accordingly [140, 184, 185]. Thus, the resulting expression for displacements is deduced from the expression for the polarisation \mathbf{P} , at a distance \mathbf{r} from the defect [184, 185]:

$$\mathbf{P} = \frac{1}{4\pi} \left(1 - \epsilon^{-1} \right) \frac{q\mathbf{r}}{r^3}$$
(2.19)

where, q is the defect charge and ϵ is the static dielectric constant of the crystal.

This approximation is, therefore, only true for small perturbations in the lattice and when the bulk has been optimised before calculating the defect effect. Ion displacements in region IIa are still considered, whereas in region IIb only the polarisation of the lattice, rather than individual ion, is considered. However, the interaction of region IIa and region I is calculated by explicit summation as described by Catlow [186].

Thus, the energy for a defect $(U_{defect}(\mathbf{x}, \mathbf{y}))$, as derived by the Mott-Littleton methodology [184], can be described as the difference between the energy of the perfect regions I and II $(U_{perfLat}(\mathbf{x}, \mathbf{y}))$ and the defective case $(U_{defLat}(\mathbf{x}, \mathbf{y}))$, with corrections due to the energy of any vacancy or interstitial species at infinite separation from the lattice (E_{∞}) as given below [140]:

$$U_{\text{defect}}(\mathbf{x}, \mathbf{y}) = U_{\text{defLat}}(\mathbf{x}, \mathbf{y}) - U_{\text{perfLat}}(\mathbf{x}, \mathbf{y}) + E_{\infty}$$
(2.20)



Figure 2.5: Diagram illustrating the Mott-Littleton approach, sub dividing the lattice into regions. Explicit calculations occur in region I. From the end of region I is region IIa where, based on polarisation, the interactions are also calculated explicitly. Region IIb represents the bulk lattice, extending from region IIa to infinity. Image modified with permission of Dr. M. Read.

The computational efficiency of these types of calculations is crucial; region I must be chosen to be large enough such that the defect energy converges with respect to region I radius, but computational time is not wasted. Figure 2.6 shows the effect of region I size on the defect energy, in this thesis region I is chosen to have a radius of 13 Å. This is because increasing region I to above 13 Å only has a very small effect on the defect energy for a considerable increase in computational cost. Furthermore, the size of region II is chosen to have a radius of 34 Å, which is decided upon by a similar method to that shown in figure 2.6.



Figure 2.6: The effect of region I size on the defect energy for an example defect calculation of a divalent defect on a Ca(1) site in FAp.

2.8 Nudged Elastic Band; Transition State Search Methodology

When both the initial and final states are known a transition state search, known as the Nudged Elastic Band (NEB) methodology, can be used to find a reaction pathway between the two points. The minimum energy pathway is calculated between this pair of stable states; both of which should be local minima on the potential energy surface. The minimum energy pathway is at an energy minimum in all directions that are perpendicular to those given by the pathway. NEB pathways are often described as linear, connecting the two given states, but this may not be the case. In particular, if the migrating atom gets too close to a lattice atom along the linear path, a repulsive force can be used to push these atoms apart, changing the trajectory to a non-linear (curved) minimum energy pathway [187].

The NEB methodology can be considered analogous to laying a chain down in a hilly land-

scape. Imagine a ridge surrounded by two valleys, see figure 2.7. Starting in the bottom of a valley, the only way to reach the valley on the other side of the hill is to climb up the slope, in small steps. The circles in figure 2.7 represent these steps or 'reaction coordinates', which are points along the proposed pathway or 'band' where the low energy regions on the energy landscape are calculated, confirming the minimum energy pathway.

In the two dimensional landscape analogy presented here the valleys represent stable, low energy regions and the hill represents a high energy, unstable, region. At each reaction coordinate on the hill the energy state is calculated, however, there will always be a driving force to pull the chain back down into the low energy valley regions, which are more energetically stable. To counteract this, the NEB methodology includes a spring force which acts parallel to the pathway to stop the moving species from falling back into a low energy region; this enables the reaction coordinates to be energetically stable at even the most unstable positions, with respect to the lattice potential energy. In this way migration through a rugged energy landscape can be calculated. A second component of the NEB methodology is a component of force that acts in the plane perpendicular to the band and ensures that the low energy area perpendicular to the band and ensures that the low energy area perpendicular to the band and ensures that the low energy area perpendicular to the band is sampled; so in the case presented in figure 2.7 the path crosses through a saddle point on the hill and not over the highest point. The migration energy between stable sites is the difference between the energy of the ion at its starting position and the energy at the highest saddle point. The activation energy is the energy required for migration and the energy to form the initial defects required for the migration process to occur.

As mentioned previously, NEB calculations use a spring force $(\mathbf{F}_i^{S\parallel})$ which enables calculations to occur anywhere along the minimum energy pathway. For example, without the spring force, an ion placed at an unstable position on the NEB pathway could move down the potential energy surface to recombine with a lattice point or low energy state [187], as depicted in figure 2.8. These calculations also rely on the force acting perpendicular to the minimum energy path, \mathbf{F}_i^{\perp} , and finds the lowest energy point within these limitations. Thus, the minimum energy pathway is achieved by combining these two individual components; that is the component of force potential perpendicular to the band (\mathbf{F}_i^{\perp}) and the spring force parallel to the band $(\mathbf{F}_i^{S\parallel})$ as given by equation 2.21 [187, 188].

$$\mathbf{F}_{i}^{NEB} = \mathbf{F}_{i}^{\perp} + \mathbf{F}_{i}^{S\parallel} \tag{2.21}$$



Figure 2.7: Minimum energy pathway over a conceived landscape as defined by NEB.

All steps taken along the NEB path are relaxed to the minimum energy through the force projection scheme, where the spring forces act along the band and potential forces act perpendicular to it, thus, the minimum energy pathway between the end points can be unambiguously identified [187, 188]. The change in the system energy (ΔE_{sys}) is then defined as the difference between the energy of the system at each step ($E_{current step}$) along the minimum energy pathway and the energy of the initial fully relaxed structure.

$$\Delta E_{sys} = (E_{\text{initial position}}) - (E_{\text{current step}})$$
(2.22)

The maximum value of ΔE_{sys} is the activation energy.

Other transition state methods have been compared to NEB by Henkelman *et al.* [188], who concluded that the NEB method was the most efficient for classical transition state searches where the initial and final points are known. A test example was compared with the same calculation from other methods such as NEB, Dimer, Ridge and Drag methods, where the NEB method was the most computationally efficient and could also assess all possible saddle points and their relative heights. As such the NEB method will be utilised in this study. The spring constant acting between the reaction coordinates used in this work was set at $1.0 \text{ (eVÅ}^{-2})$ for all NEB calculations in this thesis.



Figure 2.8: Two components make up the nudged elastic band force (F_{NEB}) ; the component of force perpendicular to the band (\mathbf{F}_i^{\perp}) and the spring force parallel to the band $(\mathbf{F}_i^{S\parallel})$. The unprojected force due to the potential Fi is also shown for completeness.

2.9 Molecular Dynamics

Molecular Dynamics (MD) is a technique that allows the time evolution of a set of atom positions and velocities to be predicted given a description of the forces acting between them. This means that MD is well suited for considering time and temperature dependent properties of a system.

The MD algorithm is based on Newton's second law [189] of motion:

$$\mathbf{F}_i(t) = m_i \mathbf{a}_i(t) \tag{2.23}$$

assuming that the mass of the object being considered is time invariant, where for an atom *i*, *t* is time, \mathbf{F}_i is force and m_i is mass and \mathbf{a}_i is the acceleration of the atom.

Newton's first law states that a body remains in a state of constant velocity unless it is acted upon by an external force [189]. For an ion at position (\mathbf{r}_i) with potential energy (ϕ) Newton's first law can be rewritten as;

$$-\frac{\delta\phi_i}{\delta\mathbf{r}_i} = m_i \frac{\delta^2 \mathbf{r}_i}{\delta t_i^2} \tag{2.24}$$

As the potential energy, ϕ_i , of an ion is dependent on the interactions with other atoms and atom positions vary with time, it is impractical to solve equation 2.24 analytically. Therefore, equation 2.24 is numerically integrated, where given knowledge of atom positions and momentum at a given time, it is possible to determine the velocities and positions of atoms at a time, $t + \delta t$. The smaller the timestep (δt), the more exact the solution to equation 2.24 becomes. Here the velocity Verlet integration method was employed [190]. This is mathematically equivalent to the original Verlet algorithm [191] but not numerically equivalent, because it does not need to store and recall data from previous timesteps in order to calculate subsequent positions. The velocity form of the improved Verlet algorithm is one where velocity appears directly in the equations to be iterated as shown in equations 2.25.

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \delta t \mathbf{v}(t) + \frac{1}{2} \delta t^2 \mathbf{a}(t)$$
(2.25)

$$\mathbf{v}(t+\delta t) = \mathbf{v}(t) + \frac{1}{2}\delta t[\mathbf{a}(t) + \mathbf{a}(t+\delta t)]$$
(2.26)

This particular algorithm directly obtains the position and velocity at the end of the time step from the position and velocity at the beginning of the step. The system state at some point in the future can be predicted by repeatedly incrementing time by δt until the required time is reached. In order to provide reliable solutions to the Verlet algorithm δt must be kept small, so the total time that can be accessed is tiny, in the order of picoseconds. Although MD simulations can accommodate a large number of atoms, the level of computing power currently available means that there is a limit to the size of the system that can be calculated. The average system size used in this thesis is in the range of half a million atoms.

Comparing the results from MD simulations to those from macroscopic samples is not straightforward. In these calculations, given the overall numbers of atoms involved, a high percentage of them appear at the 'surface' of the system contributing to the overall properties of the bulk. In real samples, the number of atoms at the surfaces compared to the bulk is very small and so the surface does not contribute greatly to the overall or average properties of the material. As a result, to avoid surface effects dominating in the relatively small systems used in MD, periodic images are introduced to approximate the effect of the simulation cell is embedded in the bulk of the material. The periodic conditions are achieved by surrounding the primary cell with images of itself, see figure 2.9. If an atom moves outside of its image, it simply wraps back around to the other side of the image. This requires the primary cell to have a sufficient size such that each atom is effectively uncorrelated with its periodic images; this is particularly important for damage cascades; figure 2.9 shows an array of periodic images. In this thesis only the bulk of the material will be examined using MD and so periodic conditions will always be used (static simulations of surfaces are described in section 2.10).



Figure 2.9: An example of periodic conditions for MD simulations in FAp for two dimensions. The central cell (shown in colour) is surrounded by tessellated images of itself in space (outlined in grey).

To bridge the gap between MD systems and macroscopic properties (such as temperature) a statistical mechanic approach is used. At the heart of statistical mechanics lies the concept of a thermodynamic ensemble. An ensemble represents all the thermodynamic states consistent with a set of variables. Inherent in the classical description of MD simulations (described above), is that the total number of atoms (N), volume of the cell (V) and the total energy of the system (E) remain constant over the duration of the calculation. Thus, the state of the system at each timestep can be said to be a member of the 'NVE' micro canonical ensemble.

Computationally speaking it is only really possible to sample a finite number of these states. Only a relatively small region of the ensemble is relevant to a given system or problem, hence, the sampling of the phase space is biased to that region. Instead of calculating each and every possible state, in order to obtain the phase state of interest, MD simulations link each state to the previous one by virtue of time. The Ergodic hypothesis states that over long periods of time all accessible phases of a system are equiprobable [192]. By starting the MD simulation with a known crystal structure, it is possible to bias the ensemble to the phase region of interest.

To enable a more realistic representation of the system, other ensembles can be used that either keep temperature or volume constant. These ensembles are known as, 'NVT' which conserves the number of atoms (N), volume (V) and temperature (T) and 'NPT' which conserves the number of atoms (N), pressure (P) and temperature (T). To maintain constant temperature and pressure the basic MD algorithm is augmented by a thermostat and/or barostat. A thermostat essentially scales velocities. However, some thermostats use the idea of an imaginary heat bath of known temperature to which energy can be transferred or removed depending upon the overall system requirements. For example, if a high energy state is experienced then the extra energy can be washed out to the heat bath over a given time period as the system is brought back down to equilibrium. This time period is known as the relaxation time and can be controlled to speed up or slow down the rate of energy exchange with the bath to better improve the system. A barostat is used to maintain constant pressure in the simulation again over a given time period by varying the volume of the cell.

In this thesis MD steps for a given system were carried out using either NVT or NPT ensembles alongside the Nosé-Hoover [193–195] and Berendsen [196] thermostat and barostat. The Nosé-Hoover [193–195] thermostat extends the initial description of the heat bath by introducing a mass concept that changes the way heat is transferred to and from the bath. This allows the simulation to reach an equilibrium state with constant statistical temperature. The Berendsen thermostat [196] differs from the Nosé-Hoover thermostat because the velocities of the ions are scaled deterministically after each step so the system is forced to its desired temperature; the Nosé-Hoover thermostat does not use a heat bath. Similarly for the Berendsen barostat the cell volume is rescaled deterministically after each step to force the system to the desired pressure. This means that the Berendsen methodology tends to allow faster equilibration and bring the system to the desired temperature and pressure over shorter timescales. However, this comes at a price in that it does not recreate the true NVT/NPT ensemble due to a lack of microscopic reversibility [196]. As a result, this thesis will employ Berendsen thermostats for equilibration runs and Nosé-Hoover type thermostat and barostats for data collection stages. To enable equilibration of the system, the relaxation time for the Berendsen thermostat [196]

was selected as 1.1 ps, and the Nosé-Hoover type barostat and thermostat were both selected to be 0.3 ps [193–195]. Furthermore, a timestep of 1 fs was used for all dynamic runs, except those simulating radiation damage. These simulations represent very high energy processes and benefitted from the use of a variable timestep algorithm, whereby if the magnitude of any atomic move exceeded 0.1 Å, the integration timestep was halved until the displacement fell below this value. Likewise, if the maximum atomic displacement fell below 0.03 Åthen the timestep was doubled. In this way, atomic positions were sampled at a higher rate for the early, high velocity stage of the cascade rather than the recovery period in which atoms have lower kinetic energies. This allowed longer timescales to be achieved than if the very short timestep necessary for the damage stage had been employed throughout.

Furthermore, a timestep of 1 fs was used for all dynamic runs, except those simulating radiation damage, which used a variable timescale, a maximum cut-off value of 0.1 Å, and minimum of 0.03 Å. This enables the timestep to vary by calculating the greatest distance a particle has moved; if the move is greater than the cut-off, the timestep is halved until this move is less than the maximum. If the move is less than the minimum value, the timestep doubles until it satisfies the cutoff. In this way the timestep changes to allow for the dynamics of the system.

2.9.1 Potentials for Molecular Dynamics

The classical potential parameters described in section 2.3 must be modified slightly if they are to be employed in MD simulations. Standard modifications to the short-range potentials (as discussed by Uberuaga *et al.* [197]) are made using the Ziegler, Biersack and Littmark (ZBL) [198] approach. This is necessary in situations where enough energy could be imparted to an atom for it to overcome the barrier to prevent close ion-ion interactions as provided by pair potentials (indicated by the arrow in figure 2.10). The high temperatures used to simulate migration here could overcome this energy barrier, as could radiation damage cascades. Thus, for both these processes the ZBL potential and appropriate spline will be applied as discussed in the following section.

The potentials defining the PO_4 tetrahedra are also altered slightly by removing the threebody and Morse potentials which strictly control the O-P-O bond angle and O-P bond length. This approach has also been adopted by Jones *et al.*[84], who removed Morse and three-body potentials governing the SiO₄ tetrahedra in silicate apatites with great success [84]. Modifying the tetrahedral potentials in this way allows for a less constrained PO₄ group, in keeping with the observed flexibility of the PO₄ substructure [96, 250] and its ability to distort to allow for changes to the structure [199]. Furthermore, altering the potentials in this way means that phosphate groups can be broken while undergoing radiation damage and the angle that defines O-P-O (109.5 °) [200] can change in accordance with the damage.

In order to achieve this the harmonic three-body and Morse potentials were replaced by a single Buckingham pair potential [153] representing the O-P ion interactions. The fitting technique outlined in section 2.2.3, was used to generate these potentials and comparison was made to experimental data as follows. Initially, the O-P potential was fitted to obtain a good representation of the FAp structure and cell parameters (compared in table 2.8), elastic constants and bulk modulus (compared in table 2.9). Once this had been achieved, the O-P potential was then tested against β -TCP and the predicted structure and lattice parameters were compared against the values in tables 2.8 and 2.10. A good fit was obtained in all cases and the full potential set derived here is reported in table 2.11.

Table 2.8: Comparison of experimental and predicted cell parameters using a two body O-P potential.

	Expe	erimenta	l (Å)	Pre	edicted (Å)		% Error	•	
Formula	a	b	С	а	b	С	a	b	С	
$Ca_5(PO_4)_3F$	9.40	9.40	6.88	9.33	9.33	6.92	-0.75	-0.75	0.61	[91]
$Ca_3(PO_4)_2$	10.29	10.39	37.26	10.34	10.34	36.35	0.49	0.49	-1.65	[119]

2.9.1.1 ZBL Potentials

The ZBL potential [198] is appropriate for describing small atomic separations; this is the region in which the Buckingham potential [153] may become unphysical. Originally the ZBL potential [198] was used in conjunction with a program known as 'Stopping and Range of Ions in Matter' (SRIM) [202], which calculates interactions of ions with matter for all ionatom collisions, up to a range of 2 GeV/amu [198]. The SRIM program is based on a Monte Carlo simulation method [203], which approximates binary collisions of ions using a random selection impact parameters and ionic distribution [198]. Thus, the ZBL potential is appropriate for instances where inter-ionic separations become suddenly smaller than those reasonably

	Simulated parameters	Experimental parameters [171]
Elastic Con	ustants (GPa)	
C ₁₁	146.93	152.00
C ₁₂	68.27	49.67
C ₁₃	54.33	63.15
C ₄₄	37.65	42.75
Bulk Modu	lus (GPa)	
K (Voigt)	86.15	93.50
K (Reuss)	86.14	92.00
K (Hill)	86.15	92.80

Table 2.9: Comparison of experimentally derived elastic constants and bulk modulii with those calculated from simulation with a two body O-P potential, for FAp.

Table 2.10: Comparison of experimentally derived elastic constants and bulk modulii with those calculated from simulation with a two body O-P potential, for β -TCP.

	Simulated parameters	Experimental parameters [169]
Elastic Con	ustants (GPa)	
C ₁₁	106.07	132.44
C ₁₂	57.83	69.53
C ₁₃	56.73	55.07
C ₄₄	35.36	24.31
C ₆₆	24.12	31.39
Bulk Modu	lus (GPa)	
K (Voigt)	74.76	76.34
K (Reuss)	74.60	61.79
K (Hill)	74.68	69.07

Species	$A_{ij} (eV)$	$\rho_{ij}({\rm \AA}^{-1})$	$C_{ij} (eV Å^6)$
0-0	22764.30	0.149	27.89
Ca-O	2036.07	0.288	0.00
F-F	1317.50	0.275	13.80
Ca-F	1534.30	0.289	0.00
O-F	583833.0	0.212	7.68
P-O	610.83	0.246	0.00

Table 2.11: The potential model for MD simulations based on table 2.3 but with no three-body or Morse potentials; core-core interactions.

modelled by the Buckingham potential sets (i.e. at much smaller separations than experienced in the experimental data sets).

An example of the energy barrier provided by a Buckingham pair potential is given in figure 2.10, where the total potential given for two similarly charged ions presents an unphysical relationship between the ions at very small ionic separations (0-0.8Å). If ions enter this atomic separation the energy is highly attractive and the ions will ultimately end up in very close proximity, if not on top of each other. This is clearly unphysical and given the potential model given in figure 2.10, this could occur for atoms with increased energy, as a result from increased system temperature or from damage cascades.

To avoid this problem, a ZBL potential can be fitted to the atom-atom interactions and is 'glued' or splined onto the Buckingham curve to give a continuous potential energy curve in both first and second energy derivatives. The ZBL potential is described in equation 2.27 [198] below;

$$V_{ij}^{ZBL} = \frac{1}{4\pi\epsilon_0} \frac{Z_1 Z_2 q^2}{r_{ij}} \phi\left(\frac{r_{ij}}{a}\right)$$
(2.27)

where

$$a = \frac{0.8854a_0}{Z_i^{0.23} + Z_j^{0.23}}$$

$$\phi\left(\frac{r_{ij}}{a}\right) = 0.1818 \exp^{-3.2\left(\frac{r_{ij}}{a}\right)} + 0.5099 \exp^{-0.9423r_{ij}} + 0.2802 \exp^{-0.4029\left(\frac{r_{ij}}{a}\right)} + 0.02817 \exp^{-0.2016\left(\frac{r_{ij}}{a}\right)}$$

where, Z is the mass number of the atom (i or j), q is the charge on an atom (i or j), ϵ_0 is the



Figure 2.10: A schematic potential energy surface for two like charged ions at a range of ionic separations.

permittivity of free space, a_0 is the Bohr radius (0.529 Å) and r_{ij} is the ionic separation.

Figure 2.11 gives an example of the use of ZBL at low separations and an exponential spline to 'glue' both the ZBL function and the Buckingham potential together.

The spline itself can be described as;

$$U = \exp(A + Br + Cr^{2} + Dr^{3} + Er^{4} + Fr^{5})$$
(2.28)

where, A, B, C, D, E and F are coefficients to be fitted so that equation 2.28 produces a curve where both U'(r) and U''(r) of the ZBL and spline potentials are equal where the spline and ZBL potentials meet (equation 2.27), but U'(r) and U''(r) of the Buckingham and spline potentials are equal where the spline potential and the Buckingham parameters meet; see figure 2.11. Table 2.12 indicates the ionic separation where this spline has been added between the Buckingham and ZBL potentials as depicted in figure 2.11. This new set of potentials will be used for the the simulations described in chapter 5.



Figure 2.11: A schematic of the ZBL potential (in blue), the Buckingham potential (in black) and an interpolated section that splines the two other potentials together (in purple) for two like charged ions.

Table 2.12: The ionic separations between which the ZBL and Buckingham potentials are splined together, for core-core interactions.

Species	Ionic separation for spline (Å)
0-0	0.558-1.000
Ca-F	0.100-0.300
F-F	0.550-1.350
O-F	0.010-0.300

2.10 Surfaces

Surfaces and interfaces are of vital importance; they are where chemical and physical processes take place between a solid and its surrounding environment. This is of particular importance when discussing waste form durability [48, 106]. In order to consider loss of material from a surface or to examine the interactions of dopant ions with respect to the surface, it is first necessary to model a set of perfect surfaces. Subsequently, particle morphologies can be predicted and dopant ion interactions can be compared to experimental observations.

To create a surface, the bulk material can simply be cleaved in any plane of interest. However, there is a thermodynamic penalty for cleaving a crystal in this way, which can be measured according to the surface energy. The surface energy density ΔU_{SE} is defined as:

$$\Delta U_{SE} = \frac{U_{surface} - U_{bulk}}{A} \tag{2.29}$$

where U_{bulk} is the bulk energy, $U_{surface}$ is an energy for the same system with a surface created and A is the resulting surface area; a negative energy implies that the surface should dissociate into the surrounding medium, implying an unstable system.

Surface energy provides a measure of how stable a particular surface is. An alternative measure that is often used is the attachment energy ($U_{attachment}$). This measures the energy for an additional stoichiometric layer to be added to the surface,

$$U_{attachment} = U_{tot}^{n+1} - U_{tot}^{n} - U_{tot}^{1}$$
(2.30)

where U_{tot}^n represents total internal energy of a surface of *n* growth layers and U_{tot}^1 is the energy of a growth layer on its own. This becomes useful when assessing surface morphology of crystals, see chapter 7.

2.10.1 Types of Surfaces

In 1979 Tasker [204] identified three distinct surface types, which will be described here. In a type I surface, the crystal consists of neutral planes with equal numbers of anions and cations, see figure 2.12. Type II consists of charged planes arranged symmetrically so that there is no dipole moment normal to the surface of the unit cell, see figure 2.13. The final classification is type III which is charged and has a dipole moment normal to the surface, see figure 2.14. These latter surfaces tend to have large (polar) surface energies, which produce a polarising electric field on the rest of the bulk. Therefore, it is debatable whether these pure surfaces exist. Stable surfaces (type I and II) can exist with only small relaxations of the bulk structure. Type III surface or stoichiometry. An example of reconstruction is given in figure 2.15, where removal of the dipole is obtained by adding an equal dipole in the opposite direction. The most stable way this can be achieved is to incorporate vacancies onto the surface and moving the displaced atoms onto the bottom of the simulation block, thereby removing the overall dipole normal to the surface.



Figure 2.12: Type I surface as defined by Tasker [204]



Figure 2.13: Type II surface as defined by Tasker [204]

2.10.2 Modelling Surfaces

A surface can be thought of as a planar defect at the edge of a bulk material, therefore, many of the methods described earlier in this chapter can be applied to surface calculations. In particular



Figure 2.14: Type III surface as defined by Tasker [204]



Figure 2.15: A reconstructed type III surface in order to remove the overall dipole normal to the surface of the crystal as indicated in figure 2.14

the description of atom-atom interactions used for bulk calculations can also be used for surface simulations, and are the same as those described in table 2.3 [153].

There are two general approaches that can be used to determine the surface energy [182].

The first, (known as the vacuum slab method) considers a three-dimensional slab of material created from the bulk, where free surfaces are formed by cleaving the material in two along a plane of interest. Thus, two surfaces are created with a sufficiently large vacuum gap between the two surfaces. The gap must be present so that the two surfaces cannot interact across the vacuum, see figure 2.16. Due to periodic conditions discussed in section 2.9, the size of slab must be carefully selected to prevent ions at the surface experiencing interactions with the other face through the slab itself. Care must also be taken to ensure that the slab itself contains enough material so the interior behaves as the bulk and allows uniform properties away from the surface.



Figure 2.16: An example of the morphology of a surface simulation created by cleaving bulk material along a plane of interest and including a vacuum to separate them, where the *c*-axis is normal to the surface.

The second method, which will be used in this thesis, gives a single surface created by using a two region configuration, see figure 2.17. Region I contains the surface (and should comprise all atoms that exhibit significant relaxation due to the presence of the surface) whilst region II represents the bulk. The ions in region I are allowed to relax explicitly (all interactions with every other ion in the region are calculated) while those in region II are held at their bulk equilibrium positions. The total energy for a surface calculation comprising of two regions can be extended (in a similar way to the Mott-Littleton approximation [184]) from the expression given in equation 2.29, to give:

$$U_{tot} = U_{11} + U_{12} + U_{22} \tag{2.31}$$
where U_{11} is the energy of region I, U_{12} is the energy of the interface and U_{22} is the energy of region II with itself. However, U_{22} is ignored in this equation as it only gives a partial representation of the infinite bulk below. Since this term, is only an additive constant that is unaltered on energy minimisation, it can be ignored. Thus, in a two region model the surface energy can be defined by the following [140]:

$$U_{surface} = U_{11} + \frac{1}{2}U_{12} \tag{2.32}$$

where $\frac{1}{2}U_{12}$ accounts for the double counting of interactions [140].



Figure 2.17: An example of the morphology of a surface simulation cell, where the c-axis is normal to the surface.

In contrast to bulk simulations region II does not extend to infinity. The size of region II is required to be large enough to ensure that any increase in size does not have an appreciable effect on any ions at the bottom of region II. In addition to this, region I needs to be large enough to ensure that during relaxation none of the ions at the bottom show a marked shift in position. Thus, the correct region sizes required for surface calculations, must be obtained. Figure 2.18 indicates convergence of region II at a fixed size, (of 30 Å to represent the bulk) and then increasing the size of region I until convergence of attachment energies was obtained. From figure 2.18, the region I size will be taken as 30 Å which corresponds to twice the *c*-axis of a $(2 \times 2 \times 2)$ supercell of FAp.



Figure 2.18: The effect of region I on attachment energy for a (1000) surface of FAp.

2.10.3 Crystal Morphologies

Crystal morphologies (or crystal shapes) are calculated from attachment energies or from surface energies, which are used to represent the crystal under growth conditions with kinetic or thermodynamic control, respectively. Wulff's theorem [205] states that the equilibrium shape of the crystal is determined from the surface energies of various minimum energy surfaces. Thus, the equilibrium crystal morphology is the shape of a crystal which has a minimum total energy; all possible surfaces should be calculated. For a given space group symmetry, many surfaces are equivalent, so the number of unique surfaces is generally small.

Unstable surfaces, with large energies, lie outside of the shape and never intersect with any other surface [206, 207]. For growth morphologies (using attachment energies) the same inverse relationship applies but with the negative value of the attachment energy. Surfaces with a highly exothermic attachment energy will rapidly grow, leaving the slow growing bounding faces in evidence.

2.10.3.1 Constructing a Wulff Diagram

Gibbs [206] proposed that a system will always minimise its free energy (at constant temperature and pressure), and as such the system will also try to reduce the total free energy associated with its surfaces and interfaces. If the surface energy were isotropic (all surfaces have the same energy), as in the case of fluids, crystals adopt a fixed shape. Therefore, for a given quantity of material one can ask the question: what shape would it adopt to minimise its free energy? The solution to this is known as the Wulff Shape, originally described by Wulff in 1901 [205].

The Wulff shape has a simple, overriding property. If the shape is centred on the centre of the crystal, and lines are drawn perpendicular to each surface from the centre of the cell, the length of each perpendicular is proportional to the surface energy of that face. The Wulff shape neglects to consider any effects from energy associated with edges or corners, surface stresses (particularly when including particles into a solid matrix) and the effect of misfit strains. All of these effects become important at the nanoscale. However, the Wulff shape gives a very good overall representation of macroscopic and larger crystals.

Crucial to the Wulff shape construction is the gamma (γ) surface. From Gibbs' argument [206], the Gibbs free energy is minimised by assuming a configuration of low surface energy. This quantity can be defined as,

$$\Delta G_i = \sum_j \gamma_j O_j \tag{2.33}$$

where γ_j represents the surface area per unit area of crystal face 'j', and O_j is the area of this face. ΔG_i represents the difference in energy between a real crystal of 'i' molecules with a surface and a similar configuration of 'i' crystals in an infinitely large crystal.

The γ surface mentioned here, is a closed surface that describes the energy of the surface as a function of orientation [208]. This is best described by imagining a set of points spread out around the origin which are then connected in a step-wise form around the origin, as indicated in figure 2.19. This process creates the γ surface [205].

The Wulff shape is constructed from the γ surface, which is traditionally done in three dimensions, as described by Herring [209]. To simplify the construction process a two dimensional explanation is given here as depicted in figure 2.20. Consider the γ surface (as shown in figure 2.19) and starting at its origin, draw a straight line out from the origin until the line intersects with the γ surface. Then draw a plane normal at this position on the γ surface (grey dotted



Figure 2.19: Creation of the γ surface, by considering surface energy as a function of orientation. The points (representing specific surfaces) are spread around the origin at a distance defined by their surface energy as indicated by the arrow. Joining all the points creates the γ surface [205].

lines). Repeat this for all points on the γ surface until the shape is bounded internally by all such planes; this forms the equilibrium shape of the crystal.





To achieve this in three dimensions and to create a true crystal morphology, the same process described above is simply used for a three-dimensional γ surface. To calculate growth morphologies for crystal systems, the attachment energies (described earlier) can be calculated, and the γ surface is created from these energies. More traditionally, however, the γ surface is created using surface energies, which generate equilibrium morphologies.

In order to create the Wulff morphologies presented here, the Qhull [210] program was used. This first involves calculating the surface energies for the surfaces of interest, here using the GULP program [140] and the methodology described earlier. With the list of planes and associated energies the 'qhalf' command from the Qhull program can be used to create the Wulff Shape. The 'qhalf' command computes the half space intersection of the planes; in other words the inner volume bounded by the intersecting planes is maintained, but the planes extending to infinity outside of this area are removed [210]. This process reveals the minimum area bounded by the planes, which gives the Wulff Construction [205].

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3

Half Occupancy of β -Tricalcium Phosphate

3.1 Structure of β -Tricalcium Phosphate

The structure of β -tricalcium phosphate (β -TCP) shows considerable compositional flexibility for incorporating such species as gadolinium, plutonium and thorium [73, 75, 76]. The structural stability and the inclusion of many waste species is a significant advantage of this material for nuclear waste forms. This feature is predominantly due to the half occupied nature of one Ca crystal site, the Ca(4) site [119] and the presence of a number of differently coordinated CaO_n polyhedra. Before the effect of this compositional variation can be examined a reliable model describing the crystal structure of β -TCP, must be determined.

 β -TCP is not a notable Ca ion conductor and therefore the disorder given by the half occu-

pancy of the Ca(4) sites is unlikely to be a dynamic mechanism in which empty Ca(4) sites are occupied by passing Ca ions. The remaining possibilities are therefore:

- 1. the Ca(4) sites are randomly occupied (i.e. the probability of finding a Ca atom at a site is independent of the occupancy of adjacent sites),
- 2. the observed partial occupancy is a symptom of a lower symmetry supercell structure, or
- 3. there is local order, so that the probability of finding a Ca atom does depend upon the occupancy of adjacent sites but this does not extend to complete long range order.

The crystal structure of β -TCP has already been discussed in section 1.5, where the Ca(4) sites have been described as having half occupancy [119, 212]. In this chapter, classical static techniques (see methodology) have been employed to consider the 48,620 different configurations possible over the (3_h×1×1) supercell and the twenty possible configurations that are possible over a (1×1×1) cell in order to obtain a more reliable structure.

3.2 β-Tricalcium Phosphate Cells

As mentioned in section 1.5, the Ca(4) site in β -TCP is considered to be half-occupied [119] and as such, it would be useful to know the arrangement of Ca(4) atoms that yields the lowest energy structure. Without this knowledge, the thermodynamic and structural consequences of loading with a waste species cannot be consistently predicted. Comparing substitution at possible sites in a well characterised material would allow the processes that are responsible for controlling the solution limit of a waste species to be identified, or would perhaps limit the durability of particular mineral waste forms. Michie [174] has previously discussed the results connected with configurations over the (1×1×1) unit cell and a (2×1×1) supercell. Here, a much larger (3_h×1×1) supercell was required to extend the configurational search and allow the discovery of a more stable configuration than any discussed previously [174]. The relative size of the search domain in this and Michie's [174] work are compared in figure 3.1.



Figure 3.1: Polygons representing the different possible basal planes for different cell sizes of β -TCP.

3.2.1 (1×1×1) Unit Cell

As discussed in section 1.5, the $(1\times1\times1)$ unit cell with the formula β -Ca₃(PO4)₂, can be described in terms of repeating columns consisting of CaO_n and PO₄ groups that run parallel to the *c*-axis, i.e. [0001], as shown in figure 1.18. In β -TCP, only the 'A' columns contain Ca(4) sites (two per column), which are all staggered with respect to each other as shown in figure 3.2. This allows for three different vertical positions of the Ca(4) sites in a $(1\times1\times1)$ unit cell. Since there are two Ca(4) sites per column, there could be a column with both Ca(4) sites occupied, one site occupied, or both sites vacant. The twenty possible arrangements across the Ca sites in a unit cell is given as $\left(\frac{6!}{3!3!}\right)$: corresponding to six total sites, three occupied and three unoccupied.

Although mathematically there are twenty possible configurations over this $(1 \times 1 \times 1)$ unit cell, due to the periodic nature of the system there are really only three symmetrically different arrangements, which will be discussed here. In first of these arrangements, the occupied Ca(4) sites are in the closest proximity to each other as illustrated in figure 3.3(a). This creates diagonal bands of occupied sites and unoccupied Ca(4) sites down the *c*-axis. The next possible arrangement consists of one fully occupied 'A' column, one half occupied 'A' column and an empty column, looking at the $(11\overline{2}0)$ plane figure 3.3(b). The final arrangement is where the



Figure 3.2: The β -TCP structure viewed parallel to the (1120) plane, illustrating the shift in Ca(4) site down the *c*-axis across the cell. In this schematic all the Ca(4) sites have been indicated as fully occupied, for ease of description. The real crystal structure is half occupied, and only three of the six Ca(4) sites shown would be occupied [119]. Here the Ca(4) groups are shown in dark blue, Ca(5) in purple and the PO₄ tetrahedra are grey. The 'B' columns have been left out and are indicated as dotted grey lines.

columns are all half filled and are staggered alternately across the columns, figure 3.3(c).

Given the nature and the proximity of these Ca(4) sites it seems likely that the relative distance between the occupied and unoccupied Ca(4) sites would have a pronounced influence on the relative lattice energies of these configurations. For example, those arrangements with unoccupied sites in close proximity may suffer from local strain in the lattice due to contraction, or too many occupied sites together may lead to greater Coulombic repulsion.

3.2.2 (2×1×1) Supercell

Michie [174] investigated all the configurations in the $(2 \times 1 \times 1)$ supercell, which is two $(1 \times 1 \times 1)$ unit cell side by side; see figure 3.1. As a result it is possible to occupy all three 'A' columns on one side of the cell and have the other three unoccupied. This leads to a spread of energies, where some are similar to those obtained with the $(1 \times 1 \times 1)$ unit cell but many lead to highly unsymmetric, unbalanced configurations which do not converge because of excessive lattice strain. This is because the $(2 \times 1 \times 1)$ supercell is very anisotropic, with a short *b*-axis (see figure 3.1). As a result the alternative $(3_h \times 1 \times 1)$ supercell is considered instead.

3.2.3 (3_h×1×1) Supercell

The $(3_h \times 1 \times 1)$ supercell was chosen to allow for a better comparison to larger β -TCP systems and can be seen in figure 3.4. As seen in figure 3.1, the $(3_h \times 1 \times 1)$ supercell contains the same atomic environments as the hexagonal setting of β -TCP, which leads to a greater number of possible configurations and longer range order to be investigated. In the $(3_h \times 1 \times 1)$ supercell there are nine 'A' columns each containing two Ca(4) sites. Which taking the same approach as the $(1 \times 1 \times 1)$ unit cell gives eighteen possible sites, nine occupied and nine unoccupied, $(\frac{18!}{9!9!})$ or 48,620 different configurations.

As in the $(1 \times 1 \times 1)$ unit cell case, a number of the configurations will be symmetrically equivalent and have identical lattice energies. Unlike the unit cell however, it is not obvious how to group so many configurations into terms of the proximity of occupied Ca(4) sites, so all possible configurations have been calculated.





Figure 3.4: Schematic showing the $(3_h \times 1 \times 1)$ supercell of β -TCP structure, with calcium as dark blue, oxygen as red and PO₄ as grey tetrahedra. The $(3_h \times 1 \times 1)$ supercell contains 819 atoms.

3.3 Atomic Scale Simulations

All the structures of β -TCP were modelled using classical static lattice techniques, described in chapter 2. The parameters used were those of Mkhonto and de Leeuw [170] and Michie *et al.* [130] which have been discussed previously in section 2.3. The potentials and charges used in this part of the thesis are reported in tables 2.7 and 2.3.

For the calculations in a single unit cell of β -TCP, the twenty possible configurations described earlier in the (1×1×1) unit cell were relaxed to zero stress and ion positions [119, 127].

In addition, a configuration in which all six Ca(4) sites were half occupied was simulated through application of the mean field theory [140], in which each Ca(4) site experiences the mean potential of all the possible configurations.

3.3.1 Configurational Averaging

The large $(3_h \times 1 \times 1)$ supercell generates vast numbers of configurations and obtaining property values for the overall β -TCP structure, including all symmetrically distinct configurations is necessary for comparing the system to experiment. This can be achieved by making a configurational average of the system as a whole, by taking a statistical thermodynamic average over the particular property values of interest [213, 214]. If a particular configuration, ('*i*'), has a property value P_i (where the property value could be, for example, lattice parameter, unit cell volume or solution energy), then the configurational average for all configurations (*P*), is given by:

$$(P) = \frac{\sum n_i P_i e^{\frac{-\Delta E_i}{k_B T}}}{\sum n_i e^{\frac{-\Delta E_i}{k_B T}}} = \sum C_i P_i$$
(3.1)

where, ΔE_i is the difference between the energy of configuration *i* and the energy of the most stable configuration, k_B is Boltzmann's constant, *T* is the temperature over which the average is taken (in K), n_i is the number of equivalent configurations generated in the unit cell. Interestingly, in these calculations the surrounding environment for each configuration is exactly the same in structure and orientation as itself due to periodic boundaries, which may not be the case in nature. Therefore, the boundary forces assumed for equation 3.1 may not be quite correct, but the effect should be small although it can only be confirmed by comparison with experiment [215], as described in the future work section, chapter 8. Data from the configurationally averaged structures of the lowest energy structures of $(1 \times 1 \times 1)$ and $(3_h \times 1 \times 1)$ will be compared.

3.4 Simulated Configurations

3.4.1 (1×1×1) Unit Cell

For the twenty different configurations possible in a $(1 \times 1 \times 1)$ unit cell there are only three energetically distinct structures, as discussed by Michie [174], which leads to three different spatial separations of the Ca(4) sites. The energies associated with these configurations can be seen in figure 3.5, where the energies for these three groups are represented as arrows at the appropriate value.

The most stable structure is where the Ca(4) sites have the greatest separation and will be referred to as the Low Energy Configuration (LEC). This arrangement can be seen in figure 3.3(c). This is in agreement with Yin *et al.* [212] who suggested that the distribution of Ca(4) ions in the β -TCP structure may affect the stability and electronic properties of the mineral, since 'defect like' electronic states are associated with the vacant Ca(4) sites [212]. Furthermore, Yin *et al.* [212] concluded that the configuration with the most even spread of Ca(4) ions was the most stable, agreeing with the results shown here (however, Yin *et al.* [212] did not investigate all configurations). The High Energy Configuration (HEC), where the Ca(4) sites are closest together, can be seen in figure 3.3(a). An example of the Intermediate Energy Configuration (IEC) is shown in figure 3.3(b). The space group P3 was determined for each of the configurations using the unrelaxed mean field positions, except for the most stable LEC structure, which exhibits R3c, space group. In all cases the structure was relaxed to zero stress, in accordance with energy minimisation (section 2.6) in order to acquire the symmetry settings.

In applying mean field theory it is assumed that all configurations are equally likely. This is possible for materials where there is little energetic difference between configurations or where formation kinetics dominate over thermodynamics, so that the structures do not approach a Boltzmann's distribution. However, a configurational average (taken at a temperature of 1000 K) for the different structures shows the LECs dominate ($C_i = 0.9995$); this explains why the LEC and configurational average results shown in table 3.1 are similar. It may, however, be

distinct from a mean field approximation.

The results shown in table 3.1 show that all the $(1 \times 1 \times 1)$ based models slightly underestimate the *a* and *b* lattice parameters. This leads to an overall reduction in the unit cell volume by 3%. Furthermore, the *c/a* ratio is close to experimentally derived parameters, this time approximately 3% larger. Unfortunately due to the similarity of the mean field and configurational average values it is difficult to distinguish between the models. However, the dominance of the LEC at high temperatures such as 1000 K, is not consistent with the average occupancy model, for this structure.

3.4.2 (3_h×1×1) Supercell

For a single unit cell only a small number of configurations exist that can be assessed. Using a $(3_h \times 1 \times 1)$ supercell it is possible to determine if a more stable configuration than the LEC from the $(1 \times 1 \times 1)$ cell could be found. A histogram of the energies for all 48,620 different arrangements of Ca(4) sites in the supercell, is shown in figure 3.5.



Figure 3.5: A histogram to illustrate the number of half occupied Ca(4) sites in β -TCP for the full hexagonal cell. The energies for the LEC, IEC and HEC (1×1×1) unit cell are indicated so the (3_h×1×1) energies are shown relative to the LEC single unit cell configuration at 0.0 eV. The histogram bin width is 0.005 (eV).

Figure 3.5 shows that more than half of the possible configurations within the $(3_h \times 1 \times 1)$ su-

Cell Parameters	Space group	a (Å)	<i>b</i> (Å)	c (Å)	α (deg)	β (deg)	γ (deg)	Volume (Å ³)	<i>c/a</i> ratio
Experimental	R3 <i>c</i>	10.44	10.44	37.40	90.00	90.00	120.00	3527.26	3.58
Mean field (Relaxed)	R3	10.29	10.29	37.26	90.00	90.00	120.00	3416.36	3.62
$(1 \times 1 \times 1)$ Configurational average at 1000 K	m R3c	10.28	10.28	37.46	89.99	90.00	120.00	3428.76	3.64
(1×1×1) LEC	R3	10.28	10.28	37.39	90.00	90.00	120.00	3423.86	3.64
Lowest $(3_h \times 1 \times 1)$ supercell	$P3_1$	10.43	10.43	37.40	90.00	90.00	120.00	3527.13	3.59
$(3_h \times 1 \times 1)$ Config.Av. at 1000K	$P3_1$	10.28	10.29	37.37	89.99	90.01	120.00	3421.40	3.63
$(3_h \times 1 \times 1)$ mapped back		10.29	10.29	37.28	90.06	90.00	120.00	3417.68	3.62



percells were found to have lower lattice energies than the LEC $(1\times1\times1)$ unit cell. Through closer inspection, the two lowest symmetrically distinct configurations are given in figure 3.6. Considering the first most stable configuration (figure 3.6 a), a longer range order of half, full and vacant columns is evident when viewed down the *c*-axis. In each of these there are three columns with a full complement of Ca(4) ions per column (F) (both Ca(4) sites are full), three that are unoccupied (E) and those that are half full (H or H⁷). The H and H⁷ differ from each other in the order of the empty and full Ca(4) sites when looking down the *c*-axis. The most stable configuration (figure 3.6a) differs from the next stable (figure 3.6b) by a subtle change of order of E and F columns around the H or H⁷ columns. This larger cell provides a more comprehensive impression of how the configurations vary only slightly from each other, which is borne out by the small differences in lattice energy, suggesting that a number of different configurations could exist in local domains.



Figure 3.6: The lowest energy configuration generated within the $(3_h \times 1 \times 1)$ cell. Each intersection of the dotted lines represents an A column which is surrounded by six B columns. The occupancy of the Ca(4) sites in the columns is represented by H for Half full (1 Ca(4)), F for Full (2 Ca(4)) and no change indicates A columns empty of Ca(4). a) represents one of the two lowest energy configurations obtained, with a symmetry of P3₁. b) represents the other low energy configuration which has a symmetry of P3₂. Both low energy configurations have symmetries which are isomorphic supergroups of the unit cell symmetry R3*c*.

In the $(1\times1\times1)$ LEC unit cell the columns are all half occupied in the $<1\overline{1}00>$ direction; see figure 3.1. Comparing this to the $(3_h\times1\times1)$ cell gives a different result as the columns along $<1\overline{1}00>$ (figure 3.6) now have a combination H, H[/], E of F. However, considering the $<1\overline{2}10>$ direction, the pattern of (F), (E) and (H) is repeated. This suggests that the low energy arrangements of the $(3_h\times1\times1)$ supercell can be related back to the original unit cell as symmetry subgroups.

The two lowest energy $(3_h \times 1 \times 1)$ supercells were investigated further and their lattice constants are presented in table 3.1. The results given for the $(3_h \times 1 \times 1)$ supercell here have been modified by dividing the a and b parameters by $\frac{1}{\sqrt{3}}$ to enable comparison to those reported for the $(1 \times 1 \times 1)$ unit cell, as observed in table 3.1. In this case the *c*-axis remains the same and the volume and lattice energy are divided by three. It is interesting to note that the predicted lattice parameters for the $(3_h \times 1 \times 1)$ supercell are all in very good agreement with the experimental data. It is perhaps easier to understand these results by considering the configurational average, due to the many configurations with very similar energies as shown by the histogram in figure 3.5. The configurational averages of the $(3_h \times 1 \times 1)$ supercell have been calculated at 300 K and 1000 K, see figure 3.7. At 1 K, only the very lowest energy configuration appears and at 300 K a small range of the lowest energy configurations exist. Intriguingly the majority of the configurations do not appear in the configurational average at 1000 K, (see figure 3.7), indicating that the configurational average is distinct from the mean. Nevertheless, the configurational average consists of a number of configurations and could explain why the average was useful in describing the experimental data. Sadly, by comparison of lattice parameters alone it is not possible to distinguish the low energy arrangement of the $(3_h \times 1 \times 1)$ supercell, shown in table 3.1, from that of the configurationally averaged structure of the $(1 \times 1 \times 1)$ unit cell. Thus, use of the full X-ray Diffraction (XRD) pattern will be considered as an alternative comparison method in the next section.

3.5 X-Ray Diffraction

3.5.1 Simulated X-Ray Diffraction

Given that the different model sizes assessed here cannot be resolved via interrogation of the lattice parameters, diffraction patterns were generated as a method of differentiating between



Figure 3.7: A graph to show the probability of the structure occupying any given state as indicated by the lattice energy per formula unit for a $(3_h \times 1 \times 1)$ supercell at 1 K, 300 K and 1000 K.

cation ordering in the models. Of particular interest is the appearance or disappearance of peaks as well as change in peak intensities. Specifically simulated XRD patterns will be compared to the low energy $(3_h \times 1 \times 1)$ supercells (see figure 3.6) since they are most probable at 300 K according to figure 3.7.

Firstly a simulated XRD pattern was produced from Yashima *et al's* final model [119] which is displayed in figure 3.8. These XRD plots are simulated using the 'Materials Studio' software [216]. This plot is compared to spectra derived from the LEC $(1\times1\times1)$ and $(3_h\times1\times1)$ cells and the configurationally averaged structure. To make identification in the diffraction patterns clear, the lattice parameters were fixed at the experimentally defined values [119]: *a* and *b* at 10.4352 Å and the *c*-axis at 37.4029 Å. The aim here is to compare the spectra from the different models investigated and assess any differences in the patterns for comparison to subsequent high resolution diffraction patterns.

Figure 3.8 shows that all the simulation patterns generated are similar to that from the model by Yashima *et al.* [119]. However, there is a change in peak intensity at 22.4 $2\theta^{\circ}$ due to the change in ordering of Ca(4) sites across the structure. The Ca(4) sites in the experimental

Yashima *et al.* model [119] have been ascribed an occupancy of 0.43. Comparing this to the same structure and assigning each Ca(4) site an occupancy of 0.5 (to maintain charge), there is no perceptible difference in the spectra. However, there is a difference in spectra (at 22.4 $2\theta^{\circ}$) if three of the sites are occupied and three are unoccupied. Conversely, the LEC (1×1×1) exhibits some additional peaks due to the change in symmetry from R3*c*, seen from the mean field calculation, to R3.

Finally, to allow a better comparison to the experimental data, the $(3_h \times 1 \times 1)$ supercell was mapped back to a $(1 \times 1 \times 1)$ geometry (as observed in table 3.1). This new cell has *c*-axes with the two Ca sites occupied as $\frac{1}{3}$ and $\frac{2}{3}$ in an alternating pattern down the axis. This modified cell displays a similar XRD pattern with a few differences in intensity to the data from Yashima *et al.* [119], which can again be attributed to different Ca(4) site occupancies. The $(3_h \times 1 \times 1)$ supercell is comparable to the mean field data as expected.



Figure 3.8: Simulated XRD patterns for the experimentally derived model [119], the lowest energy configuration for both the(1×1×1) and (3_h ×1×1) cells and the geometrically modified lowest (3_h ×1×1) (λ =1.54 Å).

3.5.2 Experimental X-Ray Diffraction

The simulated XRD patterns indicate that there is a change in peak intensity (at ~ $222\theta^{\circ}$) for the configurationally averaged ($3_h \times 1 \times 1$) supercell when compared to Yashima *et al.* [119]. In order to evaluate the effect proposed by the simulated XRD data, XRD was carried out on a real sample of β -TCP, provided by Dr P. Mallinson from AWE, via the process mentioned in section 1.5.

As mentioned previously, the area of interest in the XRD pattern at roughly ~ $222\theta^{\circ}$, so for experimental XRD plots a narrow band encompassing this region was selected to allow a finely sampled XRD spectra to be measured in a reasonable time.

The XRD was carried out using a Bragg-Brentano geometry [217], with Cu K α radiation, $\lambda(K\alpha_1) = 1.54056$ Å and $\lambda(K\alpha_2) = 1.54439$ Å. The scan step used was 0.02 Å and the angular 2θ range was from 13 to 23, in order to collect an accurate spectrum.

To encourage ordering of the Ca(4) sites, a heated stage was used during the XRD data collection period [218, 219], which increased in temperature from 308 K (room temperature) to 473 K and then in 200 K intervals up to 1073 K, as shown by the profile in figure 3.9.

In this experiment a small sample of β -TCP was mounted onto the heated stage within the X-ray diffractometer. For each data collection point the sample was heated to the desired temperature and held there for two hours for the °2 θ range spectra to be obtained before the next step in temperature. The final temperature run (at 1073 K) was carried out twice back-to-back to establish if degradation of the sample at temperature had occurred.

All the XRD spectra obtained in this way are presented in figure 3.10. The two diffraction patterns taken at 1073 K are identical, therefore no change in the sample over prolonged temperature exposure was seen. Interestingly the two sets of data collected at 308 K show almost identical patterns. Sadly, this indicates that there has been no appreciable change of the structure after being held at high temperatures for the 14 hours required for the experiment. This suggests that any ordering of cation sites occurring in the lattice cannot be discerned by this method, or does not happen. As a result a mean XRD spectrum is obtained over all configurations present within the sample, the spectrum presented in figure 3.10 is comparable to the configurationally average structure for the $(3_h \times 1 \times 1)$ supercell shown in figure 3.8.



Figure 3.9: Scanning profile for each XRD spectrum over a $13-232\theta$ range.

As temperature increases, the lattice expansion is noticeable by a shift in spectra to the left [220]. The extent of the expansion of the structure, and hence the shift in patterns, is controlled by the thermal expansion coefficient, which is discussed later in section 6.1. Here, as temperature increases, the ratio of the triplet peak at ~ $22^{\circ} 2\theta$ changes also with the right hand peak (at ~ $22^{\circ} 2\theta$) decreasing. Unfortunately, this change in relative intensity cannot be attributed to cation ordering, but instead to a change in cation position in the structure as the volume expands due to temperature.

Comparing the experimental diffraction patterns (figure 3.10) and those obtained from simulation (figure 3.8) it is possible to establish whether any ordering of Ca(4) sites takes place. Figure 3.11 demonstrates that there are a few differences between the simulated diffraction patterns, the Yashima *et al.* [119] data and the configurationally averaged (at 1000 K) ($3_h \times 1 \times 1$) supercell. This is not such an unexpected result, since diffraction experiments sample much of the crystal over a long range. Figure 3.11 shows that the Yashima *et al.* [119] model exhibits a different ratio of the triplet at ~22° 2 θ , when compared to the configurationally averaged ($3_h \times 1 \times 1$) structure and the experimental XRD patterns. Also the configurationally averaged ($3_h \times 1 \times 1$) structure exhibits two small peaks, one at ~13° 2 θ and ~23.7° 2 θ , which are shown in the experimental patterns but not in the Yashima model [119]. Conversely, the configurationally averaged structure exhibits a small peak at ~17.5° 2 θ which is not shown in the Yashima *et al.*



Figure 3.10: XRD patterns for a sample of pure β -TCP for temperature 308 K-1073 K at 200 K increments. Note the change in relative intensities of the peaks at ~ 22 ° 2 θ .

model or the experimental patterns. Thus, both the configurationally averaged structure and the Yashima model [119] differ from the experimental XRD plots, thus, more experimental data are required to properly investigate the existence of domains. Recently, Mellier *et al.* [227] have carried out synchrotron powder diffraction experiments which provide additional evidence in support of the XRD patterns exhibited in figure 3.10 as their results suggest the presence of numerous small domains, of lower energy configurations. Nevertheless, it is the order of these domains, even on a sub-grain level that will be of crucial importance in determining the behaviour of extrinsic dopants and will contribute to the overall compositional flexibility of β -TCP, so more experimental work is required to really understand ordering present in this structure, as discussed in the further work chapter, 8.



Figure 3.11: Comparison of XRD patterns at 308 K and 1073 K with the Yashima *et al.* half occupied structure [119] and the LEC $(3_h \times 1 \times 1)$ supercell. The results here have been moderated to allow for thermal expansion so the results are more comparable at the same 2θ .

3.6 Statistical Analysis

For a better understanding of cation ordering in β -TCP, all configurations possible for a large $(3_h \times 1 \times 1)$ supercell (48,620) have been calculated and relaxed. If an even larger cell size were to be used to find (potentially) lower energy configurations, the number of configurations required to be calculated would range into billions, which would require huge computational resources that are currently unavailable. Therefore, the use of statistical analysis has been considered to reduce this number and still obtain a good confidence level [221].

In order to only calculate a smaller proportion of overall configurations, it is necessary to determine how large a sample is required to still give the overall trend and to identify the very low energy configurations. To calculate so called Confidence Intervals [222] on a population of results, it is assumed that the data have a Gaussian or 'normal' distribution. Figure 3.5, which represents all 48,620 data points, shows a long tail to the right of the main body of data which suggests that the data are non-normal.

Further investigations of this data set show positive skewness, which is a measure of asymmetry of the data curve, where the positive value (given in table 3.2) indicates the tail is longer on the right hand-side of the probability density function (figure 3.5). Mathematically skewness (g) is defined as;

$$g = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^3}{(n-1)\sigma^3}$$

for a sample of data with values $x_1...x_n$, where \bar{x} is the sample mean, σ is standard deviation and *n* is the total number of data points.

The data set also presents higher measure of kurtosis (which is a measure of how peaked or broad the data curve is). The mathematical description of kurtosis(γ) can be given as;

$$\gamma = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^4}{(n-1)\sigma^4}$$

for the same sample of data as described for skewness. The results described for the lattice energies of β -TCP, deviate somewhat from those expected for a Gaussian distribution (as seen in table 3.2) which would have a kurtosis value of 3 [222, 223].

Although the data set appears to present a significant deviation from a perfect Gaussian distribution, a further investigation into how non-normal the data set is, would be useful to assess how much the values presented in table 3.2 impact on the normality of the data. If the data set

Parameter	Value
Mean	0.0355 eV
Median	0.0296 eV
Standard Deviation	0.0255 eV
Skewness	1.1550
Kurtosis	4.4178

Table 3.2: Statistical overview of energies for all 48,620 configurations shown in figure 3.5.

is particularly non-Gaussian, transformations such as the Box-Cox or Weibull transformations [224, 225] can be applied to the data to make the distribution of data more 'normal'.

A normal probability plot, Chambers *et al.* [226], is a graphical method for assessing whether or not a data set has approximately normal distribution. The data are plotted against a theoretically normal distribution in such a way that if the data set is normal, the points form an approximate straight line. A full methodology for plotting a normal probability graph can be found in the work by Chambers *et al.* [226]. The normal distribution function for the data presented here can be seen in figure 3.12. The data set shows classical non-linear behaviour [223] for data that are skewed heavily to the right. Sadly attempts to force the data into being more 'normal' using Box-Cox or Weibull transformations [224, 225] do not change the data enough to present it as a Gaussian distribution. As a result, the use of confidence intervals to suggest the size of the sample required [223] to give a good representation of the data cannot be used. Therefore, it seems that at present all possible configurations must be calculated in order to fully understand the configurational ordering of cations within β -TCP, and the largest cell that can be probed currently is the (3_h×1×1) supercell due to current computational limits.

3.7 Conclusions

In this particular study lattice energies for all possible configurations of the half occupied Ca(4) site have been calculated for the $(1\times1\times1)$ unit cell and the most stable variant, $(1\times1\times1)$ LEC, has been identified. In order to align these predictions more closely with long range order, a larger $(3_h\times1\times1)$ cell has also been examined and significantly, large numbers of lower energy configurations were determined. These latter configurations fall into isomorphic supergroups of



Figure 3.12: Normal Probability Plot for the data presented in this section vs. the standard normal distribution (z). Comparing the data to the ideal 'normal' line (shown in blue), the data show very strong non-linear behaviour .

the experimentally determined structure, which has symmetry R3*c*; the $(3_h \times 1 \times 1)$ LECs have P3₁ and P3₂ supergroup symmetries. However, the difference in energy between these low energy groups is minimal, leading to an experimental structure that is likely to exhibit many low energy configurations. This helps to justify the assumption of a configurational average.

The $(3_h \times 1 \times 1)$ supercell was chosen because it represents the full symmetry for the experimentally determined space group. Nevertheless, it has been impossible to rule out lower energy configurations arising from an even larger supercell. It is particularly clear from the $(1 \times 1 \times 1)$ results [174] that including lattice relaxation into each simulation is vital. This makes calculating the many millions of configurations possible for larger cells than the $(3_h \times 1 \times 1)$ a formidable task!

This investigation into the β -TCP structure shows that differences in stability for various configurations are not random; the probability of finding a Ca atom on a given site does depend upon the occupancy of local sites. Using the LEC for a $(3_h \times 1 \times 1)$ cell and modifying the geometry of the cell to enable comparison to experiment yield a more suitable representation of the half occupancy; this is for the Ca(4) sites to be occupied down the *c*-axis in a $\frac{1}{3}$, $\frac{2}{3}$ repeating pattern instead of simply being half occupied. Crucially, however, although many lower energy configurations have been found when considering the larger hexagonal $(3_h \times 1 \times 1)$ cell over the primitive $(1 \times 1 \times 1)$ cell, a dominant single low energy cell or structural motif was not found. Unfortunately, it is not possible to increase the size of the cell further to determine if there are any lower energy structures, as computational limits restrict the calculation of the billions of configurations that would be required. It may well be that regardless of cell size, there is no guarantee that the lowest energy system can be found. The data for the distribution of configurations presented by the $(3_h \times 1 \times 1)$ supercell is very non-normal (figure 3.12) and a smaller, but representative sample of a larger supercell cannot be calculated using confidence probabilities [223].

Finally, the present XRD experiments show that the structure is not consistent with only the low energy $(3_h \times 1 \times 1)$ structure. However, recently Mellier *et al.* [227] have carried out synchrotron powder diffraction experiments which they conclude provides additional evidence in support of the results shown here and in the paper Jay *et al.* [211] as their results indicate "the presence of a super structure with a symmetry lower than R3*c*". These experimental results are encouraging for the conjecture presented here; that there are domains of low energy configurations apparent in the structure.

The configurational ordering at atomic level will have consequences for the compositional flexibility of this system, as the ability of defect ions to substitute into the structure relies on the type and stability of sites available. In this regard, the lowest energy $(3_h \times 1 \times 1)$ structure identified here provides a useful model on which to base further investigations. Indeed it is the $(3_h \times 1 \times 1)$ LEC model which will be utilised for further studies in this thesis.

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4

Cation Substitution and Partitioning of Fluorapatite and β -Tricalcium Phosphate

4.1 Introduction

The structures and chemistry of both β -tricalcium phosphate (β -TCP) and fluorapatite (FAp) are such that numerous substitutions can be incorporated, as discussed in chapter 1. These substitutions include metal cations with a range of valences as discussed in the literature [81, 105, 108, 131, 229–231]. Indeed large swathes of the periodic table can be incorporated into the apatite structure, but normally at trace concentrations. However, for some ionic substitutions (such as Sr²⁺) complete solid solutions exist [130]. FAp has two distinct cation sites whilst β -TCP has five providing a large number of sites for cation substitution. Both structures are found

together as heterogeneous mixtures within naturally occurring mineral deposits [25], and have been proposed as components of a multiphase waste form (chapter 1). It would be beneficial to understand how the waste elements are partitioned between the two phases.

There are a number of possible substitution mechanisms possible for cations and the PO₄^{3–} anionic complex in both structures and for fluorine in FAp, which are described in detail by Pan *et al.* [230]. Understanding these defect substitutions is vital, as they represent the means by which heavy metals may be sequestered. This is of particular importance for waste forms where knowledge of the likely location of foreign species is a crucial consideration in their design. This chapter will consider a wide range of divalent and trivalent substitutions into the FAp and β -TCP lattice, comparing the relative stability of substitutions on different lattice sites within each structure and then comparing between structures. This will give a good idea of the defect distribution and partition over the potential composite waste form, which are not yet fully understood [72]. This study aims to investigate site preferences of both structures independently and together.

4.1.1 Cation Sites in Fluorapatite

FAp has two symmetrically different cation sites, Ca(1) and Ca(2), as described in section 1.4.1 and outlined in figure 4.1. The Ca(1) site (which resides further away from the anionic central channel) has been described as more covalent than the Ca(2) site and has a volume of 31.92 Å^3 [107, 110]. By contrast the Ca(2) site (which lies parallel to the central channel) is described as more ionic; it is "under-bonded" and has a smaller volume of 22.68 Å³ [107, 110]. Furthermore, Pan and Fleet [108, 109] suggest factors that control site preference for defect species remain unclear and changes in bond valence and volume could be important. Interestingly Pan and Fleet's conclusion seems contradictory to the effect expected from atomic radius size alone; they concluded that smaller defects would preferentially substitute into the larger Ca(1) site, while defects with a larger radius may substitute into the smaller Ca(2) sites [108]. In contradiction to other reports, Khattech *et al.* [111] claim that the smaller of the two sites is Ca(1) and as such, smaller defects will preferentially substitute onto the smaller Ca(1) site and *vice versa*.

Clearly there is some confusion over partitioning of these defects and which effect dominates the defect partitioning in apatites. Beevers and McIntyre [95] concluded that even very minor



Calcium polyhedra present in the β -TCP structure:

Calcium polyhedra present in the FAP structure:



Figure 4.1: Schematic of the cation sites present in both the FAp and β -TCP structures, fully discussed in sections 1.4 and 1.5 respectively.

changes in atomic radii of the species within the FAp lattice, and specifically those near the c-axis tunnel, leads to an expansion or contraction of the tunnel. Furthermore, investigations by Dong and White [232, 233] indicate that doping the Ca(1) and Ca(2) sites generates an expansion or contraction of the tunnel via distortion or twisting of the phosphate groups within the lattice.

With reference to the structure of FAp (figure 4.1), the polyhedron that surrounds the Ca(1) site can be described by the closest surrounding species, which are six O^{2-} ions in this case. This polyhedron is noted as a Ca(1)O₆ metaprism and was first described by White and Dong [96]. They noticed that this metaprism distorts or twists as the chemistry of the apatite lattice changes. The amount of twist observed was a function of the size of the ion in the *c*-axis channel and on the ions surrounding cation sites [232, 233]. The twist of the metaprism structure controls the *c*-axis tunnel diameter and height; this also impacts upon the overall lattice parameters *a*, *b* and *c*. This ability to change lattice parameter and tunnel diameter allows accommodation of a range of defect species within the lattice. The metaprism angle change with incorporation of a range of defects will be calculated and compared for each defect species in

FAp.

4.1.1.1 Cation Sites in β -Tricalcium Phosphate

 β -TCP is not expected to behave in the same way as FAp. The structure of β -TCP is different, having five symmetrically different cation sites, not two as in FAp (see figure 1.4). There is also a greater range of site size; Yashima *et al.* [119] suggest a sequence of site sizes based on differences in Ca-O bond length. The site size order is reported as: Ca(5) < Ca(1) < Ca(2) < Ca(4) < Ca(3) [119]. The Ca sites have a greater range of coordination states in the β -TCP structure (table 1.3). Generally the coordination state increases with site size, with the exception of the Ca(4) site, which has the lowest coordination number (i.e. 3) but is the second largest site. The small coordination combined with the large Ca(4)-O bond distance indicates that this site is very different from all the other sites. As discussed previously, in section 1.5, this site is described as half occupied [119, 211] and the Low Energy Configuration (LEC) determined in section 3.4.2 is utilised here.

4.2 Method

Structures of both β -TCP and FAp were simulated using classical pair potential methods and the defect energies were calculated using the Mott-Littleton methodology (described in section 2.7). A range of phosphate structures have been simulated at the dilute limit with both isovalent and trivalent cations. For both the FAp and β -TCP, cations are substituted onto each symmetrically different cation site, to allow identification of the lowest energy site. Solution energies are calculated using expressions 4.1 and 4.5 and lattice energies associated with the defect oxides given in tables 4.1 and 4.7.

Partitioning of a range of divalent and trivalent species between β -TCP and FAp will be predicted by comparing solution energies for the relevant substitution processes, as described later by equation 4.2. This is intended to lead to commensurate improvements in the understanding of the defect properties over these two structures and the likely distribution of defect species across composite materials fabricated from these phases.

4.3 Divalent Substitution

For defect cation species that are divalent, the substitution mechanism by which the defect can be incorporated into the lattice proceeds via expression 4.1, since the host cations are also divalent.

$$AO + Ca^{X}_{Ca(x)} \rightarrow A^{X}_{Ca(x)} + CaO$$
 (4.1)

4.3.1 Divalent Substitution into β -Tricalcium Phosphate

The five symmetrically different cation sites in β -TCP give rise to different isolated substitutional defect energies as shown in figure 4.2. These values represent removing one lattice cation and replacing it with a defect ion, as per expression 4.1.



Figure 4.2: Defect energies of isovalent cations in β -TCP.

First considering the defect energies for substitution into β -TCP, figure 4.2 indicates that for defects with atomic radii smaller than the lattice host ion (such as Mg, Mn and Fe), the Ca(5) site is preferred and the largest site (Ca(3)), is least preferred. The defect energies for this substitution process are displayed in table 4.3. This corresponds with the size of the Ca(1)

site, which is the smallest of all the β -TCP sites. Using the defect energies acquired, solution energies for the reaction can then be calculated using expression 4.1. The lattice energies for the oxides denoted 'AO' in expression 4.1 are given in table 4.1.

Table 4.1: Lattice energies for various oxides with a divalent cation to use in calculation of solution energies.

Oxide	Lattice energy (eV)
CaO	-141.86
MgO	-163.34
ZnO	-157.37
MnO	-152.50
FeO	-158.48
SrO	-132.10
BaO	-124.93



Figure 4.3: Solution energies of isovalent cations in β -TCP calculated via expression 4.1.

Figure 4.3 shows the solution energies for divalent cation substitution into β -TCP. These results follow the same trend as established using only defect energies; the species with atomic radii smaller than that of Ca²⁺ prefer to occupy the smaller Ca(5) site. Conversely, species with a radius larger than that of the host cation, Ca²⁺ (1.00 Å), have a preference for the Ca(4) and Ca(3) sites. This can be correlated to the site size order described by Yashima *et al.* [119].

This indicates that site preference in β -TCP is strongly correlated to the size of the cation sites as previously described. Furthermore, as the size of the defect species changes from that of the Ca²⁺ host cation, so does the difference in site preference energy; the preference becomes more apparent as the spread of solution energies between sites increases. The site preference for these divalent cations can be compared to results obtained in various experimental studies, and summarised in table 4.2. This table indicates a good correlation between experimental results available and those from the simulations described here.

Table 4.2: Comparison of predicted and experimentally determined preference for divalent cations in β -TCP at low concentrations.

Cation	Site preference		Reference	Experimental technique
	Predicted	Experimental	(experimental data)	
Mg	Ca(5)	Ca(5)	Bigi et al. [234, 235]	XRD/IR absorption
Mn	Ca(5)	Ca(5)	Mayer et al. [236]	XRD/EPR spectroscopy
Fe	Ca(5)	-	-	
Sr	Ca(3)/Ca(4)	Ca(4)	Kannan et al. [237]	XRD/Rietveld refinement
Ba	Ca(4)	-	-	

4.3.2 Divalent Substitution into Fluorapatite

FAp offers two substitutional lattice sites, Ca(1) and Ca(2) as discussed in section 1.4. The defect energies displayed in figure 4.4 and table 4.3, suggest that atoms with smaller atomic radii prefer to occupy the Ca(1) site, which is larger in volume than the Ca(2) site [106, 110] and *vice versa*. Thus, given the relative sizes of defect species compared to the lattice site, this is an unexpected and counter-intuitive result which indicates that site preference does not depend solely on the atomic radius of the defect species.

This is a consequence of how the lattice reacts to defects of different sizes, through changes to the metaprism location and twist present in apatites. Figure 4.5 shows how the metaprism geometry changes with change in angle (ϕ). Here the angle between the metaprisms change as defects are introduced into the perfect structure.

Figure 4.6, shows the change in the metaprism twist angle when divalent defects are substituted



Figure 4.4: Defect energies to substitute in a cation and remove one to infinity, for divalent cations in FAp.

Table 4.3: Defect energies (in eV), to substitute a divalent cation into FAp and β -TCP for all available cation sites. Radii data taken from Shannon [238].

Atomic radius	Defect species	FAp		β-ΤСΡ				
(Å)		Ca(1)	Ca(2)	Ca(1)	Ca(2)	Ca(3)	Ca(4)	Ca(5)
0.72	Mg ²⁺	-2.97	-2.59	-3.14	-2.95	-2.60	-3.10	-4.40
0.78	Fe ²⁺	-2.95	-2.60	-3.13	-2.91	-2.65	-3.01	-4.14
0.83	Mn ²⁺	-2.34	-2.03	-2.48	-2.28	-2.07	-2.29	-3.08
1.18	Sr ²⁺	1.77	1.62	1.87	1.68	1.52	1.50	2.30
1.35	Ba ²⁺	4.23	3.75	4.43	3.95	3.54	3.11	5.37

onto both the Ca(1) and Ca(2) sites in FAp. For substitutional species on the Ca(1) site, there is a reduction in the metaprism twist angle for species that have an atomic radius less than the host Ca²⁺ ion. In turn, this results in a reduction of the Ca(1)-O bond length and consequently the volume of the site itself. Thus, the interaction of the lattice with the smaller dopant cation is maximised efficiently. Figure 4.6 indicates that the accommodation of small dopants into the Ca(2) site, results in little change of the twist angle, therefore not altering the site volume, leading to less favourable substitution on this site, as shown by figure 4.4.


Figure 4.5: Polyhedral drawings of FAp emphasising the A(1) metaprism twist angle ϕ . The metaprism is shown in blue and example angles of twist are also shown. As the cation size increases in the Ca(1) site ϕ also increases.

For defects with atomic radii above Ca^{2+} there is an increase in twist angle, associated with the Ca(1) site, which increases the site volume. However, the Ca(2) site is in close proximity to the rather open fluorine channel which allows defects substituting at the Ca(2) site with atomic radii greater than 1.00 Å (the Ca^{2+} radius), on this site to distort into the open space. Another crucial point is that the Ca(2) polyhedra are staggered down the channel in a 'zig-zag' manner that better accommodates any volume increase, while the Ca(1) polyhedra are directly on top of each other and are less able to expand as efficiently in the *c*-axis direction.

Table 4.4: A comparison of predicted and experimentally determined preference for divalent cations in FAp, which is considered to be at the dilute limit.

Defect cation	Site preference		Reference
	Predicted	Experimental	
Mg	Ca(1)	-	-
Mn	Ca(1)	Ca(1)	Hughes et al. [239] and Suitch et al. [99]
Fe	Ca(1)	Ca(1)	Khudolozhkin [240]
Sr	Ca(2)	Both	Hughes et al. [239]
Ba	Ca(2)	-	-

For FAp the solution energies can also be calculated from the results displayed in figure 4.4.



Figure 4.6: Metaprism twist angles (θ) for divalent species in FAp, for substitution on both Ca(1) and Ca(2) sites.

These are shown in figure 4.7, which display equivalent results to figure 4.4, where for smaller species the Ca(1) site is preferred and the Ca(2) site is preferred for larger cations. As with the results for β -TCP, defects with radii that are increasingly dissimilar from that of the host lattice atom have larger solution energy differences between sites. As such, the preference for cations to occupy specific lattice sites become more marked. Again, the cation site preferences indicated by these simulations can be compared to experimental data as outlined by table 4.4.

4.3.3 Partitioning of Divalent Defects Across Fluorapatite and β -Tricalcium Phosphate.

The partitioning of divalent species in β -TCP and FAp can now be predicted. These partition energies can be calculated using expression 4.2, so that positive values indicate a preference for the β -TCP structure.

$$E_{\text{partitioning energy}} = E_{\text{solution energy } (FAp)} - E_{\text{solution energy } (\beta TCP)}$$
(4.2)

The results obtained from the partitioning energies are interesting; figure 4.8 shows all divalent defects substituted into both structures preferentially segregate to β -TCP. Furthermore, as the absolute difference between the atomic radii of Ca²⁺ and the substituting species decreases, the



Figure 4.7: Solution energies of isovalent cations in FAp via expression 4.1.



Figure 4.8: Partition energies for isovalent cations showing the absolute difference between the most favourable solution energies in β -TCP and FAp. In all cases there is a preference for solution into β -TCP.

partition energy decreases linearly, indicating that those defects with an atomic radius similar to Ca²⁺ will have no particular preference for either structure. The slopes of energy change, however, are quite different for species larger and those smaller than the original host lattice cation; a consequence of defect accommodation on different sites of β -TCP. A contributing

factor to the increase in structure preference as a function of dopant radius is afforded by the higher elastic constants and bulk modulus of FAp compared to β -TCP [77], seen in tables 2.1 and 2.2. Thus, since FAp has a stiffer lattice than β -TCP, strain induced by accommodation of defects has a greater energy penalty in FAp than in β -TCP.

Another simple way to consider the effect of incorporating ions onto the lattice is to look at the volume change in the lattice when defects are incorporated. For isovalent substitution, where no change in charge compensating defects are formed, volume change is only associated with the dopant species and is known as the 'defect volume'. When a defect is introduced into a lattice there is an associated change to the lattice volume as the lattice relaxes to accommodate the defect. Catlow *et al.* [241], developed a method in which this change in volume, v, can be calculated using the Mott-Littleton methodology [184]. This can be described as follows;

$$v = K_T V_C \left(\frac{\delta f_v}{\delta V_C}\right)_T \tag{4.3}$$

where, K_T is the isothermal compressibility, V_C is the unit volume of the perfect lattice, T is temperature and f_v is the defect formation energy (calculated from a Mott-Littleton calculation). Thus, $\left(\frac{\delta f_v}{\delta V_C}\right)_T$ is the change in volume experienced by the lattice as a function of defect formation energy at a given temperature. The isothermal compressibility for a rhombohedral structure can be calculated from the elastic compliance matrix;

$$K_T = 2S_{11} + S_{33} + 2S_{12} + 4S_{23} \tag{4.4}$$

a full description of which is given by Golubev *et al.*, Grimes *et al.*, Murphy *et al.* [242–244]. A negative defect volume indicates that the lattice has shrunk and a positive defect volume suggests an expansion of the lattice to accommodate the defect.

Defect volumes for divalent species substituting into their lowest energy (preferred) sites in FAp and β -TCP are reported in table 4.5. Each value corresponds to the total change in lattice volume incurred by the incorporation of a substitutional defect. As expected there is a decrease in the lattice volume for incorporating defects with atomic radii smaller than the native Ca²⁺, an an increase for defects with larger atomic radii. The way to convert these values into changes in average lattice parameters has been discussed previously [241–243]. For example, if the concentration of dopant species per unit cell corresponds to one cation per unit cell, the volume of the unit cell is changed by the defect volume. Defect volumes are useful in establishing dopant loadings as the volume of a unit cell will change with respect to the defect volume until the dopant limit is reached, beyond which the rate of change will alter indicating that dopant

species are no longer able to be accommodated in the lattice, although this assumes minimal defect-defect interactions. For trivalent substitutions the defect volumes will not be calculated as this requires knowledge of cluster formation, which is not considered in this thesis, but which would make a very interesting further study, as discussed in the further work chapter, 8.

Table 4.5: Defect volumes associated with divalent dopants. In each case the dopant is assumed to occupy its most stable site in the appropriate lattice. Radii data taken from Shannon [238].

Dopant	Dopant radius (Å)	Defect volume (Å ³	
		FAp	β -TCP
Mg	0.72	-7.77	-9.05
Fe	0.78	-7.34	-7.57
Mn	0.83	-5.69	-5.11
Ca	1.00	-	-
Sr	1.18	5.42	1.12
Ba	1.35	10.43	3.60

4.4 Trivalent Substitution

The substitution of trivalent cations into the FAp and β -TCP lattices requires a charge compensating mechanism. In this study the charge compensation mechanism considered is described by expression 4.5. While it is possible that other reactions may take place forming compounds with 'B' and Ca ions, as a mechanism simply to compare solution and structure preference between FAp and β -TCP; expression 4.5 is acceptable because it is used consistently for all dopants.

$$3Ca_{Ca(x)}^{X} + B_2O_3 \rightarrow 2M_{Ca(x)}^{\bullet} + V_{Ca(x)}^{//} + 3CaO$$
 (4.5)

Unlike divalent substitution, for aliovalent substitution both the atomic radii and a Coulombic effect (due to the increase in ion charge) will govern the site preference.

4.4.1 Trivalent Substitution into β -Tricalcium Phosphate

Figure 4.9 describes the effect of substituting a trivalent cation into the β -TCP structure. The defect energies are also displayed in table 4.6. As indicated in expression 4.5, the charge compensating mechanism involves placing two trivalent cations in the system, and also one vacancy. All defects in this case were considered to be spatially isolated, and all were placed on the same type of site. This does not take into account any clustering or bonding, which will be discussed in chapter 8. The defect energies for ions with an atomic radius smaller than the native Ca²⁺ (1.00Å), initially show a preference for the Ca(5) site (for Al³⁺, Ga³⁺). This then changes to the Ca(1) site for the other defects with an atomic radius smaller than 1.00 Å. The preference changes again for species bigger than 1.00 Å, which again exhibit a preference for the Ca(5) site. As with previous examples, the solution energies for the defect substitution have also been calculated. Here, expression 4.5 is used along with the lattice energies for trivalent oxides (table 4.7) using a reactants minus products approach as discussed earlier in this chapter.

Table 4.6: Defe	ct energies (ir	1 eV), to sub:	stitute a trivale	ent cation into	FAp and β -TC	P for all available	e cation sites.
Radii data takei	n from Shanno	on [238].					

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Atomic radius	Species	FA	Ąр			β -TCP		
(Å)		Ca(1)	Ca(2)	Ca(1)	Ca(2)	Ca(3)	Ca(4)	Ca(5)
0.54	Al ³⁺	-29.06	-27.42	-29.25	-28.82	-28.04	-28.28	-30.49
0.62	Ga ³⁺	-27.52	-26.04	-27.74	-27.20	-26.56	-26.36	-28.29
0.87	Yb ³⁺	-22.87	-21.95	-22.91	-22.44	-22.45	-21.20	-22.91
0.89	Er ³⁺	-22.09	-21.37	-22.12	-21.69	-21.74	-20.51	-22.02
0.94	Gd^{3+}	-20.29	-19.82	-20.26	-19.93	-20.15	-18.84	-20.02
0.95	Eu ³⁺	-20.22	-19.76	-20.19	-19.86	-20.09	-18.77	-19.93
0.96	Sm ³⁺	-19.75	-19.34	-19.70	-19.40	-19.67	-18.38	-19.41
0.98	Nd ³⁺	-19.12	-18.78	-19.07	-18.81	-19.11	-17.87	-19.00
1.01	Ce ³⁺	-18.35	-18.15	-18.34	-18.09	-18.42	-17.26	-18.73
1.03	La ³⁺	-16.47	-16.73	-16.46	-16.32	-16.77	-15.75	-18.17

Considering the solution energies of divalent defects in β -TCP (figure 4.10), those species with an atomic radius of less than 0.9 Å exhibit a preference for the smaller Ca(5) site (which compares to the defect energies calculated), with the largest site, Ca(3), being the least preferable.



Figure 4.9: Defect energies for trivalent cations in β -TCP via expression 4.5.

Table 4.7: Lattice energies for oxides with a trivalent cation to use in the calculation of solution energies.

Oxide	Lattice energy (eV)
Al ₂ O ₃	-164.95
Ga ₂ O ₃	-161.57
Yb_2O_3	-138.67
Er ₂ O ₃	-137.45
Gd_2O_3	-134.69
Eu_2O_3	-134.16
Sm_2O_3	-133.46
Nd_2O_3	-131.99
Ce ₂ O ₃	-131.22
La ₂ O ₃	-129.05

For dopants with a radius above 0.9 Å, the site preference changes to the larger Ca(2) site. The effect is equivalent to the dopant site preferences of divalent defects (which have a site-size relationship), however, here the larger dopant preference is for the Ca(2) site rather than the Ca(3) or Ca(4), which are larger. Furthermore, divalent dopant undergoes a change in site preference at 1.0 Å, equivalent to the atomic radius of the host Ca^{2+} radius. However, for trivalent

dopants, which have an additional positive charge compared to the host ion, the switch occurs at a smaller radius, which can be attributed to the Coulombic effect. This results in a far greater attraction of the surrounding anions and therefore leads to smaller effective site sizes. This has been discussed previously for ceramics with the rock salt structure [244]. The preference for rare earth elements (REEs) (Pr to Er) to occupy larger sites (Ca(1), (2) or (3)) has also been postulated by Golubev and Lazoryak [242]. Calculating the solution energies for these defects gives a more comprehensive picture of site preference than simply considering defect energies by themselves.



Figure 4.10: Solution energies of trivalent cations in β -TCP via expression 4.5.

4.4.2 Trivalent Substitution into Fluorapatite

Considering the defect and solution energies in FAp, shown in figures 4.11 and 4.12, and detailed in table 4.6, there is a strong site preference for the Ca(1) site over all dopants investigated. For small dopants (with an atomic radius less than 0.9 Å) the site preference exhibited is the same as the divalent dopants. However, as the atomic radius of dopants increases above this value, the energy for site preference decreases monotonically, but site preference does not change over to Ca(2), except for La³⁺. Here, however, the difference in energy is small, so La³⁺ is likely to occupy either site. This behaviour is quite different to that for divalent dopants in FAp.



Figure 4.11: Defect energies for trivalent cations in FAp via expression 4.5.



Figure 4.12: Solution energies of trivalent cations in FAp via expression 4.5.

4.4.3 Partitioning of Trivalent Defects

The calculation of partition energies for trivalent dopants is achieved using expression 4.2. The site preferences between FAp and β -TCP obtained by this method are shown in figure



Figure 4.13: Partition energies for trivalent cation solutions showing the absolute difference between the most favourable solution energies in β -TCP and FAp.

4.13. Thus, it can be concluded that for defects with an atomic radius of less than 1.00 Å and greater than 0.85 Å (which amounts to the majority of the dopants considered here) the partition energies are small; suggesting that these defects will exhibit little preference for either phase. On the other hand those species on either side of this region, will preferentially partition into β -TCP given a biphasic material consisting of both β -TCP and FAp.

4.5 Conclusions

Understanding the likely partitioning of waste elements between the phases and the site accommodation within each phase is vital when considering a multi component waste form.

This study concludes that isovalent divalent dopant ions Mg, Fe, Mn, Sr and Ba exhibit a strong preference for β -TCP over FAp. Furthermore, site preference of dopant ions in β -TCP is a strong function of atomic radius, with small cations occupying the smaller sites and larger dopant cations the larger sites. However, in FAp other factors than the atomic radius influences site selectivity, in particular, the induced changes to the metaprism twist angle [96] (see figure 4.5).

Interestingly the rare earth trivalent ions (Er^{3+} to La^{3+}) have no appreciable preference for either phase although the smaller ions, Al^{3+} and Ga^{3+} , demonstrate a strong preference for partitioning into β -TCP. Additionally, in β -TCP the small dopant cations occupy the smaller sites and large cations occupy the larger sites; this preference is therefore independent of cation charge. In FAp all trivalent ions, irrespective of size show preference to occupy only the Ca(1) site, except for La³⁺, which shows no real preference for either site.

Considering the idea of a composite waste form once more, this study predicts that divalent cations will preferentially migrate to β -TCP from FAp, while the majority of trivalent cations show little phase preference, except for Al³⁺ and Ga³⁺, which have a significant partition energy to β -TCP. As such, a composite material will provide a more flexible waste form with different waste species exhibiting different phase preference in addition to different site preference. This work is currently being carried out experimentally by AWE and first indications suggest a good agreement with the work presented here. Parts of this work have been published in the following papers:

E.E. Jay, P.M. Mallinson, S.K. Fong, B.L. Metcalfe and R.W. Grimes, "Divalent cation diffusion in calcium fluorapatite", Journal of Materials Science, **46**, 7459-7465 (2011). [245]

E.E. Jay, M.J.D. Rushton and R.W. Grimes, "Migration of fluorine in fluorapatite - a concerted mechanism", Journal of Materials Chemistry, DOI:10.1039/C2JM16235K (2012).[246]

5

Migration of Species in Fluorapatite

Despite its importance in biomedical, agricultural and nuclear applications, fluorapatite (FAp) still remains relatively unexplored when it comes to the migration pathways of different species [87] through its lattice. Further understanding of transport phenomena would be beneficial to many disciplines. To gain a fuller understanding of the prevalent migration processes in FAp it is essential to investigate all possible migration pathways and assess those most likely to occur. As part of this overall aim, this chapter deals with the mechanisms underpinning transport of calcium and fluorine ions.

5.1 Divalent Cation Migration in Fluorapatite

In this section cation vacancy assisted pathways are considered and migration energy barriers are calculated using a Nudged Elastic Band (NEB) transition state search [187, 188], which is described fully in section 2.8. Here migration activation energies for a range of divalent cations, in addition to calcium, are compared.

Cation migration in FAp can occur via a number of different mechanisms, indeed González-Diaz *et al.* [247] concluded a continuous network of cation migration steps exist throughout the apatite lattice. To establish the nature of these pathways the migration of cations via a vacancy mediated migration [248] will be considered. Hughes *et al.* [110] concluded that no stable interstitial sites exist that can accept a calcium or similar sized cation, because all such sites are less than 2.2 Å from an O^{2-} ion and a local minimum is unlikely. As a result, they suggested diffusion must be influenced by vacancies or structural defects, as cation movement via interstitial sites is not viable in FAp [110, 239].

5.1.1 Migration Mechanism

The hypothesis presented by Hughes *et al.* [110], that migration proceeds via a vacancy mediated mechanism for cation defects, rather than via an interstitial mechanism, has been investigated. In order to achieve this the Frenkel energy (see expression 5.1) is compared to the partial Schottky energy associated with removing one calcium and two fluorine ions (see equation 5.2). The energies for these defect processes calculated using the Mott-Littleton method [184] (section 2.7) were then normalised for the number of atoms and are 10.37 eV and 5.13 eV, for the Frenkel and Schottky formation respectively.

$$\operatorname{Ca}_{\operatorname{Ca}}^{\times} \to \operatorname{Ca}_{i}^{\bullet \bullet} + V_{\operatorname{Ca}}^{//}$$
(5.1)

$$Ca_{Ca}^{\times} + 2F_{F}^{\times} \rightarrow V_{Ca}^{//} + 2V_{F}^{\bullet} + CaF_{2}$$
(5.2)

Thus, the Schottky reaction has a much lower energy and would therefore be expected to be dominant, agreeing with the hypothesis of Hughes *et al.* [105]. So, under intrinsic defect conditions, it is likely that the concentration of calcium vacancies will be orders of magnitude grea-

ter than the concentration of calcium interstitials and so vacancy migration mechanisms offer a greater population of defects to mediate calcium migration. To quantify this, the concentration of extrinsic calcium interstitials and vacancies can be calculated using equations 5.1 and 5.2 at 1000 K as follows;

For the Schottky reaction:

$$Ca_{Ca}^{\times} + 2F_{F}^{\times} \rightarrow V_{Ca}^{//} + 2V_{F}^{\bullet} + CaF_{2} = 5.13 \text{ eV}$$

$$\left[V_{Ca}^{//}\right] \left[V_{F}^{\bullet}\right]^{2} = e^{\frac{-5.13}{kT}}$$
(5.3)

Given electroneutrality:

$$\begin{bmatrix} V_{Ca}^{/\prime} \end{bmatrix} = 2 \begin{bmatrix} V_{F}^{\bullet} \end{bmatrix}$$
(5.4)

Thus, substituting equation 5.3 into 5.4:

$$\frac{1}{4} \left[V_{Ca}^{//} \right]^2 \begin{bmatrix} //\\Ca \end{bmatrix} = \frac{1}{4} \left[V_{Ca}^{//} \right]^3 = e^{\frac{-5.13}{kT}} \\ \left[V_{Ca}^{//} \right] = 4e^{\frac{-5.13}{3kT}}$$
(5.5)

For the Frenkel reaction:

$$Ca_{Ca}^{\times} \rightarrow Ca_{i}^{\bullet\bullet} + V_{Ca}^{//} = 10.37 \text{ eV}$$

$$\left[V_{Ca}^{//}\right] \left[Ca_{i}^{\bullet\bullet}\right] = e^{\frac{-10.37}{kT}}$$
(5.6)

Again, substituting equation 5.5 into 5.6:

$$\begin{bmatrix} Ca_i^{\bullet\bullet} \end{bmatrix} = \frac{e^{\frac{-10.5/}{kT}}}{4e^{\frac{-5.13}{3kT}}}$$
Using T=1000 K

$$\begin{bmatrix} Ca_i^{\bullet\bullet} \end{bmatrix} = 5.65 \times 10^{-45}$$
(5.7)
Substituting for $\begin{bmatrix} Ca_i^{\bullet\bullet} \end{bmatrix}$, equation 5.6 into 5.7:

$$\begin{bmatrix} V_{Ca}^{//} \end{bmatrix} = 9.63 \times 10^{-9}$$

From this the concentration of calcium interstitials is 5.65×10^{-45} while the concentration of calcium vacancies is, 9.63×10^{-9} ; the Schottky reaction (which requires vacancies) is entirely dominant.

While this conclusion is certainly consistent with the vacancy dominated migration suggested by Hughes *et al.* [105], extrinsic doping could result in a greater concentration of interstitial calcium. However, that would require either substitution of F^- or A^+ onto the Ca site. In the absence of these extrinsic defects, and given the higher concentration of vacancies, migration via vacancies will be the dominant process unless the vacancy activation energy is prohibitively high. Therefore, following the previous hypothesis [110], this section will only consider migration of cations via vacancy mechanisms. In all vacancy migration pathways the movement of the vacancy is in opposition to the movement of the X^{2+} ions (where X is any of the divalent cations investigated).

5.1.2 Calcium Vacancy Migration

There are a number of different migration pathways for Ca^{2+} cation transport within the FAp lattice. These can be categorized into five groups; the first involves only Ca(1) sites, the second uses only Ca(2) sites and the remaining three use a combination of Ca(1) and Ca(2) sites. For each migration process a contiguous pathway across an entire unit cell has been identified and these are highlighted in figures 5.1-5.9. In some cases migration across the cell occurs via a sequence of identical hops, but in others the pathway is via non-identical hops. The activation energy for a migration pathway corresponds to the greatest energy profile; the rate limiting barrier to migration.

First consider the migration of Ca^{2+} cations via a $V_{Ca(1)}$, down the *c*-axis utilising four identical sites to give a $Ca(1) \rightarrow Ca(1) \rightarrow Ca(1) \rightarrow Ca(1)$ pathway across the apatite unit cell. A schematic of this migration pathway is shown in figure 5.1.

A plot of the migration pathway energy as a function of the reaction coordinate is presented in figure 5.2. The current pathway is directly down the *c*-axis with no component in either the *a*-axis or *b*-axis. The migration mechanism shown in figure 5.1 describes minima only on Ca(1) sites and no local minima at interstitial sites. The migration passes through four identical Ca(1) sites with two symmetrically different arrangements of the PO₄ groups surrounding the migration pathway. This generates two different energy profiles for the migration between the Ca(1) sites. One has a migration energy of 1.0 eV and the other has a slightly higher barrier of 1.42 eV. The activation energy of the whole migration therefore, is 1.42 eV, since this is the largest barrier to migration via Ca(1) sites.

The next migration pathway considered involves only the Ca(2) sub-lattice, a schematic of which can be seen in figure 5.3. In FAp the Ca(2) sites form a hexagonal array and are lin-



Figure 5.1: Pathway 1: Schematic representations of calcium migration down the *c*-axis, via $Ca(1) \rightarrow Ca(1) \rightarrow Ca(1) \rightarrow Ca(1)$. The migration pathway taken is outlined by the arrows.



Figure 5.2: Pathway 1: Graphical representations of calcium migration down the *c*-axis, via $Ca(1) \rightarrow Ca(1) \rightarrow Ca(1) \rightarrow Ca(1)$. Activation energies are shown for each hop. The starting point refers to the fully relaxed structure, before migration.

ked down the *c*-axis in a zig-zag pattern. Unlike the previous migration, the actual pathway veers off from a straight line and goes in towards the central anion channel and away from the phosphate backbone; a small displacement of the fluorine atom can also be observed as a result of the migrating calcium's proximity. Here, at each point along the pathway the coordination environment is similar and as such, the energy for each step is the same. The activation energy for the migration down Ca(2) sites in the *c*-axis as given by figure 5.4, is 1.1 eV.

The next three migration series all consist of a series of hops around and through the central anion channel (in the basal plane) involving an exchange of vacancies between the Ca(1) and Ca(2) sublattices in the following order: Ca(1) \rightarrow Ca(2) \rightarrow Ca(2) \rightarrow Ca(1). Given the number of calcium sites in FAp there are a number of different possibilities for this migration, many of which are symmetrically equivalent, allowing for three separate migration pathways of this type. The first path goes directly through the middle of the channel, (named pathway 3, see figure 5.5), one that passes at the edge of the channel (pathway 4, see figure 5.7) and one path that lies between these two (pathway 5, see figure 5.9).

Migration through the very centre of the channel, as shown in pathway 3 (figure 5.5), requires the migrating calcium to pass from a Ca(2) site on one side of the anion channel, to another symmetrically equivalent site on the other side of the channel. Transport directly between two of the fluorine ions in the channel gives rise to a large migration energy peak at this location, as the calcium passes by the highly polarised fluorine ions. This migration causes a shift in the position of the fluorine ions in the channel, away from the migrating calcium and a slight bend in the migration pathway. The energy along this pathway is shown in figure 5.6, where the barrier to migration can be seen to be 5.6 eV.

Pathway 4 is the next migration route of interest: this involves two adjacent Ca(2) sites around the central of the fluorine channel, see figure 5.7. Figure 5.8 indicates the energy given by this pathway that reveals an interesting feature, the two local minimum either side of a central maximum. The minimum energy pathway for the Ca(2)-Ca(2) hop deviates slightly towards the centre of the anion channel away from the phosphate groups. Figure 5.7 indicates a central maxima at "B" but different energy profiles for the "A" and "C" points in the diagram. This is attributable to the differences in the positions and rotation of the phosphate groups relative to the two Ca(1)-Ca(2) paths. The activation energy for this interim pathway (pathway number 4) is 1.7 eV.



Figure 5.3: Pathway 2: Schematic representations of calcium migration down the *c*-axis, via $Ca(2) \rightarrow Ca(2) \rightarrow Ca(2) \rightarrow Ca(2)$. The migration pathway taken is outlined by the arrows.



Figure 5.4: Pathway 2: Graphical representations of calcium migration down the *c*-axis, via $Ca(2) \rightarrow Ca(2) \rightarrow Ca(2) \rightarrow Ca(2)$. Activation energies are shown for each hop. The starting point refers to the fully relaxed structure, before migration.



Figure 5.5: Pathway 3: Schematic representation of calcium migration via the centre anion channel, via Ca(1) \rightarrow Ca(2) \rightarrow Ca(2) \rightarrow Ca(1). The migration pathway taken is outlined by the arrows.



Figure 5.6: Pathway 3: Graphical representation of calcium migration via the centre of the anion channel, via $Ca(1) \rightarrow Ca(2) \rightarrow Ca(2) \rightarrow Ca(1)$. Activation energies for each hop. The starting point refers to the fully relaxed structure, before migration.



Figure 5.7: Pathway 4: Schematic representations of calcium migration via the side of the anion channel, via Ca(1) \rightarrow Ca(2) \rightarrow Ca(2) \rightarrow Ca(2). The migration pathway taken is outlined by the arrows.



Figure 5.8: Pathway 4: Graphical representation of calcium migration via the side of the anion channel, via Ca(1) \rightarrow Ca(2) \rightarrow Ca(2) \rightarrow Ca(2). Activation energies are shown for each hop. The starting point refers to the fully relaxed structure, before migration.

The final migration process is pathway 5, which shows that the calcium ion partly cuts the fluorine channel, in between the central anions and the bounding outer calcium ions; a schematic of this is shown in figure 5.9. As expected, the activation energy for this pathway is highest when the calcium ion passes close to the fluorine ion in the lattice. As discussed for pathway 3, the migrating calcium ion shifts slightly from a straight pathway (away from the *c*-axis fluorines), at the same time the fluorine ions shift in the opposite direction to accommodate the cation motion. Figure 5.10 displays the energy profile for migration at each stage. The activation energy for this pathway is 2.9 eV.

A comparison of all migration energy barriers for calcium ions is given in table 5.1. Interestingly this identifies those pathways that occur parallel to the *c*-axis as having the lowest barrier to migration. This preference for *c*-axis migration has previously been reported for F^- [110, 239, 249]. Although previous work agrees with the directionality of F^- migration as *c*-axis, the nature of the pathway is contentious as discussed in section 5.2. The lowest migration path for transport in the *ab* plane is via pathway 4, which passes around the outside of the fluorine channel. However, this energy is significantly larger than those processes that operate in the *c*-axis (pathways 1 and 2), so that these migration processes are less preferable. This leads to distinct transport anisotropy for migration in FAp with transport along the *c*-axis dominating.

5.1.3 Transport of Dopant Species

Transport of a range of different dopant species in FAp is also an important consideration for both nuclear waste hosts and for many biomaterial applications. As a result, the migration of other divalent cations, namely Sr^{2+} , Zn^{2+} , Mg^{2+} and Ba^{2+} ions, has been considered. Migration of each species is based on the same five migration paths as those identified for the calcium ions, and numbered 1-5 in the same manner.

Table 5.1: Activation energies for cation migrations in FAp

Migration pathway	Schematic figure	Activation energy (eV)
$Ca(1) \rightarrow Ca(1) \rightarrow Ca(1) \rightarrow Ca(1)$	Figure 5.1	1.42
$Ca(2) \rightarrow Ca(2) \rightarrow Ca(2) \rightarrow Ca(2)$	Figure 5.3	1.10
$Ca(1) \rightarrow Ca(2) \rightarrow Ca(2) \rightarrow Ca(1)$	Figure 5.5	5.60
$Ca(1) \rightarrow Ca(2) \rightarrow Ca(2) \rightarrow Ca(1)$	Figure 5.7	1.70
$Ca(1) \rightarrow Ca(2) \rightarrow Ca(2) \rightarrow Ca(1)$	Figure 5.9	2.90



Figure 5.9: Pathway 5: Schematic representation of calcium migration in-between the *c*-axis fluorine ions and the outside of the anion channel, via $Ca(1) \rightarrow Ca(2) \rightarrow Ca(2) \rightarrow Ca(1)$. The migration pathway taken is outlined by the arrows.



Figure 5.10: Pathway 5: Graphical representation of calcium migration in-between the line of central fluorine atoms and the outside of the anion channel, via $Ca(1) \rightarrow Ca(2) \rightarrow Ca(2) \rightarrow Ca(1)$. Activation energies are shown for each hop. The starting point refers to the fully relaxed structure, before migration.

Figure 5.11 reveals that each of the cations chosen exhibits a similar response to migration in the FAp lattice. Each migration pathway also follows the same relative spread of energies exhibited by calcium ions (as summarised in table 5.1).

In accordance with the transport of Ca^{2+} ions, the lower energy pathways are parallel to the *c*-axis; pathways 1 and 2. Thus, migration via Ca(2) sites or migration via Ca(1) sites is dominant, these being only slightly different to each other. Transport in the *ab* plane is lowest in energy via pathway 4, however, this energy is sufficiently higher than those processes that operate in the *c*-axis that it leads to distinct transport anisotropy.

Considering the changes to the barrier for migration as a function of cation size, there is only a small increase in migration activation energy as atomic radius increases for pathways 1, 2, 4 and 5. Significantly, the differences in activation energy hardly change, maintaining anisotropy. Pathway 3 changes the most with atomic radii; this can be attributed to the proximity of the fluorine ions during the migration.



Figure 5.11: Graph to show maximum activation energy of various dopant cations for the five different pathways discussed above, labelled 1-5.

5.1.4 Conclusions

This part of the work presents a number of useful conclusions. For Ca²⁺ transport in FAp, the lowest barriers to migration occur for those pathways (1 and 2) that lie parallel to the *c*-axis pathways, where the activation energies are 1.4 eV and 1.1 eV respectively. The three pathways (3-5) that occur in the *ab* plane, have migration energies ranging from 1.7 eV to 5.6 eV. The migration energies for pathways 3-5 are significantly higher in energy than pathways 1 and 2, leading to considerable anisotropy in Ca²⁺ ion transport, which has a significant preference for migration parallel to the *c*-axis. This preference for *c*-axis migration has previously been reported for F⁻ [110, 239], so it is interesting to find that the same trends occur for calcium.

The transport mechanisms for a range of divalent cations yielded similar results to those for Ca^{2+} . The relative activation energies were also similar regardless of the cation considered. This suggests that all divalent cation loss from FAp will occur preferentially parallel to the *c*-axis. Clearly, this has implications for the design of any waste host based on FAp and those materials used to surround it. Interestingly the morphology of FAp crystallites is often reported as having a high *ca* ratio (that is the crystallites are long and thin) [106]. This would be beneficial with regard to inhibiting the transport of divalent cations, which would have to travel through more material in the *c*-axis to reach the edge of the crystal than in the *ab* directions, limiting the overall loss of cations in the *c*-axis. The crystal morphology will be considered further in chapter 7.

5.2 Fluorine Migration in Fluorapatite

As discussed previously, understanding the mechanisms controlling both the divalent cation migration and fluorine ion migration in FAp is important. Section 5.1 described the migration of calcium and a range of divalent cations within the lattice and concluded that there is a preference for migration in the *c*-axis direction, via Ca(2) sites. In this section, the migration mechanism of fluorine ions within the FAp lattice will be discussed.

Apatites, one of the most abundant group of minerals on earth [250], are also found to be present in many biological tissues, in particular the mineral component of human hard tissues such as bones and teeth. FAp is therefore used in bio-medical applications, such as bone replacements and coatings for prostheses [251, 252]. A better understanding of fluorine migration into and out of FAp would therefore be of considerable interest. For example, acidic conditions within the mouth can lead to chemical attack on teeth and the formation of undesirable caries. Fluoride is known to significantly increase resistance to the formation of caries and subsequent tooth decay [253–255]. Furthermore, as formerly discussed in chapter 2, apatites can accommodate species (such as halides) that cause problems for nuclear waste hosts [230] that are currently employed. In both applications it would, therefore, be useful to predict the rate of migration of F^- ions within FAp and the mechanism by which this takes place [256].

Given the crystal structure of FAp, it is natural to assume migration of F⁻ ions occurs along the *c*-axis. Indeed, Tse *et al.* [249] suggested "the mechanism of ionic motion is probably an interchange of ions with vacancies", directly down the *c*-axis. However, as discussed in section 1.4.1, other anions such as OH⁻, Cl⁻, or F⁻ can fill other positions within the channel. F⁻, the smallest of these species, can fit into the triangle created by the Ca(2) sites forming the channel; larger anion species occupy other sites in the channel as depicted in figure 1.16. In this figure, the crosses marked 'F[•]_i' denotes three symmetry related interstitial sites, that can be temporarily occupied by F⁻ [84], though only one at a time.

Interestingly, Royce *et al.* [253], Tse *et al.* [249] and Welch *et al.* [254] concluded that the lowest activation energy for migration of any species in FAp is for F^- ions in the *c*-axis, which was calculated using a Born model of the crystal and correlated random walk statistics. However, a full description of F^- ion migration (including the possibility of an interstitial mechanism) has not been described in the literature, even by Tse *et al.* [249] and Welch *et al.*

[254].

Here the migration mechanisms for F^- in the FAp lattice will be investigated to identify the lowest energy, rate limiting step for migration. To achieve this, Molecular Dynamics (MD) simulations using the DL_POLY [141] code (over a range of temperatures) and static simulations using the GULP [140] code will be described. Utilising both methodologies together will help to establish both isolated defect energies and activation energies.

5.2.1 Molecular Dynamics

For the MD simulations presented in this section, the initial equilibration period was performed using an NVT ensemble using the Berendsen thermostat [196]. Subsequently, after equilibration, calculations using the NPT Nosé-Hoover [193, 195] thermostat and barostat were carried out. Using this regime, true thermodynamic ensemble members could be sampled during data collection.

To examine the effect of temperature on migration, simulation temperatures in the range of 300 K to 1500 K at 200 K intervals were considered. Prior to each data collection run, the system was equilibrated for 20 ps (or ten thousand timesteps) to bring the system to temperature and to allow the system volume to relax. This was followed by another 20 ps of dynamics during which atomic positions were sampled every 100 fs. The simulations were performed using a $20 \times 20 \times 20$ supercell containing 350,000 atoms.

Alongside the MD simulations, static calculations using the GULP code [140] were performed to calculate energies associated with defects and specific migration pathways, using the Mott-Littleton methodology [184]; see section 2.7. Finally, to investigate specific migration pathways a NEB method [187, 188] was used, as described in section 2.8.

5.2.2 The Isolated Defect Model: Using Static Approximations

 F^- ion migration in FAp has been previously described as a vacancy mediated migration mechanism that proceeds directly down the *c*-axis channel [249, 254]. For this process to occur classical diffusion theory first requires the formation of vacancy defects through a disorder process [230]. Thus, the energy for Frenkel pair formation was calculated, using the Mott-Littleton methodology [184], with the defects at the dilute limit. This defect process can be described using Kroger-Vink [136] notation, as follows:

$$F_F^{\times} \rightarrow V_F^{\bullet} + F_i^{/}$$

$$\Delta H_{Fre} = 4.177 \text{ eV} + (-1.654) \text{ eV}$$

$$= 2.52 \text{ eV}$$
(5.8)

where F_F^{\times} is a F⁻ ion on a fluorine site, V_F^{\bullet} is a fluorine vacancy and $F_i^{/}$ is a F⁻ interstitial.

Defect energies for V_F^{\bullet} and F_i^{\prime} were calculated to be 4.17 eV and -1.65 eV respectively (using the Mott-Littleton methodology, see section 2.7). Thus, the total energy for Frenkel pair formation (ΔH_{Fre}) in FAp is 2.52 eV, as described in equation 5.8. Applying the law of mass action [257] to equation 5.8 yields the expression;

$$[V_F^\bullet][F_i'] = e^{\frac{-\Delta H_{Fre}}{kT}}$$
(5.9)

In an intrinsic material, electroneutrality will require that the concentration of fluorine vacancies $[V_F^{\bullet}]$ is equal to the concentration of fluorine interstitials $[F_i^{\prime}]$. It follows that,

$$[V_F^{\bullet}] = e^{\frac{-\Delta H_{Fre}}{2kT}} \tag{5.10}$$

where T is temperature in Kelvin and k is Boltzmann's constant (8.617⁻⁵ eV K⁻¹).

Using the concept of F^- ion migration via a vacancy method (as suggested by Tse *et al.* [249]), the NEB methodology [187] was used to identify an activation energy for vacancy migration (ΔH_{act}) of 0.90 eV, as seen in figure 5.12 and shown in the FAp lattice in figure 5.13. The diffusion coefficient (D) is the product of the concentration related formation term and the activation energy so that,

$$D = D_o \ e^{-\frac{\Delta H_{acl} + \frac{\Delta H_{Fre}}{kT}}{kT}}$$
$$D = D_o \ e^{-\frac{0.90 + \frac{2.52}{kT}}{kT}}$$
$$= D_o \ e^{-\frac{2.16}{kT}}$$
(5.11)

where D_o is the maximum diffusion coefficient at infinite temperature. The value of 2.16 eV assumes a dilute concentration of defects. Thus, considering F⁻ ion migration using a static approach, the energy sum for Frenkel pair formation and migration is equal to 2.16 eV. This value can then be compared to any values obtained for F^- ion migration using MD.



Figure 5.12: Calcium migration down the *c*-axis via a vacancy mechanism. Activation energies are shown for each hop. The starting point refers to the fully relaxed structure, before migration.



Figure 5.13: Fluorine migration down the *c*-axis, via $F \rightarrow F \rightarrow F \rightarrow F$. The migration pathway taken is outlined by the arrows and the figure shows the vacancy (as a box) initially at the second site as an example.

5.2.3 The Molecular Dynamics Model

Results from the MD simulations offer a different approach to that described previously. In particular, starting the simulation with an assumed migration mechanism is unnecessary as the mechanism will become apparent through the simulation, if it occurs on the MD timescale. Simulations at temperatures below 1100 K, over a 20 ps time period show that F^- ions only moved over distances comparable with atomic vibrations. As such, F^- transport at temperatures below 1100 K are not accessible to these simulations. For each calculation the mean squared displacement (MSD or $< r^2 >$) for F^- ions was determined and plotted against time, using:

$$\langle r^2 \rangle = 6Dt + c \tag{5.12}$$

where, D is the diffusion coefficient, c is a constant and t is time. Thus, the diffusion coefficient can be determined at each simulation temperature (T). The general equation for the diffusion coefficient is:

$$D = D_o \exp\left(\frac{-Q_d}{kT}\right) \tag{5.13}$$

where k is Boltzmann's constant and Q_d is the sum of both activation energy and defect formation energy.

The Frenkel pairs [139] required for F^- ion migration are an intrinsic defect within the system. However, due to the short simulation times accessible by MD simulations (20 ps) it is a concern that the formation of these Frenkel pairs might not have reached equilibrium within this time. To ensure that during the course of the equilibration time Frenkel pairs are formed appropriately, two types of system were considered. The first is a perfect system and the second is one seeded with a concentration of Frenkel pairs above that expected at equilibrium. Both of these systems were equilibrated as discussed previously and the MSD for F^- ions was determined and then compared. Figure 5.14, which presents the natural log of the calculated F^- ion diffusivity as a function of inverse temperature, shows that both methods provide the same result. This, indicates that the timescales used for equilibration of these simulations is sufficient to realise the formation intrinsic defects.

$$D = D_o \exp\left(\frac{-Q_d}{RT}\right) \tag{5.14}$$

$$\ln(D) = D_o - \frac{Q_d}{RT}$$
(5.15)

Rearranging equation 5.14 as shown in equation 5.15 and using the gradient from the MSD plot (figure 5.14) the value of Q_d , which predicts the diffusion activation energy and Frenkel

pair formation, has a value of 0.55 eV. This contrasts with the value of 2.16 eV (for the same process) calculated by the static NEB and defect energy calculations, as discussed previously.

Activation energies obtained in this way include contributions due to both the migration activation energy and the energy required to introduce the defects into the lattice (Frenkel pair formation). Considering again the static simulations and equation 5.11, the value for Q_d is expected to be equal to 2.16 eV, if the vacancy mechanism proposed previously [249] was the operating migration method. This suggests that the vacancy mediated mechanism is not consistent with the one operating in the MD simulations. Analysing the MD results further as discussed in the following section, a different mechanism is proposed which explains why these two predictions are so different. (Unfortunately, replicating the mechanism identified by the MD simulations in a static calculation was not possible, since the MD gives rise to long range coupled PO₄ movements that are difficult to replicate using static methods, accounting for the difference in Q_d .



Figure 5.14: The calculated diffusivity of F^- ions as a function of temperature, from 1100-1500 K. Two sets of data are presented, one that started from a perfect lattice equilibrated to temperature and a second initially seeded with Frenkel pairs and then equilibrated to temperature.

5.2.4 Fluorine Migration in Molecular Dynamics

The transport mechanism generated by MD can be partly understood through a series of figures that show relative F^- ion density at different temperatures. Density plots (figures 5.15-5.17) show the position of all F^- ions at a given temperature, averaged over the 20 ps of the data collection period. Density plots were calculated by decomposing the simulated supercell into many unit cells, then calculating the local number density of F^- ions within each cell and then averaging the densities back into one unit cell forming a density plot. The individual unit cell densities from the whole system were averaged to produce a mean F^- ion density represented in a single FAp cell. Therefore, it is possible to calculate contour plots taken as slices across the unit cell to show the proportion of ions at a given position in terms of the inverse natural log of the density, ln(particles/Å³). Thus, the iso-surfaces (shown in green) suggest probable migration pathways (at a given temperature). The value of the iso-surface was chosen to be ln(-4.5) particles/Å³, which corresponds to a density of about 1.0×10^{-2} particles/Å³, which enabled identification of the migration pathway as it evolved with increasing temperature.

The absence of observable migration (at the timescales available in MD) at temperatures lower than 1100 K is clear in figure 5.15, which shows the migration of F^- ion density at 900 K. Both the iso-surface (shown in green) and the contour plots indicate that there is no contiguous pathway at this temperature (on the time scale accessible to present MD simulations): the F^- ions simply oscillate around their lattice sites with no migration between sites. In figures 5.15-5.17 the contour plots show the density of the F^- ions, with the highest density localised around the fluorine lattice sites (indicated by the lightest colour); the volume enclosed within the iso-surface indicates that at this temperature the F^- ions vibrated around their lattice sites.

Figure 5.16 shows the effect of F^- ion migration after increasing the temperature to 1100 K. It indicates that migration of F^- ions has started to occur. Considering the iso-surface, the volume explored by the F^- ions has extended from that shown in figure 5.15; in particular the F^- ions begin to occupy interstitial sites. The contour plots show a contiguous F^- ion density extending between neighbouring fluorine sites indicating that some F^- ions have hopped between crystal sites. The two iso-surfaces that bisect the *c*-axis in figure 5.16 are rotated around a mirror plane, which is defined by the location of the Ca(2) ions, which are distributed in triangular planes rotated on the mirror plane [96]. This pattern is visible throughout all the contour plots presented in this work.



Figure 5.15: This figure shows the overall iso-surface for F^- ions at 900 K, wrapped back from the supercell into a unit cell. Four contour plots of slices through the unit cell, as indicated as *bc*, *ac* and two *ab* planes, are also shown. The coloured crosses inside the unit cell represent the position of all other atoms within the FAp lattice, as seen more fully in figure 1.15.

Given the existence of stable interstitial sites (figure 1.16), it is not surprising that figure 5.16 shows the F^- ion migrating via the interstitial nodes and not straight down the *c*-axis. The migrating F^- ion maintains its proximity to Ca(2) sites that surround the anion channel. As mentioned previously, apatites can have other halide end-members, for example Cl⁻ and OH⁻, where their positions in the anion channel are not the same as F^- but are located away from the F^- site, as discussed by Rakovan *et al.* [106] and indicated in figure 1.16. Cl⁻ and OH⁻ are much larger ions than F^- and cannot occupy a site in the triangular plane of calcium ions, but sit at a position above the F^- site directly in line with the *c*-axis. Significantly the F^- ion does not occupy the Cl⁻ site during its migration in MD. A rationale for this is provided by the relative shortest inter-ionic separations associated with each of the possible intermediary sites; for the F^- site and the Cl⁻ site and fluorine interstitial site, these are 2.3 Å, 2.9 Å and 2.2 Å respectively (as shown in figure 1.16). Thus, the migration pathway goes through the smallest inter-ionic separation, which is the interstitial position, as this maximises the F^- and Ca²⁺ interactions.

The highest temperature illustrated is 1500 K (figure 5.17), which shows a more extensive migration pattern from that in figure 5.16. The ions now have considerably greater energy and can occupy a great proportion of the space within the channel. However, the contour plots show that the Cl^- position is still not significantly occupied, although the excluded area is diminished. The overall iso-surface has increased so that it occupies nearly the entire anion channel, thus giving rise to a larger migration pathway for F^- ions.

5.2.5 The Fluorine Migration Mechanism

While average density plots provide a time averaged picture of where F^- ions were found during the simulation, they do not explain the mechanism by which F^- ions moved through the crystal. This is demonstrated by investigating individual F^- ions. In this regard, transport of F^- ions always involved an F^- interstitial ion but not via a simple interstitial or interstitialcy mechanism.

Figure 5.18 shows an example of an F^- ion migration by following a sequence of timesteps over 10 ps of an MD simulation. The migration pathway shows movement of F^- ions down the anion channel via interstitial sites. The interstitial species have already been formed. The F^- ion (at the top of the migration pathway) is initially in an interstitial site, while the rest



Figure 5.16: This figure shows the overall iso-surface for all F^- ions at 1100 K, wrapped back from the supercell into a unit cell. Four contour plots of slices through the unit cell, as indicated as *bc*, *ac* and two *ab* planes, are also shown. The coloured crosses inside the unit cell represent the position of all other atoms within the FAp lattice, as seen more fully in figure 1.15.



Figure 5.17: This figure shows the overall iso-surface for all F^- ions at 1500 K, wrapped back from the supercell into a unit cell. Four contour plots of slices through the unit cell, as indicated as *bc*, *ac* and two *ab* planes, are also shown. The coloured crosses inside the unit cell represent the position of all other atoms within the FAp lattice, as seen more fully in figure 1.15.

of the F^- ions in the pathway occupy their lattice sites. The initial positions of all ions are shown as green spheres at t=0 ps. The colours shown in the pathway are indicative of time and subsequent spheres along the pathway of the same colour occur simultaneously. This explains the average result shown by the iso-surfaces (figures 5.15-5.17), that the migrating ions pass through interstitial sites. Crucially, however, a set of F^- ions move at the same time; their motion is coupled and thus, migration is occurring through a concerted mechanism. By the time the first interstitial ion nears its final position at a lattice site, the second ion in the sequence has already moved from its site, it has dwelt in an interstitial site and then moved down to the next lattice site. The final ion in the sequence depicted in figure 5.18 has also been displaced and now occupies an interstitial site. This process does not necessarily finish after two lattice ions have been displaced, as in figure 5.18; the sequence can be longer or shorter. Nevertheless, whatever the sequence length, the process results in the transport of F^- ions down the *c*-axis, since the beginning and ending configurations are equivalent.

While the sequence of interstitial to interstitial motion provides the low energy pathway for migration, it is also necessary to form the interstitial defects from the perfect lattice. The isolated Frenkel reaction described in section 5.2.2 is clearly too high an energy process to be consistent with the overall MD activation energy of 0.55 eV. An alternative mechanism, related to the interstitial to interstitial migration mechanism was observed in the MD simulations. This can be considered as a lattice fluorine to interstitial movement, which leaves behind a vacant fluorine lattice site. This process is illustrated in figure 5.19. In this case the initial green $F^$ ions at t=0 are all at their lattice sites. The process begins with one lattice F^- being displaced towards an interstitial site. Simultaneously other lattice F^- ions proceed to be displaced and a sequence of concerted events occur. This finishes with a vacant F^- lattice site at one end and an interstitial F^- at the other. This constitutes an interstitial F^- ion formation sequence. It is then possible that the sequence may reverse, annihilating the vacancy or, that the interstitial ion proceeds further via another sequence of events as described by figure 5.18, that is, a transport sequence. Finally, the MD simulations are consistent with no migration in the *ab* direction; migration occurs solely along the c-axis [78, 79, 239] highlighting the highly anisotropic nature of diffusion in this material.


Figure 5.18: A complete sequence of the coupled F^- interstitial migration process over 7.1 ps. The migration pathway in this example, is denoted by time, so all ions with the same colour occur at the same time. The initial and final position of the migrating interstitial F^- ion is given as a cross. The location of F lattice atoms are given as dotted circles. This image shows migration across the *a*-axis and *b*-axis as shown by a) and b) respectively. This system temperature was 1300 K.



Figure 5.19: Formation of a Frenkel pair in an anion channel; the initial positions of the migrating F^- ion are given as dotted black circles, the final interstitial position is denoted as a cross and the final vacancy position is labelled as a dotted square. The migration pathway, is coloured by time, so all ions with the same colour occur at the same time as indicated by the key.

5.2.6 Conclusions

This study has revealed a new quasi-one-dimensional concerted mechanism for F^- ion migration in FAp. The mechanism occurs with a sequence of F^- ions moving along the *c*-axis in a concerted mechanism, via lattice and interstitial sites. An initial F^- interstitial ion displaces and replaces a lattice F^- ion which may replace the next F^- lattice ion and so on until a $F^$ interstitial ion is left further down the *c*-axis between two lattice F^- ions. This contrasts markedly with the previous proposed mechanism that suggested a vacancy mediated process where the F^- ion moved straight down the *c*-axis channel [249, 254], although both mechanisms imply highly anisotropic F^- ion migration, the movement of F^- ions through the interstitial sites, which are not directly along the *c*-axis is related to maintaining the proximity of the migrating F^- ion and the surrounding Ca(2) ions. The formation of the required F^- interstitial species also proceeds via a sequential process which forms a relatively immobile fluorine vacancy and F^- interstitial pair. The total activation energy for migration identified via the MD simulations is 0.55 eV. This low value is consistent with fast F^- ion transport along the *c*-axis.

Although, transport of F^- ions is predicted to occur preferentially along the *c*-axis, crystallites

of FAp are long and thin and have a high *c*-axis aspect ratio, thus any migrating F^- ion must travel a long way down the channel before reaching a grain boundary. Furthermore, since the whole anion channel is involved in the migration process, any contraction or expansion of the channel due to impurities or other defects [96, 228] will affect the transport of F^- ions within the lattice and may increase or decrease the movement accordingly.

6

Radiation Damage of Fluorapatite and β -Tricalcium Phosphate

Molecular Dynamics (MD) simulations can help reveal properties and structural features that cannot be calculated with static energy calculations. This includes the effect of radiation damage on the structure, an important consideration for the purposes of designing a nuclear waste host [10]. This chapter aims to explore the effects of a range of damage cascades using different Primary Knock on Atom (PKA) energies and initial directions. In addition, amongst other characteristics, the effect of damage on PO₄ bond angles, the number and type of defects and PKA trajectory length, will be considered, as these are of significant interest to understanding the progress of radiation damage [258].

The results presented in this chapter are calculated using MD which is described in section

2.9. The potential sets used to represent both fluorapatite (FAp) and β -tricalcium phosphate (β -TCP) lattices are discussed in section 2.9.1. Here two-body potentials are used to represent P-O interactions (as discussed by Jones *et al.* [84]) and these are augmented by the Ziegler, Biersack and Littmark (ZBL) potentials at small inter-atomic separations. The potential parameters themselves and the regions in which the ZBL potentials act are reported in tables 2.11 and 2.12.

6.1 Thermal Expansion Coefficient

As suggested by Gale [259], calculating the Thermal Expansion Coefficient (TEC) [260] of structures modelled with pair potentials can give a good indication of the reliability of the potentials to represent the structure at various temperatures.

Thermal expansivity relates the change in temperature to the change in shape of the lattice. This will manifest itself as a change in total cell volume or in individual lattice parameters. The fractional change in volume per unit of temperature change is given in equation 6.1.

$$\alpha_L = \frac{1}{L_0} \left(\frac{\delta L}{\delta T} \right)_p \tag{6.1}$$

where α_L is the thermal expansion coefficient for a cubic system, *T* is the temperature, L_0 is the original length. All the derivatives are taken at constant pressure, *p*. It is possible, in a cubic system, to relate the volume of the structure to a change in length, as shown in equation 6.2.

$$\alpha_V = \frac{1}{V} \frac{\delta V}{\delta T} = \frac{1}{L_0^3} \frac{\delta L^3}{\delta T} = \frac{1}{L_0^3} \left(\frac{\delta L^3}{\delta L} \cdot \frac{\delta L}{\delta T} \right) = \frac{1}{L_0^3} \left(3L^2 \frac{\delta L}{\delta T} \right) = 3 \cdot \frac{1}{L_0} \frac{\delta L}{\delta T} = 3\alpha_L \tag{6.2}$$

However, both systems considered in this thesis are not cubic and so calculating the TEC must be carried out in a slightly different way as described by Lundström *et al.* [261]. In this, the total linear thermal expansion for a rhombohedral system (α_m) is calculated as shown in equation 6.3.

$$\alpha_m = \frac{(2\alpha_a + \alpha_c)}{3} \tag{6.3}$$

where α_a and α_c are the thermal expansion coefficients for the *a* and *c* parameters respectively which can be calculated from equation 6.1, by substituting in the appropriate parameters for '*L*'.

Figure 6.1 shows the changes in the lattice parameters with temperature. The $\frac{\delta L}{\delta T}$ parameter (from equation 6.1) can be obtained from the gradient of figure 6.1 and can be utilised in equation 6.1 and 6.3, to generate the thermal expansion coefficient, α_m .

$$\alpha_m = \frac{(2\alpha_a + \alpha_c)}{3}$$

$$= \frac{(2 \cdot 1.29141 \times 10^{-5} + 1.29140 \times 10^{-5})}{3}$$

$$= 1.29 \times 10^{-5} K^{-1}$$
(6.4)

Equation 6.4 gives the TEC for β -TCP as 1.29×10^{-5} K⁻¹, which is comparable to the experimentally derived value from Krajewski *et al.* [262] and Perdok *et al.* [263], shown in table 6.1. Therefore, the potential set derived for MD simulations, shown in table 2.11, appears to describe the materials' temperature response well and so will be utilised for MD simulations.

Phase	Thermal expansion coefficient (K^{-1})
α -TCP	6.00×10^{-5}
β -TCP	1.31×10^{-5}
Hydroxyapatite	1.16×10^{-5}
FAp	1.14×10^{-5}

Table 6.1: Experimentally derived TEC of phosphatic phases [262-264]

6.2 Threshold Displacement Energies

The Threshold Displacement Energy (E_d) , is an important physical parameter for understanding and describing radiation damage in crystal structures. E_d is the minimum kinetic energy an atom requires to be permanently displaced from its lattice site to another low energy position within the structure, thereby creating a stable defect such as a Frenkel pair (see section 1.6.2.2).



Figure 6.1: Lattice parameters for β -TCP versus temperature, in the range of 300-800 K. Here the gradient is equal to $\frac{\delta L}{\delta T}$, as discussed in equation 6.2.

Kinchin and Pease [265] were the first to develop a model to describe the accumulation of damage created by radiation processes in crystalline solids. The Kinchin-Pease model [265] provides an estimate for the number of atoms to be displaced permanently from their lattice sites for a PKA with an energy above the E_d and below a cut-off value provided from electron stopping, E_c ; this is shown graphically in figure 6.2. The number of ions displaced (N) can be described as a function of the PKA kinetic energy (P) and is inversely proportional to the E_d as described in equation 6.5 [265, 266].

$$N(T) = \begin{cases} 0, & 0 < P < E_d \\ 1, & E_d < P < 2E_d \\ \frac{P}{2E_d}, & 2E_d < P < E_c \\ \frac{E_c}{2E_d}, & P \ge E_c \end{cases}$$
(6.5)

The Kinchin-Pease model concludes that if an atom is given an energy greater than E_d , the atom will move permanently off its lattice position (creating a Frenkel pair), the energy required to move the ion is E_d . If an energy less than E_d is imparted to the atom, then it will simply fall back into its original lattice site.



Figure 6.2: Kinchin-Pease model, where E_d is the threshold displacement energy which moves an atom permanently off its site giving rise to one Frenkel pair, E_c is the value over which electronic stopping will occur and the gradient of the line is $\frac{P}{2E_d}$.

In crystalline materials such as FAp and β -TCP the energy to displace symmetrically equivalent atoms can be different even for the same crystallographic directions due to the small thermal vibration differences of surrounding ions (although this can be averaged out). Of course, since the surrounding environments are not isotropic for a given ion, the energy for displacement is directionally dependent even when averaged over time. Therefore, it is often necessary to consider a large number of energies and directions to obtain a complete overview of atomic displacement (this is discussed in further work, chapter 8). In this chapter only the low index directions will be reported.

Knowledge of E_d is particularly important for understanding radiation damage cascades. During radiation damage the initial cascade can give rise to many subcascades, which will eventually stop when the moving particles have a kinetic energy that is smaller than E_d .

The E_d value described here was calculated using MD at a simulated temperature of 300 K, within a 20×20×20 supercell. The supercell was initially equilibrated using a NVT Berendsen thermostat [196] to ensure rapid convergence to the equilibrium structure. Subsequently, after equilibration, a particular atom of a chosen species was given a velocity appropriate to a specified kinetic energy in the specified direction; this is the displacement atom. The energy given to

the initial atom was increased in 5 eV increments, until the PKA was permanently moved from its lattice site. The lattice was simulated using the NVE ensemble over a 10 ps time period, and the movement of the displacement atom was monitored. The energy imparted to the atom to permanently move it off its lattice site was then classified as the E_d .

The same procedure was then performed for a number of low index directions (<0001>, < $\overline{1}2\overline{1}0$ >, < $\overline{1}2\overline{1}3$ >, < $2\overline{1}\overline{1}0$ >, < $2\overline{1}\overline{1}1$ >, < $11\overline{2}0$ > and < $11\overline{2}1$ >) and for species in both β -TCP and FAp structures. The threshold displacement values for both structures were then compared. This method gives an approximation of E_d for both β -TCP and FAp, but for statistically significant results a number of equivalent calculations should be carried out at different points in both lattices and the average E_d taken, as described in the further work section (chapter 8).

The minimum energy for the displacement of each atomic species and direction are shown in tables 6.2 and 6.3 for FAp and β -TCP respectively. It is possible to use the Kinchin-Pease model (equation 6.5) to predict lattice damage during a cascade. Considering the E_d values for the FAp structure shown in table 6.2, two general trends can be seen. The first is that on average, the cations (P and Ca) exhibit larger E_d values than any of the anions, suggesting that during damage cascades a smaller proportion of cation defects will be generated in comparison to anions. Interestingly, this trend was also noted by Veiller *et al.* [258] in zirconolites and by Lian *et al.* [267], Chartier *et al.* [268] and Purton *et al.* [269] in pyrochlores. This can be related back to the energy required to create a vacancy or a Frenkel pair in the lattice. The defect energies required to create a vacancy in both the FAp and β -TCP lattices are compared in table 6.4. This indicates that the anions require much smaller energies to create a vacancy, which goes some way to explaining the overall trend exhibited by the displacement energies.

Table 6.2: Calculated threshold displacement energies (in eV) for FAp in the hexagonal directions indicated. The lowest energies are shown in bold, for each ion type.

	<0001>	< 1210>	< 1213>	<2110>	<2111>	<1120>	<1121>
Ca(1)	40	45	45	80	70	80	45
Ca(2)	50	90	45	60	55	65	95
F	10	30	25	80	15	30	30
0	10	55	15	25	15	25	10
Р	30	20	25	65	20	50	10

	<0001>	< 1210>	< 1213>	<2110>	<2111>	<1120>	<1121>
Ca(1)	90	40	40	50	45	40	45
Ca(2)	25	20	10	35	15	10	20
Ca(3)	40	45	45	80	70	80	45
Ca(4)	100	30	85	20	50	20	20
Ca(5)	25	40	60	20	30	30	40
0	10	20	25	10	35	10	10
Р	25	15	10	15	30	15	25

Table 6.3: Calculated threshold displacement energies (in eV) for β -TCP in the hexagonal directions indicated. The lowest energies are shown in bold, for each ion type.

Table 6.4: Calculated defect energies to create vacancies for lattice species in both the β -TCP and FAp structures. Oxygen, fluorine, calcium and phosphorus vacancies ($V_O^{\bullet\bullet}$, V_F^{\bullet} , $V_P^{/////}$ and $V_{Ca}^{//}$ respectively).

	Species	Defect energy (eV)
FAp		
	0	9.93
	F	4.94
	Р	30.40
	Ca(1)	22.12
	Ca(2)	22.79
β -TCP		
	0	10.06
	Р	29.11
	Ca(1)	22.46
	Ca(2)	21.26
	Ca(3)	22.77
	Ca(4)	19.85
	Ca(5)	21.90

The E_d for an atom is influenced by the proximity of the displaced ion to other lattice atoms, and as such the trends seen for FAp suggests that the E_d is strongly directional. This is an effect that is not considered in the original Kinchin-Pease model, but has been observed in a number of other studies [270, 271]. This can be seen in particular for the < 0001 > direction, which has some of the lowest E_d values (shown in bold) compared to other directions such as the two related < $2\overline{1}\overline{1}0$ > and < $\overline{1}2\overline{1}0$ > directions. This can be explained by the relative density of ions in the < 0001 > direction which is generally less than other directions across the lattice, especially down the anion channel in FAp. With reference to the Kinchin-Pease model (equation 6.5), and the results shown in table 6.2 it is likely that a larger defect population for damage initiated in the < 0001 > direction will be seen when compared to other directions. Furthermore, the model suggests that more anion defects are likely to form than cation defects.

The E_d values for β -TCP (shown in table 6.3), suggest that like FAp there is a directional effect, especially down the *c*-axis, which can be related back to the symmetry of β -TCP (as discussed in section 3), which shows a pattern of repeating columns creating channels parallel to the *c*-axis. Furthermore, the E_d value for anions seen in table 6.3, is lower than the E_d seen for cations, which again is a similar effect to that seen in FAp.

Overall, for both structures the two minerals exhibit similar E_d values, with β -TCP values being slightly lower than those shown in FAp. Thus, β -TCP is likely to have "slightly larger" damage cascades than FAp, as less energy is required to move ions off their lattice sites. Even though both structures can be damaged easily they are known to recover from damage, and in the case of apatites, this has been seen over geological timescales [73, 77–80]. The rest of this chapter will concentrate on radiation damage of FAp, and will compare the trends predicted by the Kinchin-Pease model [265] with those generated from lengthy and computationally expensive damage cascades obtained using MD.

6.3 Radiation Damage of Fluorapatite

6.3.1 Previous Studies

The suitability of several phosphate based materials, as waste hosts, has been investigated via fission-track thermochronometry; apatites were found to be the most useful [79].

Fission-track thermochronometry is a method widely used to measure geological time and processes in the Earth's crust [272]. This approach compares the abundance of naturally-occurring radioactive isotopes and their decay products within a sample and measures the size and shape of fission tracks [80]. Interestingly, through studies such as this it has been found that the exact composition of FAps has a profound effect on the rate of fission-track annealing [273, 274]. Specifically the inclusion of rare earth elements (REEs) in the apatite structure, alters the cell parameters, thereby affecting the annealing process [273]; so that slower annealing times are noted for crystals with shortened *c*-axis and larger *a* or *b* axes. Furthermore, Weber *et al.* [275] suggested that the nature of the central damage track and its surrounding lattice is little investigated and has not yet been characterised as amorphous or crystalline. To be able to understand the effect of compositional changes on the FAp structure (as suggested in chapter 8, as future work), radiation damage effects must first be examined for the perfect FAp lattice.

Gleadow *et al.* [79] describe the mechanism of track formation as the combination of two coincident and brief processes. Upon decomposition of an atomic nucleus, fission fragments with excess kinetic energy move in opposite directions and interact with the host lattice (observed in figure 1.3). Electronic stopping of the fast moving ion occurs when it undergoes inelastic collisions with lattice ions. The number of these collisions is large and the fast moving ion loses energy and imparts it to lattice atoms. As the projectile loses energy it slows downs and nuclear stopping becomes the more important effect. Nuclear stopping is dominated by elastic collisions between two bodies at low velocities, just as when billiard balls collide [276]. Classical MD simulations (described in section 2.9) do not take into account charge transfer interactions between ions, so only elastic collisions will be well represented in this discussion of radiation damage.

One of the main sources of defect production and modifications of the crystalline structure in waste host materials occurs when the lattice is subjected to α -decay irradiation in a repository environment [258], as discussed in section 1.2. Under such irradiation conditions it is likely that FAp will undergo local deformation and amorphisation. The extent and type of damage suffered by the lattice is of interest to waste form developers and will be assessed here over the timescales currently accessible via MD using the computing power available, about ~100 ps. This timescale allows for the initial damage to form and although subsequent damage evolution can take place over geological timescales (>10⁵ years) [258], the initial damage processes described by MD are nevertheless crucial as the beginning point for other longer-term models. Furthermore, modelling damage cascades probes timescales that are inaccessible by experimental means and gives a good overall picture of damage evolution.

6.3.2 Damage Cascade Simulations

The anisotropy of the fluorine environment, discussed in chapter 5.2, suggests that fluorine ions might channel down the *c*-axis (due to its low atom density). Furthermore, it is also the most mobile species in the structure (see section 5.2) and as such this ion will be used as the PKA for these simulations. As discussed for future work, in chapter 8, all atoms should be considered as potential PKAs in damage cascades, to obtain a full understanding of the system, but this chapter will concentrate only on fluorine. With reference to table 6.2 the low index directions of <0001> and <2110> were chosen as PKA directions; these represent directions with low energy and high energy threshold displacements, respectively.

The cascades considered here simulate the effect of an α decay recoil nucleus. The cell used in these calculations is a 20×20×20 supercell of FAp containing 336,000 atoms, in which *a* and *b* = 188 Å and *c* = 138 Å. Prior to initiating damage the supercell was first equilibrated at 300 K for 20 ps, using the Berendsen thermostat [196]. For the data collection stage, the NVE ensemble was used to reduce any damping of the PKA from velocity scaling due to the ensemble itself. After the PKA was initiated, subsequent movements of the impacted ions and the surrounding lattice were followed until a metastable state was reached, after around 30 ps. To count the defects produced from a damage cascade a sphere of radius 0.8 Å around each lattice site was considered. If the sphere is empty, the site is considered to be vacant, otherwise it is occupied. This allows for thermal vibrations of ions adjacent to the lattice site. If an atom is not contained within any spheres it is considered to be an interstitial. If an ion recombines with a vacant lattice site then this is classified as a substitutional defect, only if the recombining atom type is different to the original atom occupying the lattice site. If the defect recombines with another lattice site previously occupied by an atom of the same species, it is no longer counted as a defect as this constitutes lattice recovery. All of these point defects are described more fully in section 1.6.2.2.

To enable a statistically significant picture of a damage effect for a specific PKA in a specific direction, a larger number of simulations must be performed and an average taken (to account for thermal fluctuations). However, given the size of cell and number of possible energies and directions such an approach is computationally not feasible. The work presented here uses a different approach to the description of radiation damage effects but a similar approach as taken by Veiller *et al.*, which has been described as suitable for obtaining general trends [258], described below and in section 6.3.3.

The PKA ions were given initial energies corresponding to kinetic energies of 0.25 to 5 keV. These energies are substantially smaller than those expected in the waste form [258], where they would be in the region of 100 keV [14]. However, these smaller values correspond to the maximum damage region that is possible in this size of supercell while avoiding overlapping cascades through periodic boundaries. Increasing the size of the supercell would significantly increase the computational requirements.

6.3.3 Characteristics of Damage Cascades

To assess damage cascades the types, numbers and recovery profiles of defects have been calculated. This gives a good overview of the development of the damage cascade and the types of defects likely to be created.

Figures 6.3 and 6.4, present the general pattern for damage and recovery for each PKA energy in <0001> and <2110> directions respectively. After maximum damage is reached, the lattice immediately starts to recover, although recovery is incomplete with some retained damage at the end of the simulation. A similar effect is seen experimentally by Afra *et al.* [277]. An example cascade is shown in figure 6.5, which reports lattice damage and recovery during a 3 keV cascade in <0001> over 25 ps. Here, extent of the initial damage and subsequent recovery of the damage cascade can be seen, as well as the remaining amorphous core of the cascade at the end of the simulation.

It is likely that the recovery process will continue over geological timescales, obviously not



Figure 6.3: Number of atoms displaced as a function of simulation time for a range of PKA energies, initially displaced in <0001>. The cutoff distance here is >0.8 Å.



Figure 6.4: Number of atoms displaced as a function of simulation time for a range of PKA energies, initially displaced in $\langle 2\bar{1}\bar{1}0 \rangle$. The cutoff distance for defects is $\rangle 0.8$ Å.



Figure 6.5: Damage induced by a 3 keV F⁻ PKA in <0001> at various times throughout the cascade. Cubes indicate vacancies, spheres indicate interstitials and pyramids represent substitutional ions. Ca²⁺ ions are blue, F⁻ ions ions are green, O²⁻ spheres are red and P⁵⁺ are purple. The cut-off distance for defects is >2 Å to generate a less cluttered image.

considered here [278]. However, within a few picoseconds of displacement around 50%-70% of atoms displaced by more than 0.8 Å return to either their original position or to another equivalent site within the lattice (see tables 6.5 and 6.6 and figures 6.3 and 6.4).

Both sets of cascades show that the total number of defects produced increases with PKA energy, which agrees with the Kinchin-Pease model [265]. Also, interestingly, the direction in which the PKA is initiated makes a difference to the total number of defects. In the 5 keV cascades, there is an increase in defect population by ~25% when moving from the $\langle 2\bar{1}\bar{1}0 \rangle$ to $\langle 0001 \rangle$ directions, see figure 6.6. This can be related back to the threshold displacement trends for FAp shown in table 6.2. Here displacement of F, O and Ca(1) ions in the $\langle 0001 \rangle$ direction have the lower E_d values.

While the graphs (figures 6.3 and 6.4) show the timescale over which recovery occurs for each PKA, the tables (tables 6.5 and 6.6) give a quantitative indication of recovery of the damaged lattice. The recovery shown here is a simple ratio between the maximum number of defects achieved by the damage cascade and the number of defects left at the end of the simulation.

For damage cascades in the <0001> direction (table 6.5), the overall percentage recovery of FAp after damage averages 70 % (as compared with 64 % for the <2110> direction) across all energies. Overall, as the energy of the PKA increases the percentage recovery also increases.

As the energy of the PKA increases still further, it imparts greater energy to the system, which in turn provides the system with an equivalent temperature (as a function of the increased energy). In effect the damaged region can be thought of as higher in 'temperature' than the surroundings and annealing of damage in this region is more effective as a result [275]. The equivalent temperature of the system, created by the additional energy from the PKA, does diminish over the course of the cascade, however, due to the use of the NVE ensemble, the effective temperature is not reduced fully to its starting point of 300 K. It is possible to reduce the heat sink problem by equilibrating the cascade using the NVT or NPT ensembles, which would reduce the temperature of the whole system back to 300 K. This is suggested as further work section, section 8.3.

The equivalent temperature effect is also true for damage in the $\langle 2\overline{1}\overline{1}0 \rangle$ direction, although the overall average recovery rate is lower, at 63.5%. This lower rate of recovery can be attributed to the migration energies associated with migration in the *ab* direction over the lower migration

Table 6.5: Characteristics of damage cascades in FAp in a <0001> direction. The cut-off distance for defects is >0.8 Å. For individual ion species, count is taken at the end of the simulation.

PKA energy (keV)	0.25	0.50	0.75	1.00	2.00	3.00	4.00	5.00
Trajectory length (Å)	5.47	7.85	6.43	4.89	15.99	16.90	18.77	28.50
Max. temperature (K)	305	311	316	321	345	367	390	413
No. of interstitials								
Ca	41	137	1103	870	3687	5156	7813	11108
F	140	331	671	736	1680	2747	3751	4709
0	2175	4091	8650	8779	20038	34592	45766	56128
Р	156	369	1208	1204	3495	5730	7817	9805
No. of vacancies								
Ca	41	138	1139	896	3725	5219	7892	11078
F	140	305	656	670	1605	2674	3644	4634
0	2176	4109	8628	8814	19977	34667	45735	56089
Р	155	376	1209	1209	3593	5665	7876	9949
No. of substitutionals								
Ca	0	1	66	31	224	158	203	213
F	0	0	2	2	21	41	45	48
Ο	1	27	47	80	237	254	318	463
Р	0	8	76	39	171	133	283	350
Peak no. of defects	251	414	1031	1515	3950	5059	7955	10379
Resdiual no. of defects	81	151	403	354	896	1502	2111	2502
Total no. of defects	2513	4964	11823	11741	29553	48811	65996	82824
dpa	0.8	1.5	3.5	3.5	8.8	14.5	19.6	24.7
Lattice recovery (%)	67.7	63.5	60.9	76.6	77.3	70.3	73.5	75.9

Table 6.6: Characteristics of damage cascades in FAp in a $\langle 2\overline{1}\overline{1}0 \rangle$ direction. The cut-off distance for defects is $\rangle 0.8$ Å. For individual ion species, count is taken at the end of the simulation.

PKA energy (keV)	0.25	0.50	0.75	1.00	2.00	3.00	4.00	5.00
Trajectory length (Å)	2.29	2.62	1.48	8.22	9.56	3.95	9.22	4.40
Max. temperature (K)	305	311	316	320	343	367	389	412
No. of interstitials								
Ca	60	245	352	905	3457	4855	5694	5249
F	214	366	547	778	1885	2526	3342	3718
0	2704	4356	6816	9029	22000	30213	40386	45521
Р	197	513	702	1299	3613	5017	6376	7022
No. of vacancies								
Ca	60	245	352	943	3522	5020	5733	5341
F	190	366	521	777	1766	2411	3224	3565
0	2726	4353	6835	8997	21998	30099	40394	45644
Р	199	516	709	1294	3669	5081	6447	6960
No. of substitutionals								
Ca	0	1	0	49	158	158	139	213
F	0	0	0	1	4	41	20	48
0	1	0	29	6	166	254	227	463
Р	0	3	10	26	143	133	167	350
Peak no. of defects	251	414	1031	1515	3950	5059	7955	10379
Resdiual no. of defects	81	151	403	276	896	1502	2111	2502
Total no. of defects	3176	5484	8456	12093	31426	43197	56351	62584
dpa	1.0	1.6	2.5	3.6	9.4	12.9	16.8	18.6
Lattice recovery (%)	59.0	45.5	58.7	67.7	63.4	72.6	70.2	71.2



Figure 6.6: Comparison of defects generated during a 5 keV PKA cascade in $<2\overline{110}>$ and <0001> directions.

energies in the *c* direction, as discussed in chapter 5. Furthermore, experimental work by Donelick *et al.* [279], suggested that the length and width of damage tracks in the *c*-axis were much longer and thinner than those in either the *a* or *b* axes. This behaviour is also seen in the cascades presented here and is reported in tables 6.5 and 6.6, where the average trajectory length for the PKA in the <0001> direction is always longer than that in the <2110> direction, although the extent to which it is longer tends to vary markedly. Rabone *et al.* [280] suggest that this effect is due to the anisotropy in the dielectric constants [131], where a charged ion moving parallel to the *c*-axis interacts more strongly with ions closer to the central damage track, thereby shielding the anions further away, creating a long and thin damage track. For damage tracks perpendicular to the *c*-axis the opposite is true; this effect, which has also been observed by Rabone *et al.* [280], is seen in figure 6.7. For both damage directions, the ability of FAp to undergo significant recovery is quite remarkable and is corroborated by a number of previous experimental studies [80, 273, 275, 281].

For the damage cascades initiated in the <0001> direction (figure 6.3) a secondary peak is evident for the 5 keV cascade, after about 12 ps. This can be directly related to the shape of the cascade at this point. The following figures 6.8 and 6.9 provide an idea of the shape and size of cascades, by showing only those defects that have moved more than 2 Å over the course of the entire simulation. The cascade images produced by this method show even those defects that



Figure 6.7: Optical micrographs taken from the work of Rabone *et al.* [280]. Etched tracks in apatite are a) longer and thinner near the *c*-axis axis (average diameter of 5 nm) and b) shorter and thicker 85° to the *c*-axis axis (average diameter 9 nm), with respect to the principal axis of the material [280].

have recombined with the lattice, allowing the cascade to be visualised without any recovery processes.

Figure 6.8, shows a schematic of the defects in the damage cascade produced in the <0001> direction with a 2 keV PKA; this cascade measures about 50 Å in diameter. Increasing the PKA energy to 5 keV (figure 6.9), not only increases the size of the main cascade, but also produces a subcascade to the side of the main damage region. It is this subcascade which causes the deviation in the recovery curve at 12 ps in figure 6.3. Interestingly, this is the only subcascade seen, but increasing the PKA energy could generate further subcascades, however, the cell size for this exceeded available computational resources.

6.4 Nature of Defects in Damage Cascades

For each cascade a central damage track is created by the PKA. The area of lattice directly in the track is highly disordered during the cascade generation and ends in a quasi-amorphous state depending on the rate of recovery [258]. The damage cascade also creates point defects further away from the central damaged zone, which are spread around the track. In this region fast recovery occurs after the initial ballistic phase of the cascade as discussed previously [258, 275]. Even so, these defects can be easily identified as interstitials, vacancies and substitutional species.



Figure 6.8: Main cascade created from a 2 keV PKA in a <0001> direction, viewed in a <0001> direction. Defects here represent any atom that moves more than 2 Å from its original lattice site over the entire length of the simulation.



Figure 6.9: Main cascade and subcascade created from a 5 keV PKA in a <0001> direction, viewed in a <0001> direction. Defects here represent any atom that moves more than 2 Å from its original lattice site over the entire length of the simulation.

6.4.1 Defect Population

Tables 6.6 and 6.5, indicate the total number of defects produced. This table suggests that the greatest proportion of defects was O^{2-} species. However, when compared to the relative number of atoms in the supercell by virtue of the chemical formula (Ca₅(PO₄)₃F) a different picture appears. To compare the numbers of defects, a normalised defect population (normalised to the chemical formula) has been produced, which accounts for the differences in the number of each atom in the chemical formula. The defect numbers are taken at the end of the simulation after the initial recovery phase has taken place and the defect population has stabilised.

Figures 6.10 and 6.11 report the normalised number of defects produced over the course of each cascade, for the <0001> and <2110> directions respectively. Both figures give the same overall pattern. As predicted by the E_d values in table 6.2, more anion defects are produced than for cations. In both examples, O^{2-} and F^- ions form the largest population of defects with little difference between the two. This is similar to the effects predicted by the E_d values calculated earlier in this chapter. P^{5+} ions represent the next highest proportion of defect, which is followed by Ca^{2+} defects. Furthermore, the profiles presented here for the two directions describe the Kinchin-Pease profile illustrated in figure 6.2 and described in section 6.2.

6.4.2 PO₄ Tetrahedra

Knowledge of the types of defects produced is important, especially when considering ionic migration through the lattice (which will be suggested as further work in chapter 8). However, of particular interest is the effect of damage on the phosphate tetrahedra, which as mentioned previously, are important structural units that allow the incorporation of a wide range of cations with different sizes into the structure by twisting and rotating. If these units were to degrade during damage cascades, then the stability of the structure could be reduced. Thus, this subsection will concentrate on how the P-O coordination number and O-P-O bond angles are altered by the damage process.

As mentioned by White *et al.* [96] and Madhavi *et al.* [199] and discussed in section 4.3.2, the PO₄ tetrahedra and the metaprism formed by Ca sites twists and moves to accommodate changes in the lattice. This process controls defect incorporation on the lattice sites and can also effectively open and close the anion channel, altering the c/a ratio. The c/a ratio is of



Figure 6.10: Normalised number of species displaced over the timescale of the simulation for different energy PKA displaced in the $\langle 2\bar{1}\bar{1}0 \rangle$ direction. The cutoff distance for defects is $\rangle 0.8$ Å.



Figure 6.11: Normalised number of species displaced over the timescale of the simulation for different energy PKA displaced in the <1000>) direction. The cutoff distance for defects is >0.8 Å.

interest as a change could lead to mismatched strain within the lattice, which could in turn lead to micro cracking; the formation of micro cracks in a waste host would be detrimental to waste form's durability [10].

6.4.2.1 P-O Coordination

Developing an understanding of the stability of PO₄ tetrahedra during and after the damage cascade would aid in understanding the response of the lattice to damage. Firstly, it is important to establish the nature of bonding in the phosphate unit during damage. This can be calculated by considering the coordination number of each phosphorus atom. The coordination environments in the following sections were calculated using an absolute distance criterion. The distance criterion used here is from 0-1.9 Å, which accounts for the P-O bond length of 1.58 Å [200] plus 25 % to allow for thermal vibrations (although these are much smaller than 25 %), but rather to identify the different O^{2-} ions coordinated to P^{5+} ions.

To assess the effect of maximum damage on coordination number, the 5 keV PKA cascades for both directions are compared over the entire cell. For comparison three different time periods during the course of the cascade are considered; i) the beginning, ii) at 8 ps (corresponding to maximum damage) and the end of the simulation, iii) after recovery. The results for both PKA directions considered are shown in figures 6.12(a)-6.12(c) and 6.13(a)-6.13(c).

For both coordination profiles before the initiation of the cascade (figures 6.12(a) and 6.13(a)) the P atoms are all tetrahedral units. Figures 6.12(b) and 6.13(b), depict the coordination profile at maximum lattice damage, where the coordination environments have shifted. Here coordinations of 1, 2, 3, and 5 (along with a vast majority of 4) become apparent. These over or under coordinated P-O groups are a product of the disordered central track zone of the cascade, which is often described as amorphous or quasi-amorphous [258, 275]. Figures 6.12(c) and 6.13(c) show the coordination of P after recovery has occurred, at the end of the simulation. For both directions, there are no 1 or 2 fold coordinated P-O units after recovery and the number of three fold coordinated units has diminished substantially, as might be expected as a consequence of the recovery of the lattice. Overall a larger percentage of 4 fold coordinated P ions are retained at the end of the simulation than during peak damage.



(a) Coordination state before the initiation of the PKA, ta-



(b) Coordination state at the point of the simulation that corresponds to maximum damage (at 8 ps).



(c) Coordination state at the end of the simulation and after recovery has occurred.

Figure 6.12: Evolution of the PO₄ coordination state over three time periods 0 ps, 8 ps and 27 ps, for a damage cascade created with a 5 keV PKA in <0001>. The break in the y-axis in these graphs lies between 4-94% and allows the smaller bars to be viewed.



(a) Coordination state before the initiation of the PKA, ta-







(c) Coordination state at the end of the simulation and after recovery has occurred.

Figure 6.13: Evolution of the PO₄ coordination state over three time periods 0 ps, 8 ps and 27 ps, for a damage cascade created with a 5 keV PKA in $\langle 2\bar{1}\bar{1}0 \rangle$. The break in the y-axis in these graphs lies between 4-94% and allows the smaller bars to be viewed.

Coordination of Phosphorus in the Central Damage Track

The bonding results presented above have been calculated over the entire cell. As such it is possible that the unaffected PO₄ (away from the damage cascade) could affect the overall coordination environments and dilute the specific P-O coordination environments within the most damaged region. Considering the damage cascade created by the 5 keV <0001> PKA, it is possible to calculate the P bonding only in the central damaged region. With reference to figure 6.14, the central damaged core for this cascade is highlighted in blue. The atoms in this section of the cascade were removed from the rest of the supercell, and the coordination environments of all P ions within it were calculated. The coordination of P ions were calculated using the absolute distance as discussed in section 6.4.2.1, previously.

The coordination environments of P ions in the central damage region are shown over the same three time periods (0 ps, 8 ps and 27 ps) in figure 6.14. For t=0 ps, the section of the lattice exhibits full 4 fold coordination as expected from a perfect lattice. At maximum damage, t=8 ps, the P ions exhibit a large number of 1, 2, 3 and 5 coordinated environments, but the majority (70%) of the P ions still exhibit tetrahedral environments as suggested in the previous section and in figure 6.12. The percentage of the 4 fold coordinated P ions is different to that shown in figure 6.12 due to the inclusion of non-damaged regions in the lattice, however, the general trends are similar.

At the end of the calculation (at 27 ps) after peak damage and during recovery, the same section of the cascade shows higher coordination numbers for P ions. In this region of the cascade there are fewer 2 and 3 coordinated P ions and a larger number of 5 and a few 6 coordinated ions. Furthermore, the area of damage here is diminished and there is a larger percentage of 4 coordinated ions (81 %). Over the course of the cascade it appears that the PO₄ tetrahedra break apart in the centre of the damaged region and then as recovery progresses P^{5+} and O^{2-} ions start to recombine to form higher coordinated units, including those which become PO₄ tetrahedra but also 5 and 6 coordinated units. The exact structures of these latter units remains unclear. Possible further work on this issue is suggested, in section 8.3. However, some insight into the coordination environments of the highest coordinated units may be gained by considering the O-P-O bond angle which will be considered next.



Figure 6.14: Coordination environments of P ions over the course of a <0001> 5 keV PKA cascade, in the central damage region shown in the blue box in the supercell. The P ions presented over three time periods (0 ps, 9 ps and 27 ps) are coloured by coordination as shown in the key.

6.4.2.2 O-P-O Bond Angle

The effect of damage to the bond angle, O-P-O, is also a useful way to characterise the effect of radiation on P containing structural units. If the O-P-O angle has altered significantly, then it is likely that during the damage cascade the tetrahedra are significantly distorted.

As mentioned by Martin *et al.* [200], the average PO₄ bond angle is 109.5° corresponding to the angle in a regular tetrahedron. Deviation from the mean bond angle, by broadening or shifting of the distribution maximum, would indicate a change in the tetrahedra. For both PKA directions considered here, the bond angles from the end of three different PKA simulations (after recovery) have been calculated and are reproduced in figures 6.15 and 6.16. From both graphs, it is clear that the smooth spread of observed PO₄ bond angles of the perfect lattice is maintained in the damaged lattice. Furthermore, the effect of radiation damage on the PO₄ tetrahedra suggests that there is little change to the O-P-O bond angles, up to ~20 displacements per atom (dpa). However, as the PKA energy increases (as indicated by the arrows), there is a slight broadening as more of the lattice is damaged.



Figure 6.15: Change in O-P-O polyhedra angle with increasing PKA energy in the <0001> direction. The perfect lattice has been left off this image for clarity, as the angle distribution is similar to that represented by the 0.25 keV cascade.

The O-P-O angles and the coordination of the tetrahedra change slightly during the damage cascade, however, the change to the units is slight. This suggests that the majority of the PO_4 units stay intact during and after the damage cascades form. However, this seems to be at odds with the number of defects that are seen throughout the cascades; there are a substantial number of oxygen defects. This suggests that during damage any remaining PO_4 tetrahedra move, or twist from their original lattice positions in response to the damage, remaining as a complete unit. Thus, the individual ions of the tetrahedra would be counted as defects if they



Figure 6.16: Change in O-P-O polyhedra angle with increasing PKA energy in the $\langle 2\overline{1}\overline{1}0 \rangle$ direction. The perfect lattice has been left off this image for clarity, as the angle distribution is very similar to that represented by the 0.25 keV cascade

moved away from their original positions, which accounts for the high levels of O^{2-} defects. This idea changes the way that radiation damage is considered in FAp; damage is not just a product of the movement of single ions, but also of whole structural units in the case of PO₄, this is discussed further in chapter 8.

6.5 Conclusions

To carry out radiation damage cascades of FAp and β -TCP it has been necessary to develop a new set of potentials. The two body potentials, complete with a ZBL spline, represent the structures well and provide thermal expansion values comparable to experiment.

Displacement of stationary lattice atoms is a fundamental process, that controls the way the lattice responds to radiation damage and how it evolves. As such the E_d values generated here provide trends for the effect of damage on the lattice and can be used to predict the overall trends seen in the full damage cascade simulations. As mentioned in their original paper, Kinchin and Pease [265] did not include the effect of incident PKA direction on damage, which is shown to be an effect in this study (tables 6.3 and 6.2) and in previous investigations [270, 271].

This is reflected in the anisotropic nature of displacements; in FAp the E_d values in <0001> are lower than in <2110>. For both structures investigated here, there is a clear difference for the E_d values between the anions and cations; the anions generally have lower energy E_d values, whereas the cations require more energy to be displaced, this trend is also reflected in the defect energies for vacancy formation.

As suggested by Kinchin-Pease [265], the E_d values give a good indication of the overall trends expected from full radiation damage cascades formation. The effect of direction for cascades in FAp is evident as well as the effect of species type, which is consistent with anions having lower E_d values than cations.

The effect of damage cascades on the phosphate tetrahedra suggests that the majority of the units stay intact during the cascade. Both the coordination numbers and the O-P-O bond angles for the unit after the cascade and recovery processes, suggest that the PO₄ unit generally remains whole, unless in the central damage core, where some units display different coordination and O-P-O angles. Since defects are recorded for O^{2-} and P^{5+} ions independently it is likely that the units move and twist as a whole unit during the cascade. Further work is required on the effect of P-O coordination during damage, which is discussed in section 8.3.

7

Fluorapatite Surfaces

The properties of the surfaces of materials are often more important than their bulk properties; they control the interactions between the bulk and its external environment. For example, it would be interesting to know if defects migrate preferentially to a surface or if they stay in the bulk. Behaviour of this nature is crucial when considering fluorapatite (FAp) for use as a potential waste host; if defect species migrate to the surface of crystals, they could build up and alter the stress distribution or even destabilise the structure as a whole [282, 283].

To understand better the effect of surfaces on the bulk and on the incorporation of defects a number of surfaces, of which FAp exhibits both II and III types [204], will be considered. As described in section 2.10.1, type III surfaces require significant rearrangement to alter the inherent dipoles. This is a complex process that requires careful consideration and assessment of multiple configurations, in this chapter only type II surfaces are considered. Analysis of type

III surfaces is outlined as further work in section 8.4.

7.1 Crystal Morphology

The morphology of a crystal is the macroscopic shape that the crystallite exhibits. Crystal morphologies are easy to observe with the naked eye, or for smaller crystals, using an optical or electron microscope. As such, the validity of simulation models can be tested against crystal morphologies. Section 2.10.3.1 describes the calculation methods used to generate the Wulff construction which allows the morphology to be predicted from surface or attachment energies.

To calculate the crystal morphologies of FAp, first the attachment energies and surface energies for all the low index type II surfaces exhibited by FAp were considered, as reported in table 7.1. Using these results and the Wulff construction method [205], it is possible to generate both the equilibrium morphology (the equilibrium energy is inversely proportional to surface energy [206]) and the growth morphology (which is inversely proportional to negative attachment energy [207]); these are displayed in figures 7.1 and 7.2 respectively.



Figure 7.1: Crystal morphology showing the attachment energy for FAp (growth morphology), surfaces are labelled with arrows accordingly.



Figure 7.2: Crystal morphology showing the surface energy for FAp (equilibrium morphology), surfaces are labelled with arrows accordingly.

Comparing the morphologies shown in figures 7.1 and 7.2 with Transmission Electron Microscope (TEM) images of apatite, (see figures 7.3 and 7.4) it is clear there is good agreement. Figure 7.3a, b, c and d, show the growth of apatite crystals as observed by Nylen *et al.* [284]. These crystals represent cross sections of material taken from lower molars and upper incisors of developing rats. Nylen *et al.* observed that at the beginning of crystal formation, the apatite crystals were long in the *c*-axis and that as mineralization progressed, the long thin crystals gradually developed into larger, hexagonal, crystals [284]. This pattern supports the crystal morphologies predicted for the growth and equilibrium morphologies in figures 7.1 and 7.2.

Another interesting feature is the flat surfaces seen at the end of the apatite crystals in figure 7.4. Rakovan [250] concludes that the top and bottom of the needle-like crystals (figure 7.1) are flat due to the (0001) and (0001) surfaces, which in FAp are type III surfaces (not considered here), the effect suggested by Rakovan [250] is indicated on those morphologies calculated in figure 7.5. This indicates that it is possible to use the prismatic planes to investigate defect distribution in FAp, although in future it would be preferable to also consider basal planes. For the remainder of this chapter, the (2110) surface (representative of the prismatic planes, shown to be stable in figure 7.1) will be used to consider the effect of defect distribution near the surface.
hkl shift	Esurf	Eatt	hkl shift	Esurf	Eatt	hkl shift	Esurf	Eatt
(1100)			(2113)			(4510)		
0.12	2.82	-5.69	0.25	2.46	-33.49	0.25	3.22	-41.35
0.38	2.82	-5.69	0.75	2.46	-33.49	0.75	3.22	-41.35
0.62	2.82	-5.69	(1101)			(4510)		
0.88	2.82	-5.69	0.25	2.46	-33.49	0.25	3.22	-41.35
(1100)			0.75	2.46	-33.49	0.75	3.22	-41.35
0.12	2.82	-5.69	(1101)			(5410)		
0.38	2.82	-5.69	0.00	2.46	-33.49	0.25	3.22	-41.35
0.62	2.82	-5.69	0.50	2.46	-33.49	0.75	3.22	-41.35
0.88	2.82	-5.69	(1101)			<u>(1120)</u>		
(2110)			0.00	2.46	-33.49	0.25	3.22	-41.35
0.12	2.82	-5.69	0.50	2.46	-33.49	0.75	3.22	-41.35
0.38	2.82	-5.69	(1101)			(2113)		
0.62	2.82	-5.69	0.25	2.46	-33.49	0.25	2.46	-33.49
0.88	2.82	-5.69	0.75	2.46	-33.49	0.75	2.46	-33.49
(1210)			(2113)			<u>(1213)</u>		
0.12	2.82	-5.69	0.00	2.46	-33.49	0.00	2.46	-33.49
0.38	2.82	-5.69	0.50	2.46	-33.49	0.50	2.46	-33.49
0.62	2.82	-5.69	(1213)			<u>(1213)</u>		
0.88	2.82	-5.69	0.25	2.46	-33.49	0.00	2.46	-33.49
(1210)			0.75	2.46	-33.49	0.50	2.46	-33.49
0.12	2.82	-5.69	(1213)			(1120)		
0.38	2.82	-5.69	0.25	2.46	-33.49	0.25	3.22	-41.35
0.62	2.82	-5.69	0.75	2.46	-33.49	0.75	3.22	-41.35
0.88	2.82	-5.69	(2113)					
(2110)			0.00	2.46	-33.49			
0.12	2.82	-5.69	0.50	2.46	-33.49			
0.38	2.82	-5.69	(5410)					
0.62	2.82	-5.69	0.25	3.22	-41.35			
0.88	2.82	-5.69	0.75	3.22	-41.35			

Table 7.1: Surface (Esurf) and attachment (Eatt) energies calculated for various surfaces (underlined) and the associated hkl shifts, required to generate type II surfaces. All energies are in eV.



Figure 7.3: A bright field TEM image of hydroxyapatite crystals as depicted by Nylen *et al.* in their paper [284]. These images show the stages of crystal growth illustrated through changes in "cross-sectional dimensions of the crystals". In a) the crystals are "initially long and thin" changing to a "more hexagonal shape" in b) and finally increasing in size in c) and d).



Figure 7.4: A secondary SEM image of hydroxyapatite crystals. Taken from [284].



Figure 7.5: The equilibrium crystal morphology (left) and growth morphology (right) that have been derived in this work. The dotted lines roughly indicate the location of type III surfaces as suggested by Rakovan [250] and Nylen *et al.* [284].

7.2 Distribution of Defects at the $(2\overline{1}\overline{1}0)$ Fluorapatite Surface

Previous chapters have been confined to calculating properties of the bulk, where it was predicted that defect cations can occupy the lattice of FAp and β -tricalcium phosphate (β -TCP) and that these are relatively low barriers to cation migration in FAp. In this chapter, the effect of divalent defect species on the surface of FAp is investigated. To determine defect segregation, the crystal is transformed to have a surface morphology suitable for use in the GULP code [140] (with appropriate region sizes shown in figure 2.18), as described in section 2.10.2. An example of the ($2\overline{1}\overline{1}0$) surface produced in this is reproduced in figure 7.6.

After the surface calculation is set up, each fission product is introduced into the bulk, where a relaxation calculation is performed to obtain the energy for the species at that specific site. Here the divalent cations will be substituted for lattice cations using the same formula and defects as described in section 4.3, which is:

$$AO + Ca^{X}_{Ca(x)} \rightarrow A^{X}_{Ca(x)} + CaO$$
 (7.1)

but it is the relative energies that will be used for discussion. AO and CaO simply provide consistent reference compositions.



Figure 7.6: The (2110) type II surface [204] in FAp, indicating region I and region II.

The defect is placed at a cation position nearest the surface and is then moved systematically down, away from the surface; the defects investigated in this chapter are placed only on lattice substitution sites. A calculation is then performed at each of these possible cation positions. An example of the possible Ca(1) and Ca(2) sites in a $(2\overline{1}\overline{1}0)$ surface can be seen in figures 7.7 and 7.8 respectively. The energies obtained for these stepwise movements away from the surface are then compared and plotted as a function of depth. This gives a good indication of the effect of the surface on the accommodation of defect ions. Energy profiles with negative gradients away from the surface indicate a move to a more stable structure (lower energy) and hence segregation away from the surface into the bulk. Energy profiles with a positive gradient away from the surface correspond to decreased stability and hence segregation towards the surface.

Performing calculations at many layers below the surface allows for sub-surface segregation effects to be noted (as proposed by Battaile *et al.* [285]). Nevertheless, this technique does not give migration barriers for ions to move from one site to another explicitly, as discussed in section 5.1.2. Rather, this technique allows the relative stability of specific sites in the lattice to be determined.



Figure 7.7: The $(2\overline{1}\overline{1}0)$ surface of FAp where the large bright blue cations indicate the Ca(1) sites and the grey region represents region II.



Figure 7.8: The $(2\overline{1}\overline{1}0)$ surface of FAp where the large bright blue cations indicate the Ca(2) sites and the grey region represents region II.

7.2.1 Divalent Defects At A (2110) Surface

The segregation trends for a range of divalent cations, whose radii are reported in table 7.2, in a sample of FAp exhibiting a $(2\bar{1}\bar{1}0)$ surface, are shown in figure 7.9. From this it is clear that different cations respond to the surface in two main ways. It appears that the divalent cations Mn^{2+} , Fe^{2+} and to a lesser extent, Ba^{2+} and Sr^{2+} indicate a "trapping effect" [286] just below the surface and that the most stable defect configurations appear in the top layers of the material. The trapping energy is defined as the difference between the energy of the less stable point surrounding the trapping sites (which will have higher energies) and the energy at the bottom of the stable trap site. Sr^{2+} ions do not appear to indicate a strong 'trapping' effect, which can perhaps be attributed to the very similar size of these ions to the host Ca^{2+} ions, as indicated in table 7.2.

The defect energy profiles discussed here indicate that the surface has an effect on the first 14 Å to 18 Å of the lattice away from the surface until bulk properties resume (14 Å for Ba, Sr and Mn and 18 Å for Fe). Stanek *et al.* [287], saw a similar effect in zirconia where the top 10 Å was affected by the surface and then below that, bulk properties of the material were apparent. Finally, the difference in site preference between the Ca(1) and Ca(2) sites as discussed in section 4.3, is appreciable only when bulk properties become apparent.

Dopant	Dopant radius (Å)				
Mg	0.72				
Fe	0.78				
Ca	1.00				
Sr	1.18				
Ba	1.35				

Table 7.2: Atomic radii of divalent defects, data taken from Shannon [238].

Looking more closely at the results for Fe^{2+} (figure 7.10), defects in the region between 4- and 10 Å experience the surface 'trapping' effect described by Slater *et al.* [286]. Here the energy difference between the stable sites (at 7-10 Å) and the less stable sites surrounding the trapping zone is 2.8 eV, which is a significant energy. Thus, it is possible that defect species from the bulk may become trapped underneath the $(2\overline{1}\overline{1}0)$ surface, particularly if the migration energy



Figure 7.9: The calculated relative energies for specific divalent cations as a function of depth from the $(2\overline{1}\overline{1}0)$ surface, for cations on both the Ca(1) and Ca(2) sites.

is large, preventing their transport, as discussed further in section 8.4.

At distances greater than 18 Å the effect of bulk cation site preference becomes apparent, as previously discussed in section 4.3. Here the energy for substitution onto a Ca(1) site is lower than incorporating defects onto a Ca(2) site, which matches the trend for divalent cations smaller than Ca ions in section 4.3. Although the difference in lattice energy for defects on either site is small, migration between the two sites could be substantial and further work is required to assess this. The migration pathways and activation energies for transport may not be comparable to those discussed in chapter 5.1, since the substantial lattice rearrangements possible at the surface are likely to affect these migration trends. This is further discussed in section 8.4.

Introducing Mn^{2+} defects into the lattice, as shown by figure 7.11, yields similar results to those shown by Fe²⁺, which is to be expected as their atomic radii are similar, (see table 7.2). The site preference exhibited here at distances greater than 18 Å again agrees with the conclusions from section 4.3, with the Ca(1) site being preferred. One difference between the Fe²⁺ and Mn^{2+} profiles is the trapping energy for Mn^{2+} is 2.6 eV which is smaller than that for Fe²⁺ (the two profiles are comparable as the atomic radii for both ions are similar). However, this is still a significant energy, which would decrease the tendency of defects to occupy sites nearer to the



surface, again suggesting trapping of ions just below the surface.

Figure 7.10: The calculated relative energies for Fe^{2+} as a function of depth from the $(2\overline{1}\overline{1}0)$ surface, for cations on both the Ca(1) and Ca(2) sites as marked.



Figure 7.11: The calculated relative energies for Mn^{2+} as a function of depth from the (2110) surface, for cations on both the Ca(1) and Ca(2) sites as marked.

The larger cations Sr^{2+} and Ba^{2+} exhibit slightly different trends as shown by figures 7.12 and

7.13. The larger cations also experience trapping below the surface, although for Sr^{2+} it is small. Considering the Sr^{2+} species explicitly (figure 7.12), the bulk properties of the material resume at a slightly smaller distance away from the surface, at 14 Å which can be attributed to the size of Sr^{2+} which is very similar to that of Ca^{2+} . The site preference discussed earlier in this thesis (in chapter 4) also holds true, with the Ca(2) sites preferred over the Ca(1) sites.

The results for the Ba^{2+} defects, figure 7.13, show that there is significant difference in energy between the two sites, which again agrees with the results reported in section 4.3, as the energy discrepancy between the sites increases with cation size. Again the Ca(2) sites are significantly lower in energy when compared to the Ca(1) sites.



Figure 7.12: The calculated relative energies for Sr^{2+} as a function of depth from the $(2\overline{1}\overline{1}0)$ surface, for cations on both the Ca(1) and Ca(2) sites as marked.



Figure 7.13: The calculated relative energies for Ba^{2+} as a function of depth from the $(2\overline{1}\overline{1}0)$ surface, for cations on both the Ca(1) and Ca(2) sites as marked.

7.2.2 Conclusions

This preliminary investigation into surface structures and the effect of defect distance from the $(2\bar{1}\bar{1}0)$ surface on energy has yielded some interesting results. Defect ions with an atomic size different from the cation host ion, such as the Mn²⁺, Fe²⁺ and Ba²⁺ ions show a trapping effect just a few layers below the $(2\bar{1}\bar{1}0)$ surface. This suggests that these ions may segregate to the surface. Sr²⁺ on the other hand does not exhibit this effect; this can be related to the relative similarity of of Ca²⁺ and Sr²⁺ ion sizes, whereas Mn²⁺, Fe²⁺ and Ba²⁺ are significantly more different. As defect radii alter from that of the host cation, a greater strain is placed on the lattice and rearrangements inherent in the surface can be taken advantage of causing a trapping effect.

The crystal morphologies predicted here with the type II surfaces show good agreement with experimental micrographs even though the type III surfaces are not included in this study. However, for future investigations it would be interesting to investigate (0001) and (000 $\overline{1}$) surfaces, as these seem to be the relevant type III surfaces, as observed experimentally [250]. Ionic rearrangements to the type III surface are needed to remove the inherent dipole, requiring multiple configurations and atomic rearrangements to be considered. To simplify this process

hydroxyl groups (which are naturally occurring in apatites formed in geological conditions) can be used on the surface of the type III surface to counteract the dipole and also to create a more realistic surface structure, which seems likely to happen in real FAp crystals [181, 287]. This is discussed further in section 8.4.

8

Further Work

In this thesis, classical, static lattice modelling techniques have been used to investigate fluorapatite (FAp) and β -tricalcium phosphate (β -TCP) minerals. In particular, this study has examined how and where radioactive waste species will be accommodated within both structures and how the species partition between them. The migration of anions and cations within the FAp structure has also been studied, with, for example, transport of material in the *c*-axis shown to occur preferentially for all species probed.

As discussed in chapter 6, for radioactive waste applications it is essential that the response of the lattice is understood. Section 6.3, goes some way to explaining the recovery exhibited by the FAp lattice. However, recovery from radiation damage is not the only desirable behaviour of a waste form; the influence of an aqueous environment on these materials also needs to be investigated. Any effect from an aqueous environment will occur predominantly at the

surface of the waste form, thus, the surfaces of FAp and β -TCP need to be understood. In this regard, supplementary research, in addition to that discussed in chapter 7, is required which is outlined below. However, following the order of chapters in the thesis, issues that deserve further consideration are now summarised.

8.1 Structure of β -Tricalcium Phosphate

With respect to the configurations of β -TCP discussed in chapter 3, the larger (3_h×1×1) supercell gives rise to a greater number of low symmetry settings with low energy configurations. However, the differences in energy between each configuration are, generally, small. As discussed (in section 3.5.2) it is, therefore, possible that under normal thermal conditions a number of the low energy configurations could co-exist. As discussed in this thesis and corroborated by the work of Mellier *et al.* [227], it is possible that β -TCP adopts domains with low symmetry structures.

Another method of calculating low energy configurations is known as Special Quasirandom Structures (SQS) [288]. This method first proposed by Zunger *et al.* [288], avoids the need to construct large supercells. This method was originally developed to allow disordered structures to be considered using the computationally demanding Density Functional Theory method [289]. A comparison between the pair potential results obtained in this thesis (chapter 3) and results using SQS and DFT methodologies would be of interest, not only for β -TCP but for other large data sets, relating to disorder in ceramics.

As reviewed in section 3.5 the experimental X-ray Diffraction (XRD) patterns, unlike the simulated XRD, show no preference for any one configuration of β -TCP over another. This can be attributed to the structure presenting many low energy arrangements in various domains, not present in the simulated structure. However, it is possible to probe the structure further still using a neutron Time-of-flight Spectrometer (such as the 'Pelican' at the Australian Nuclear Science and Technology Organisation) which can give information concerning local short range order in a number of crystal domains, by measuring the inelastic neutron scattering response. In this way a broader picture of the β -TCP structure and the prevalence of possible low symmetry and energy domains can be better understood.

8.2 Substitutions and Migration in Fluorapatite and β -Tricalcium Phosphate

Chapter 4 presents a prediction of cation partitioning across both β -TCP and FAp structures. Discussions with AWE, have suggested that the trends reported in this thesis are also observed in biphasic samples of FAp and β -TCP, where Gd³⁺ partitions into the β -TCP phase, thereby destabilising the FAp phase. Later in this chapter the possibility of simulating an interface between these two phases is considered. However, for partitioning (and transport) of cations to occur across such grain boundaries a better understanding of the migration of divalent ions in β -TCP and trivalent ions in both FAp and β -TCP must first be obtained. The diffusion of both divalent cations and F⁻ ions in FAp is already discussed in chapter 5, but to do the same for trivalent defects requires a better understanding of defect clustering in both structures.

As considered previously in chapter 4, when incorporating trivalent defects onto a calcium site in either phosphate structure, the compensating mechanism involves two substitutions and one charge compensating vacancy to be created, as described by the following reaction:

$$3Ca_{Ca(x)}^{X} + M_2O_3 \rightarrow 2M_{Ca(x)}^{\bullet} + V_{Ca(x)}^{\prime\prime} + 3CaO$$

Thus, the site preferences of all three defects and the binding energy between the cluster could be calculated to ascertain how these defects exist together. If the cluster shows a particularly large binding energy, it may be that migration of the trivalent defect also involves the rest of the cluster. This could be examined for both structures via Molecular Dynamics (MD) and Nudged Elastic Band (NEB) calculations.

As discussed in chapter 1, apatites have a particularly flexible chemical structure, and along with cation substitutions, apatites with different end-members or anionic tetrahedral units exist in nature. For example, SiO₄ or GeO₄ tetrahedral units can substitute for the PO₄ groups in FAp. Full substitution of these groups causes the apatite structure to become an oxide ion conductor [83–86], which is important in solid oxide fuel cells. The migration simulations presented here could be extended into this field, where there is increasing interest in oxide migration and the effects of defect incorporation. Furthermore, the FAp structure has also been found to incorporate carbonate groups CO_3^{2-} . Previous work [290], indicates that the charge compensation mechanism for this substitution is promoted by adding an additional F⁻ or OH⁻ to the lattice, or substituting a monovalent ion for a Ca²⁺ lattice ion. The CO₃ group is planar

(unlike the PO_4) and as such will impose a particular distortion on the lattice. CO_3 substituted apatites are of importance in biological applications, associated with teeth and bone [291]. Lastly, the solution energies and site preference of the cation substitutions as a function of anion composition could also be investigated, with particular interest in chlorapatites, which are also of interest as multi-phase waste forms [14, 107, 109].

 F^- migration through the FAp lattice is predicted to proceed in a concerted mechanism which differs markedly from those predicted by Welsh *et al.* and Tse *et al.* [249, 254]. Jones *et al.* [87] and Tamm *et al.* [292]. Of course, OH⁻ ions can substitute easily for F⁻ ions in the apatite structure. Similarly Cl⁻ ions can also substitute for F⁻ ions leading to a polymorphic change to the monoclinic structure. For both these substitutions it would be interesting to ascertain if the migration mechanisms throughout the FAp lattice are similar to those described for F⁻ ion migration. More intriguing still would be to investigate the effect on F⁻ migration in a FAp lattice that has been seeded with, for example, 50% Cl⁻ or 50% OH⁻. It is possible that changing the anions in the channel has an effect on the rate and mechanism of F⁻ ion migration [293]. As discussed in chapter 1, the effect of fluorine in teeth and bones (i.e. hydroxyapatite) is to increase resistance to caries and improve hardness, which are both desirable qualities.

Regarding the migration pathway of F^- , it might be possible to obtain more information about the migration route of this anion by again using a cold-neutron Time-of-flight Spectrometer, which can give information about ion diffusion through a crystal lattice.

8.3 Radiation Effects

The ability of waste host materials to recover and repair after radiation damage is central to waste form studies. Section 2.9.1 introduces the necessary alterations to the original potentials [170, 174] in order to use them for MD simulations. The radiation damage cascades presented in this thesis give an overall trend for damage in two directions for FAp. To obtain a better statistical analysis of the cascades it would be useful to undertake a number of similar simulations using different Primary Knock on Atoms (PKAs) and taking an average over the parameters of interest. In this way any directional effects due to slight differences in symmetry in the lattice can be incorporated into the overall description of radiation damage.

Further to the radiation damage effects observed here for FAp in section 6.3, many more direc-

tions could be investigated, again using a F^- ion as the PKA. Also, other lattice ions could be used as the PKA to simulate damage in the lattice and these could be compared to the trends predicted by the Threshold Displacement Energy (E_d) in section 6.2. The effect of radiation damage on the PO₄ units investigated in the simulations shown in this thesis suggest an inherent stability of the group itself, which appears to stay as a whole unit during cascades. To obtain more information about this effect it would be useful to explore more fully the central damage core with respect to the phosphorous ion coordination and any amorphous regions.

As proposed by Carlson *et al.* [274] compositional variation in apatites is sufficient to produce marked differences in recovery and resistance to annealing of the lattice after damage. As a result it would be interesting to correlate resistance to damage to properties such as anion content, anion type (Cl⁻, F⁻, OH⁻...) and lattice imperfections such as voids. Furthermore, several studies [78, 273, 274] have suggested that substitution of other cations can affect annealing and fission track evolution. The effect of cation incorporation on the stability and the lattice's ability to recover is an important consideration for a waste host [169]. In addition the ensemble used during the recovery stage of the damage cascades in this thesis is the NVE ensemble, which will not remove all the additional energy or thermal components from the simulation. Thus, during the recovery stage it would be useful to introduce the NVT or NPT ensemble that will remove any additional thermal components from the simulation and perhaps produce a different recovery profile. Lastly, the effect of radiation damage on the β -TCP structure is of equal interest and could also be investigated in a similar way to the calculations carried out on FAp presented here.

8.4 Simulations of Surfaces

Permanent immobilisation of radioactive waste species into a waste host requires that there is little or no loss of waste species from the material. The loss of material will ultimately occur from the surface of the waste form. Surfaces behave differently from the bulk material as rearrangements of the ions at the surface will occur. Thus, a more thorough understanding of surfaces and their interaction with defects is required.

Chapter 7 goes some way to investigating the type II surfaces of FAp and crystal morphology. The particle morphologies produced in this work match well with experiment and confirm the surface model used is suitable. However, for a true description of the crystal morphologies, type III surfaces must be considered. To do this, the surface structure must be rearranged to remove the dipole that is inherent for type III surfaces as described by Tan [294]. However, given the complex arrangement of PO₄ groups and F^- ions at the surface this is a formidable task with many different configurations possible. However, in reality crystals of FAp will eventually be in contact with water and may form surface hydroxide species [169]. This can change the relative stability of surfaces and could go some way to creating a stable type III surface. Thus, a better understanding of the type III surfaces in FAp could be achieved in this way, and the crystal morphologies compared again to experimental observations.

The transport mechanisms discussed in chapter 5.1, are not necessarily comparable due to lattice rearrangements experienced at the surface. Thus, it would be interesting to consider transport of defect ions near the surface using the NEB migration methods discussed in chapter 5.1. This would enable a better idea of the trapping effect and likelihood of segregation of species to the surfaces of FAp.

In parallel to the results produced in this thesis for FAp, the same simulations could be applied to the β -TCP structure to obtain a fuller understanding of the surface. The interface between FAp and β -TCP could then be investigated. Understanding the interface and its response to radiation damage, defect immobilisation and partitioning would be very interesting as the stability of the two phases in a multi-phase waste form is not completely understood.

Finally, it is guaranteed that at some point the waste form will come in contact with water. Most ceramics in this situation form surface hydroxide species (as mentioned above); and additional water could cause dissolution of the mineral. There are a variety of models for surface water that will have to be critically assessed. MD simulations of water interacting with the surfaces of FAp and β -TCP will be somewhat challenging, but will provide further steps towards a better understanding of the durability of a multi-phase waste form, formed from FAp and β -TCP.

Publications

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