Chapter 5

Computer modelling of rutile-liquid trace element partitioning: implications for the fate of HFSE in subduction zones
Abstract

The exceptionally large range in reported rutile/melt and rutile/fluid partition coefficients ($D$ values) complicates their application to geochemical models of subduction zone magmatism. Here, we use classical and first principles molecular simulations to shed light on the mechanisms and energetics of trace element incorporation into rutile relative to melt- and aqueous fluid-like environments.

Using computed solution energies of tetravalent ions substituting for titanium in TiO$_2$-rutile, we demonstrate that both modelling methods constrain the optimum ionic radius $r_0$ of substituents close to that of the anticipated value ($r_0$ $\approx$ $r_{Ti}$ = 0.605 Å). The radius derived from first principles simulations (0.60 Å) more closely resembles that of the displaced host cation than the classically derived value (0.66 Å). Relative solution energy differences between elements qualitatively resemble measured partition coefficient trends in rutile that show $D_{U}$ > $D_{Th}$ and $D_{Hf}$ > $D_{Zr}$. In contrast to results from rutile-melt solution energies, simulations combining ion exchange in rutile with hydration enthalpies and gas-phase total energies show that small cations preferentially partition into the fluid while large cations are energetically more favourable in rutile. In addition, the variation between elements is much larger.

We show that trivalent elements may charge-compensate the incorporation of pentavalent ions (Nb, Ta, V, Pa) with an optimum trivalent ionic radius close to Sc and Lu. Results show the difference between Nb and Ta solution energies in rutile compared to a melt-like environment are negligibly small. Comparing the energy difference between Nb and Ta in relation to a hypothetical aqueous fluid shows the smaller cation (Ta) is on average $427\pm4$ kJ mol$^{-1}$ more favourably incorporated in rutile than Nb, indicating fluids have a stronger potential to fractionate Nb from Ta than melts.

Using Bader-partitioning of the charge density, we are able to show that atomic charges and radii of tetravalent defects are different in rutile compared to values obtained for the elemental bulk phases. All tetravalent defects studied have a charge larger than that of the host (titanium), that is charge-balanced by a mechanism involving polarisation of the octahedral oxygen atoms in combination with charge reduction of non-nearest neighbour titanium atoms. This demonstrates the power of quantum-chemical over classical simulations to rationalise trace element partitioning data, and provides a first step towards truly atomic-scale models of mineral-liquid partitioning.
Chapter 5

Introduction

The high field strength element (HFSE, Ti, Zr, Hf, Nb, Ta, W, Th) signatures of major terrestrial reservoirs such as continental crust, mid-ocean ridges, ocean islands and subduction zones provide first-order constraints on the chemical and physical mechanisms responsible for their origin and evolution (Ryerson and Watson 1987; Brenan et al. 1994; Salters and Longhi 1999; Kamber and Collerson 2000; Klemme et al. 2002; Rapp et al. 2003; Münker et al. 2004; Klemme et al. 2005; Xiong 2006; Pfänder et al. 2007; Ireland et al. 2009; Takamura et al. 2009; Fulmer et al. 2010; Nebel et al. 2010). In subduction-derived volcanic rocks, HFSE are generally depleted relative to other incompatible trace elements such as the large-ion lithophile elements (LILE, e.g. Rb, Pb, Sr, Ba, Cs). The cause of this relative depletion is subject of intense debate. It is thought to be the result of either dehydration reactions in subducting slabs, partial melting of the mantle wedge or melting of the subducting slab (Foley et al. 2000 and references therein).

Deciphering which of these processes dominates is crucial for the development of more realistic models of subduction zone thermal structures, small-scale transport pathways, and large-scale chemical differentiation in the Earth. To assess the extent to which these processes are responsible for the observed HFSE depletion, quantitative information is needed concerning the mineral-melt and mineral-fluid partitioning behaviour of the HFSE, as well as the solubility of HFSE-bearing minerals.

Models of HFSE retention usually involve a mechanism associated with residual titanium-rich minerals that remain immobile during fluid or melt generation. Titanium-bearing minerals such as ilmenite (e.g. (Fe,Mg)TiO$_3$), titanium-perovskite (CaTiO$_3$) or titanite (CaTiSiO$_5$) are likely candidates to host, and thereby possibly retain HFSE. Rutile (TiO$_2$) has also attracted considerable attention because its strong affinity for HFSE is combined with high durability during fluid fluxing or partial melting of the subducting oceanic lithosphere (Green and Pearson 1986; Ryerson and Watson 1987; Peacock 1990; Ayers and Watson 1991; Ayers and Watson 1993; Brenan et al. 1994; Poli and Schmidt 1995; Keppler 1996; Foley et al. 2000; Audétat and Keppler 2005; Kessel et al. 2005; Klemme et al. 2005; Tropper and Manning 2005; Antignano and Manning 2008).

However, recent observations from both subduction-related rocks in high-pressure metamorphic terranes (Sorensen and Grossman 1989; Selverstone et al. 1992; Scambelluri et al. 2001; Zack et al. 2002; Rubatto and Hermann 2003; John et al. 2008; Schmidt et al. 2008; Zhang et al. 2008; Beinlich et al. 2010), solubility experiments (Antignano and Manning 2008; Manning et al. 2010; Rapp et al. 2010), and first principles computer simulations (van Sijl et al. 2009; van Sijl et al. 2010) have revealed a much more complex picture, that weakens the argument that rutile is a wholly immobile phase.

Rutile is the most common natural polymorph of TiO$_2$. Under relevant geological conditions, titanium is present in rutile in a tetravalent oxidation state (Waychunas 1987; Brenan et al. 1994; Watson and Harrison 2005; Watson et al. 2006). Titanium is six-fold coordinated by oxygen in a slightly distorted octahedral geometry (Figure 5-1) in a tetragonal (P4$_2$/mmm) unit cell (Vegard 1916; Bokhimi et al. 2002). Rutile in eclogites at ~1 modal percent level has the potential to control more than 90% of the whole rock Ti, Nb, Ta, Sb and W (Zack et al. 2002).

Published rutile/melt HFSE partition coefficients ($D_{HFSE}$ defined as concentration
Figure 5-1. Unit cell of rutile-$\text{TiO}_2$ (a,b=4.591 Å, c=2.954 Å, $\alpha, \beta, \gamma$=90°, this study). Each titanium atom is surrounded by six oxygen atoms in a slightly distorted octahedral coordination, depicted by yellow shading.

Figure 5-2. Compilation of (a) rutile-melt and (b) rutile-fluid trace element partition coefficients from literature sources (see Table 5-1 and Table 5-2 for a summary)
ratios by weight between rutile and co-existing melt) show a wide range of values (Table 5-1, Figure 5-2). Data for Nb vary between 0.7 – 540 and for Ta they range from 2 - 210 (Table 5-1). Moderately compatible are Zr (0.57 – 8.8), Hf (0.93 – 12.0) and U (0.2 – 3.8), whereas thorium, the rare earth elements (REE) and LILE (Rb, Sr, Ba) are incompatible. Rutile/aqueous-fluid partition coefficients, summarised in Table 5-2, again show an enormous range, and generally display an even higher affinity for rutile of Nb (38-484) and Ta (41-2400), and to a lesser extent Zr (2.7-206) and Hf (3.9-94). Tantalum is more compatible in rutile relative to niobium and Nb/Ta ratios in rutile are between 0.61 and 1.02, depending on melt composition. Partition coefficient ratios are between 0.41 and 1.00 (Schmidt et al. 2004).

The exceptionally large range in reported rutile/melt and rutile/fluid partition coefficients for individual elements as well as element ratios complicates application of $D$ values to geochemical models of subduction zone magmatism. Although it is clear that $D$ values are thermodynamic variables changing with pressure, temperature and composition, these variables alone do not provide an explanation for the large range in published $D$ values. The effects of complexation reactions with ligands such as chloride or fluoride dissolved in aqueous fluids or melts on rutile/liquid partitioning are currently particularly poorly quantified. It has been noted that the local environment surrounding trace elements in melts can have a major impact on partition coefficients (van Westrenen et al. 2001; Linnen and Keppler 2002; O’Neill and Egger 2002; Blundy and Wood 2003b; Schmidt et al. 2006). For example, Schmidt and co-workers (2004) observe that with increasing melt polymerization, the partitioning of Nb and Ta in rutile relative to melts increases by almost an order of magnitude, possibly due to the decreased availability of non-bridging oxygens to accommodate these elements in the melt. Similarly, the effect of ligands in solution could partly account for the local (re-)mobilization of nominally insoluble HFS elements observed in high-pressure rocks exposed at the surface.

Explanations for differences in $D$ values between elements at the same conditions are also plentiful. For example, the higher affinity for Ta relative to Nb in rutile has been rationalised in various ways:

1. Differences in electronic polarisability of Ta relative to Nb and a larger covalent character of Nb relative to Ta (Horng and Hess 2000).
2. A slight difference in ionic radii between octahedrally coordinated Ta$^{5+}$ (0.64 Å) and Nb$^{5+}$ (0.66 Å) (Tiepolo et al. 2000), which, oxidation state being equal, converts to a slightly higher charge density of Ta compared to Nb (Schmidt et al. 2004).
3. Non-equilibrium and kinetic effects; e.g. a significantly higher mobility of Nb compared to Ta in rutile (Dohmen et al. 2009).

Incorporation mechanisms for HFSE in rutile are also debated. Tetravalent ions substitute readily for Ti$^{4+}$ in rutile as there are no charge balance constraints. The incorporation of pentavalent Nb and Ta in rutile is thought to be accommodated by charge-balancing mechanisms involving trivalent counter-ions, or by a Ti vacancy mechanism with or without the involvement of divalent cations (Horng and Hess 2000). The concentrations of trivalent and divalent ions in natural rutile are larger than required for charge balancing Nb and Ta by such mechanisms, and are likely not a limiting factor for pentavalent ion solubility in rutile (Schmidt et al. 2004).
Table 5-1. Experimental rutile-melt partition coefficients summary from literature sources. Where more than one datapoint exists, a range of values is given. *Increasing aluminium saturation index (ASI).

<table>
<thead>
<tr>
<th>Reference</th>
<th>System</th>
<th>P (kbar)</th>
<th>T (°C)</th>
<th>Zr</th>
<th>Hf</th>
<th>Nb</th>
<th>Ta</th>
<th>Th</th>
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Table 5-2. Experimental rutile-fluid (H$_2$O) partition coefficients summary from literature sources. Where more than one data point exists, a range of values is given.

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Computer models of trace element incorporation

Many explanations for observed differences in element partitioning behaviour originate from Goldschmidt’s predictions regarding the importance of the size and valence of cations in controlling trace element incorporation at a specific lattice site in a mineral (Goldschmidt 1927). Although valence is not taken into account directly, the lattice strain model (Brice 1975; Beattie 1994; Blundy and Wood 1994) has often been used to rationalise Goldschmidt’s predictions. This model is based on the elastic response of the crystal upon insertion of a defect with a different effective size relative to the lattice site on which substitution occurs. It relates the strain energy \( U_{\text{strain}} \) to the optimum radius \( r_0 \), the site apparent Young’s modulus \( E_x \) and size misfit \( r_i - r_0 \):

\[
U_{\text{strain}} = 4\pi E_x N_A \left[ \frac{1}{2} r_0 (r_i - r_0)^2 + \frac{1}{3} (r_i - r_0)^3 \right]
\]

where \( N_A \) is Avogadro’s constant.

Under the assumption that the strain energy dominates the free energy change upon exchanging major and trace elements between mineral and co-existing liquid, the partition coefficient \( D_i \) of element \( i \) can be written as:

\[
D_i = D_0 \exp\left( -\frac{\Delta G_{\text{crystal}}}{RT} \right) = D_0 \exp\left( -\frac{-4\pi E_x N_A \left[ \frac{1}{2} r_0 (r_i - r_0)^2 + \frac{1}{3} (r_i - r_0)^3 \right]}{RT} \right)
\]

with the maximum \( D \) corresponding to \( D_0 \), the strain-compensated partition coefficient at the lattice site of interest, yielding the approximate parabolic dependence of \( D_i \) on ionic radius as first noted by Onuma and co-workers (Onuma et al. 1968). Empirical modelling of trace element partitioning is thus readily accomplished by fitting isovalent trace element partitioning data with only three parameters and, optionally, as a function of any intensive variable (Blundy and Wood 1994; Wood and Blundy 1997; van Westrenen et al. 1999).

Computer simulations can be used to provide an atomic-scale picture of these processes (e.g. Allan et al. 2001 and references therein). By comparing the energies of the perfect lattice with that of the defective lattice, the energetic cost or gain of trace element insertion can be determined. Because crystal lattices are more ordered and rigid compared to melts or aqueous fluids, they will be less tolerant of misfit cations. Hence, it is often assumed that the local environment in a crystal lattice dominates the energetics of partitioning. However, to make a connection between measured partition coefficients and computer simulations, the effect of element exchange in the melt or aqueous fluids has to be incorporated. Commonly, a simple binary oxide model is used to simulate the local melt environment and to provide a first-order estimate for the energetic difference between the exchanged ion pair in the form of solution energies. Although this method does not explicitly yield absolute values for partition coefficients, it has proven to be a valuable tool to evaluate and rationalise experimental trace element data in many mineral-melt systems (e.g. Blundy and Wood 1994; Purton et al. 1996; Purton et al. 1997a; van Westrenen et al. 2000; Allan et al. 2003; Blundy and Wood 2003b; van Westrenen et al. 2003; van Kan Parker et al. 2010).

Here, we perform detailed computer simulations of trace element substitutions in rutile to...
provide new insights into rutile-melt and rutile-fluid partitioning. Using classical ionic model simulations with such highly charged ions may be problematic since the covalent contributions to the bonding are more important than for cations with lower charge. Therefore, the results of simulations based on classical mechanics are compared to results from first principles simulations (density functional theory) to establish a full quantum mechanical picture of trace element incorporation at the atomic scale. With the necessary approximations of local environments in melts and fluids, we establish an atomistic simulation analogue to trace element partitioning between rutile and liquids in the static limit.
Technical details of the simulations

Classical simulations

Static lattice energy calculations based on the Born ionic model of solids (Born and Mayer 1932) use interatomic potential functions to describe the non-Coulombic contributions to the energy of a system in terms of the atomic coordinates. Ions are assigned formal charges in accordance with usual chemical rules. The short-range interactions are described with an internally consistent set of two-body Buckingham interatomic potentials of the form \( \phi(r_{ij}) = A \cdot \exp(-r_{ij}/\rho) - C/r_{ij}^6 \), where \( A \) and \( \rho \) determine the Pauli repulsion between two ions \( i \) and \( j \) separated by a distance \( r \) with a cutoff distance of 15 Å, and \( C \) determines the attractive dispersion interaction term. Interactions involving tetrahedrally coordinated silicon include a three-body O-Si-O bond-bending term \( \frac{1}{2}k_B(\theta - \theta_0)^2 \), where \( (\theta - \theta_0) \) is the deviation from the ideal tetrahedral angle (109.47°) and \( k_B \) is the corresponding harmonic force constant.

Long-range coulombic interactions are summed using the Ewald technique (Ewald 1921). The electronic polarisability of the oxygen atoms is described with the shell model of Dick and Overhauser (1958), dividing the ion in a core and a massless “shell” coupled by a harmonic spring with force constant \( k_B \). The simulations are performed with the General Utility Lattice Program (GULP, Gale 1997; Gale and Rohl 2003; Gale 2005).

Interatomic potentials for Nb and Ta

Two new potentials for Nb\(^{5+}\) and Ta\(^{5+}\) were developed. Following Donnerberg \textit{et al.} (1989) and Jackson \textit{et al.} (2005), we fit the \( A \) and \( \rho \) parameters of the Nb-O Buckingham potential to the crystal structures of LiNbO\(_3\) (Hsu \textit{et al.} 1997), Li\(_2\)O (Zintl \textit{et al.} 1934) and Nb\(_2\)O\(_5\) (Ercit 1991) simultaneously, and include a bond-bending term. The potential for Ta\(^{5+}\) is obtained by a fitting setup identical to that for Nb\(^{5+}\), but using KTaO\(_3\) (Zhurova \textit{et al.} 2000), K\(_2\)O (Zintl \textit{et al.} 1934) and Ta\(_2\)O\(_5\) (Zibrov \textit{et al.} 2000) as the bases for fitting. The fitting runs make use of the Davidon-Fletcher-Powell (DFP, Fletcher and Powell 1963) updating scheme for the Hessian matrix and were performed at constant pressure and in the static limit (0 K in the absence of lattice vibrations). Rational Functional Optimisation (RFO, Banerjee \textit{et al.} 1985) was used to accelerate convergence towards the end of the optimisation (defined as the point where the root mean square energy gradient falls below 0.001), while at the same time verifying that the Hessian has the required structure. The shell positions and radii were both optimised during fitting. As there are no obvious physical grounds to use a polarisable shell model, Nb and Ta were treated as rigid non-polarisable ions.

The full set of interatomic potentials used in this work is given in Table 5-3. It is consistently based on the oxygen-oxygen potential of Catlow, Lewis and co-workers (Catlow \textit{et al.} 1982; Lewis and Catlow 1985) and has previously been applied in static lattice energy simulations of trace element incorporation into a variety of silicates and oxides (see for example Blundy and Wood 1994; van Westrenen \textit{et al.} 2000; Corgne \textit{et al.} 2003; van Kan Parker \textit{et al.} 2010).
### Table 5-3. Interatomic potential parameters used in this study

<table>
<thead>
<tr>
<th>Element</th>
<th>Element</th>
<th>$q_{ion}$</th>
<th>$A$ (eV)</th>
<th>$\rho$ (Å)</th>
<th>$C$ (eV Å$^6$)</th>
<th>Cutoff (Å)</th>
<th>Ref.</th>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Sc 3+</td>
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<td>15.0</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr 3+</td>
<td>Cr 3+</td>
<td>1734.100</td>
<td>0.3010</td>
<td>15.0</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe 3+</td>
<td>Fe 3+</td>
<td>1102.400</td>
<td>0.3299</td>
<td>15.0</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>Y 3+</td>
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<td>0.3491</td>
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<tr>
<td>La 3+</td>
<td>La 3+</td>
<td>1439.700</td>
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<td></td>
<td></td>
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<tr>
<td>Lu 3+</td>
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<td></td>
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<td>Hf 4+</td>
<td>1454.600</td>
<td>0.3500</td>
<td>15.0</td>
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<td>Ce 4+</td>
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<td>Tb 4+</td>
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<td>Th 4+</td>
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<td>0.3949</td>
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<td>Sn 4+</td>
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<td>V 4+</td>
<td>V 4+</td>
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<tr>
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<td>1283.909</td>
<td>0.3205</td>
<td>10.6545</td>
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<tr>
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<td>1218.6325</td>
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<tr>
<td>Ta 5+</td>
<td>Ta 5+</td>
<td>1026.8046</td>
<td>0.3765</td>
<td>15.0</td>
<td>*</td>
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<tr>
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<td>O 2-</td>
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<td>27.8800</td>
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#### Three-body potential

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<th>$\Theta_0$ (°)</th>
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<tr>
<td>O-Si-O</td>
<td>2.094</td>
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<tr>
<td>O-Nb-O</td>
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<td>90</td>
</tr>
<tr>
<td>O-Ta-O</td>
<td>0.5776</td>
<td>90</td>
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#### Core-shell potential

<table>
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<th>$q_{core}$</th>
<th>$q_{shell}$</th>
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<td>O$<em>{core}$ - O$</em>{shell}$</td>
<td>74.92356</td>
<td>0.86902</td>
<td>-2.86902</td>
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*Buckingham potential describing the cation-oxygen interaction.

**Point defects**

Two widely used methods for introducing point defects (trace elements and/or vacancies) in the simulations were tested:

1. An embedded cluster method treating an inner region (I) around the defective site explicitly and estimating the interactions contributing from a second region (II) further away via an intermediate region (IIa) (Mott-Littleton approximation, Mott and Littleton 1938; Hardy and Lidiard 1967; Lidiard 1989). All embedded cluster calculations in the rutile system employ a radius of 10.0 Å for region 1 and 16.0 Å for region 2. This is equivalent to 599 and 1988 atoms respectively with a 2a region consisting of 298 atoms. Resulting defect energies are converged to better than 0.01 eV.

2. The supercell approach, i.e. a periodic lattice consisting a non-primitive unit cells containing one or more defects. At little extra computational expense, we determine the effect of supercell size on computed energies, and compare these to energies obtained with the embedded cluster method. Successively larger supercells were investigated \((X_{2-4} \times Y_{2-4} \times Z_{2-6})\,\text{subscript denotes the unit cell multiplier in the X, Y or Z direction})\. Results show that a 3×3×3 supercell reproduces the embedded cluster energies of isovalent point defects in \(\text{TiO}_2\)-rutile to within 1.3‰, depending on the defect type.

Both approaches are difficult to extend beyond the static limit (Allan et al. 2001). It has been shown however, that defect energies obtained this way are a good approximation to defect enthalpies at elevated temperatures (Taylor et al. 1997).

**Quantum mechanical simulations**

The interatomic potential based methods mentioned above do not consider electrons explicitly, and their success requires the development of accurate and transferable interatomic potentials. The goal of electronic structure methods is to solve the Schrödinger equation approximately for the system of interest, and evaluate the resulting total energies, forces and other quantities of interest. To include the electrons explicitly and keep the problem at hand computationally tractable, density functional theory (DFT) has proven to be a powerful tool. DFT relies on the insight of Hohenberg and Kohn (1964) that the ground state electronic energy is determined completely by the electron density. The framework of Kohn and Sham (1965) further reduces the many-body problem of interacting electrons to one that relies on the electron density through the use of functionals of the electron density which describe the exchange and correlation contributions to the total energy.

Here, we rely on the gradient-corrected method (GGA) to include the exchange and correlation energies dependent on the electron density and its derivative using Perdew and Wang’s (PW91) exchange correlation functional (Becke 1988; Perdew et al. 1992; Perdew et al. 1996). Interpolation of the correlation part of the exchange correlation functional is accomplished with the formulation by Vosko, Wilk and Nusair (Vosko et al. 1980).

Core (i.e. non-valence) electrons of the atoms are usually replaced with an effective potential (pseudopotential). Here, we formally retain all the core electrons by performing...
simulations that employ the projector augmented wave (PAW) method (Blöchl 1994; Kresse and Joubert 1999), as implemented in the Vienna \textit{ab-initio} simulation package (VASP) (Kresse and Hafner 1993; Kresse and Furthmüller 1996). The smaller core radii of the PAW potentials and the exact reconstruction of the valence wavefunction including the core region, make PAW potentials generally more accurate than pseudopotential-based approaches (Blöchl 1994; Kresse and Joubert 1999). The details of the PAW potentials used here are given in Table 5-4. Several parameters were investigated \textit{a priori} to study their effect on the accuracy and precision of the computations. The objective of this investigation was to obtain:

(a) An optimal representation of structures and energies of the binary oxides of many different elements throughout the periodic system.

(b) A computationally feasible supercell size from which energies can be compared directly to the energetics of binary oxide structures (i.e. the same parameters throughout all reported computations).

The cut-off energy for the plane-wave basis set is 400 eV and the energy cut-off for augmentation charges, which are evaluated on a second, finer grid at a relatively small computational cost, is 750 eV. Spin polarisation effects are also accounted for. The Brillouin-zone integrals are calculated using the tetrahedron method with Blöchl corrections (Blöchl et al. 1994). Special \textit{k}-point positions for sampling the Brillouin zone are automatically determined from a shifted 6×6×9 Monkhorst-Pack \textit{k}-points mesh (Monkhorst and Pack 1976; Moreno and Soler 1992). This results in a total of 162 special \textit{k}-points for the reported supercells and binary-oxide structures based on TiO$_2$-rutile (P4$_2$/mnm). Calculations involving trivalent –and pentavalent elements use a non-shifted 6×6×9 \textit{k}-point mesh resulting in 164 irreducible \textit{k}-points per rhombohedral (R-3cR/R3cR) primitive unit cell.

The wavefunction is initialised randomly and subsequently optimised with the residual vector minimisation direct inversion in the iterative subspace algorithm (RMM-DIIS) of Kresse and Furthmüller (1996) converged to values better than 10$^{-4}$ eV. The cell shape, cell volume and ions are relaxed with a quasi-Newton algorithm that uses the forces and stress tensor to determine the equilibrium shape and positions to the point where forces on the atoms converged to better than 10$^{-3}$ eV/Å. Because of changes in cell dimensions, the final basis set might not be isotropic leading to spurious effects on the final energies. Therefore, all energies reported are computed from an additional wavefunction optimisation taking the final relaxed geometry as input. The residual external pressure of the supercells at the end of the relaxations involving isovalent point defects is in the range of -0.53 to 0.02 kbar, with typical absolute values less than 0.02 kbar. However, it must be noted that due to plane-wave basis set incompleteness upon volume changes, a residual stress exists unless absolute convergence with respect to the basis set has been achieved. The so-called “Pulay stress” that remains after the final energy optimisation (i.e. after obtaining final energies with an isotropic basis set) is in the range -4.63 to 1.91 kbar. This is considered to be sufficiently low to allow further use of the resulting energies without additional compensation for the Pulay stress.

The computational strategy outlined above results in energies of pure TiO$_2$-rutile better than -3.6 kJ mol$^{-1}$ compared to calculations with a 50 eV higher cutoff. The chosen \textit{k}-point sampling yields binary oxide energies converged to less than -1 kJ mol$^{-1}$ (at the given plane-wave and augmentation charge cut-offs).
To simulate the local environment of elements in aqueous fluids, we compute hydration enthalpies of ion-water clusters according to the scheme detailed in van Sijl et al. (2009). Tetravalent and pentavalent atoms are described with the revised basis sets for the LANL Hay-Wadt relativistic effective core potentials (LANL08, Wadt and Hay 1985; Roy et al. 2008), which were obtained for use with Gaussian03W from the Basis Set Exchange (BSE) software and the EMSL Basis Set Library (Feller 1996; Schuchardt et al. 2007). We take the energy-consistent set of effective core potentials (ECP's) derived by Dolg et al. (1989; 1993) to describe the electronic structure of lanthanide-water clusters. The latter ECP's replace a Kr[4d\(^{10}\),4f\(^{1}\)] electronic core configuration, where \(i\) takes values from 0-14 for the lanthanides (La-Lu). For all elements, 6-311++G(d,p) standard basis sets were used for the hydrogen and oxygen atoms (Ditchfield et al. 1971; Harihara

### Table 5-4.

<table>
<thead>
<tr>
<th>Element</th>
<th>Core radius (Å)</th>
<th>electronic configuration</th>
<th>(n)(_{\text{valence}})</th>
<th>(n)(_{\text{core}})</th>
<th>(n)(_{\text{total}})</th>
</tr>
</thead>
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<tr>
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<td>4</td>
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\*electronic groundstate of the bulk atom used to generate the pseudopotential

### Molecular Orbital Calculations

To simulate the local environment of elements in aqueous fluids, we compute hydration enthalpies of ion-water clusters according to the scheme detailed in van Sijl et al. (2009). Tetravalent and pentavalent atoms are described with the revised basis sets for the LANL Hay-Wadt relativistic effective core potentials (LANL08, Wadt and Hay 1985; Roy et al. 2008), which were obtained for use with Gaussian03W from the Basis Set Exchange (BSE) software and the EMSL Basis Set Library (Feller 1996; Schuchardt et al. 2007). We take the energy-consistent set of effective core potentials (ECP’s) derived by Dolg et al. (1989; 1993) to describe the electronic structure of lanthanide-water clusters. The latter ECP’s replace a Kr[4d\(^{10}\),4f\(^{1}\)] electronic core configuration, where \(i\) takes values from 0-14 for the lanthanides (La-Lu). For all elements, 6-311++G(d,p) standard basis sets were used for the hydrogen and oxygen atoms (Ditchfield et al. 1971; Harihara
and Pople 1973).

Geometries were optimised accounting for long-range interactions according to the polarisable continuum model (Cossi et al. 2002) using pure water (dielectric permittivities $\varepsilon_0=78.39$, $\varepsilon_\infty=1.776$, solvent radius 1.385 Å) at 298.15 K with a solvent-dependent electrostatic scaling factor (1.2 for water) (see for instance Curutchet et al. 2003). All simulations employed Becke’s three parameter hybrid exchange functional (Becke 1993) combined with the correlation functional by Perdew and Wang (B3PW91, Perdew and Wang 1992). Simulations were performed on a pruned ultrafine grid yielding converged electronic energies to less than a microhartree (~2.7·10^{-5} eV). Frequency calculations, gas-phase binding energies and solvation energies were calculated using B3PW91 DFT with the software package Gaussian03W (Frisch et al. 2005).
Results and Discussion

Rutile-melt trace element partitioning model

Structures and energetics

The calculated lattice parameters for pure oxides of all elements listed in Table 5-3 (GULP) and Table 5-4 (VASP) are given in Table 5-5, together with experimental values. Simulated oxides (rutile structure) based on classical interatomic potentials (GULP) show reasonably good agreement with experimentally determined lattice parameters (reproduced to within approximately 5.4 per cent), with the exception of vanadium-oxide. The unit-cell volume of TiO$_2$-rutile is slightly overestimated by 3.2 Å$^3$, mostly due to poor representation of the lattice vector $c$ (6.6 per cent too large). More advanced interatomic potentials exist to describe the Ti-O interaction in titanium-oxides, either aiming at a more accurate description of the structure and elastic moduli of rutile (e.g. Swamy and Gale 2000), or more tuned towards fitting its dielectric properties (e.g. Ogata et al. 1999). For consistency, we adopt the simplest interatomic potential whose precision and method of derivation is the same as that of other interatomic potentials listed in Table 5-3, all based on the O$^2-$-O$^2-$ potential of Lewis and Catlow (1985).

Density functional theory (DFT) calculations performed with VASP making use of the PAW potentials (Table 5-4) reproduce the experimental TiO$_2$ geometry very well. The unit-cell volume is underestimated by only 0.55%, with very good representation of the $c$ direction (-0.08% compared to experiment) contrary to the classical potential method. The small difference may be rationalised in part by the absence of temperature and lattice vibrations in our simulations. Two TiO$_2$ supercells were constructed taking the simulated unit cells (Figure 5-1 on page 92) as structural bases. A 3×3×3 (162 atoms) cell was used for simulations performed with GULP and a 2×2×2 (48 atoms) supercell was used for DFT simulations (Figure 5-3). Isovalent trace elements substitute for the titanium atom. The system is fully relaxed optimising the unit cell and all atomic positions without symmetry constraints. The exchange reaction is written as:

$$\text{Ti}_n\text{O}_{2n} + M^{4+} \rightleftharpoons M_n\text{Ti}_{1-n}\text{O}_{2} + \text{Ti}^{4+}\quad (3)$$

The defect formation energies, $E_{\text{defect}}$, in the static limit and at zero pressure are given by:

$$E_{\text{defect}} = E_{\text{lat}}(M_n\text{Ti}_{1-n}\text{O}_{2}) - E_{\text{perfect}}(\text{Ti}_n\text{O}_{2}) + nE_{\text{Ti}}^{4+} - nE_{\text{M}}^{4+}\quad (4)$$

where $E_{\text{perfect}}$ and $E_{\text{lat}}$ are the computed total energies of the perfect and defective super cells. $E_{\text{Ti}}^{4+}$ and $E_{\text{M}}^{4+}$ denote the total energies of the isolated ions. The last two terms vanish in classical simulations, and only have to be accounted for in the first principles calculations. As the total energies reported in VASP already include the atomic energy of the reference state of the PAW potential (see electronic configuration in Table 5-4), we include experimental ionization energies taken from (Lide 2003) to correctly include the last two terms in equation 4. For Th, U and Pa, the
ionization energies were also computed from simulations on single atoms in a 10 Å³ simulation box at the gamma point. The computed and experimental ionization energy of Th differ by < 5%, which adds to our confidence that for our purpose, computations and experimental energies can be combined.

The calculated defect formation energies from both classical and DFT simulations are shown in Figure 5-4. In classical simulations, the defect energies show a roughly linear increase with ionic radius, with negative defect energies for cations with a smaller radius than that of the displaced host ion ($r_{\text{Ti}}=0.605$ Å). Defect energies based on DFT calculations show a similar trend compared to GULP results, but defect energies of larger cations are more positive. These large differences (on the order of a few eV) may be due to the problematic representation of covalent bonding terms with classical potentials.

Defect energies as defined by eqs. 3 and 4 do not fully cover the exchange reaction between minerals and liquids, but instead refer to a reservoir of ions at infinite distance from the supercell. In processes that (re-)distribute elements between minerals and melts, a starting point to properly take into account the melt is to assume that the local environment surrounding the
Table 5-5. Comparison between calculated (GULP, VASP) and experimental lattice parameters of binary oxides in the rutile, corundum, and fluorite structures.

<table>
<thead>
<tr>
<th>Rutile ($P4_2/mnm, Z=2$)</th>
<th>GULP</th>
<th>VASP</th>
<th>Exp</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>IR a (Å)</td>
<td>a (Å)</td>
<td>c (Å)</td>
<td>V (Å³)</td>
</tr>
<tr>
<td>Ge</td>
<td>0.870</td>
<td>5.027</td>
<td>3.569</td>
<td>90.199</td>
</tr>
<tr>
<td>Ge</td>
<td>0.530</td>
<td>4.257</td>
<td>3.019</td>
<td>54.712</td>
</tr>
<tr>
<td>Hf</td>
<td>0.710</td>
<td>4.716</td>
<td>3.364</td>
<td>74.832</td>
</tr>
<tr>
<td>Si</td>
<td>0.400</td>
<td>4.016</td>
<td>2.785</td>
<td>44.921</td>
</tr>
<tr>
<td>Sn</td>
<td>0.690</td>
<td>4.707</td>
<td>3.333</td>
<td>73.852</td>
</tr>
<tr>
<td>Tb</td>
<td>0.760</td>
<td>4.879</td>
<td>3.455</td>
<td>82.252</td>
</tr>
<tr>
<td>Th</td>
<td>0.940</td>
<td>5.190</td>
<td>3.691</td>
<td>99.415</td>
</tr>
<tr>
<td>U</td>
<td>0.890</td>
<td>5.080</td>
<td>3.609</td>
<td>93.150</td>
</tr>
<tr>
<td>Pa</td>
<td>0.900</td>
<td>n.c.</td>
<td>n.c.</td>
<td>n.c.</td>
</tr>
<tr>
<td>V</td>
<td>0.580</td>
<td>4.234</td>
<td>3.852</td>
<td>69.053</td>
</tr>
<tr>
<td>Zr</td>
<td>0.720</td>
<td>4.731</td>
<td>3.358</td>
<td>75.145</td>
</tr>
<tr>
<td>Ti</td>
<td>0.605</td>
<td>4.570</td>
<td>3.151</td>
<td>65.816</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Corundum (R-3c, Z = 6)</th>
<th>GULP</th>
<th>VASP</th>
<th>Exp</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>IR  a (Å)</td>
<td>a (Å)</td>
<td>c (Å)</td>
<td>V (Å³)</td>
</tr>
<tr>
<td>Cr</td>
<td>0.615</td>
<td>5.014</td>
<td>13.170</td>
<td>286.674</td>
</tr>
<tr>
<td>Fe</td>
<td>0.645</td>
<td>5.060</td>
<td>13.368</td>
<td>296.420</td>
</tr>
<tr>
<td>Sc</td>
<td>0.745</td>
<td>5.294</td>
<td>13.959</td>
<td>338.746</td>
</tr>
<tr>
<td>Y</td>
<td>0.900</td>
<td>5.701</td>
<td>15.035</td>
<td>423.120</td>
</tr>
<tr>
<td>La</td>
<td>1.032</td>
<td>6.117</td>
<td>16.129</td>
<td>522.717</td>
</tr>
<tr>
<td>Lu</td>
<td>0.861</td>
<td>5.578</td>
<td>14.710</td>
<td>396.427</td>
</tr>
<tr>
<td>Nb'</td>
<td>0.640</td>
<td>5.244</td>
<td>13.190</td>
<td>314.091</td>
</tr>
<tr>
<td>Ta'</td>
<td>0.625</td>
<td>5.251</td>
<td>13.118</td>
<td>313.209</td>
</tr>
</tbody>
</table>
Fluorite (*Fm-3m, Z=4*)

<table>
<thead>
<tr>
<th>Element</th>
<th>IR' (Å)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>0.970</td>
<td>5.447</td>
<td>-</td>
<td>161.648</td>
<td>n.c.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>5.411 -</td>
</tr>
<tr>
<td>Ge</td>
<td>n.a.</td>
<td>4.613</td>
<td>-</td>
<td>98.135</td>
<td>n.c.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>n.a. -</td>
</tr>
<tr>
<td>Hf</td>
<td>0.830</td>
<td>5.096</td>
<td>-</td>
<td>132.353</td>
<td>n.c.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>5.063 -</td>
</tr>
<tr>
<td>Si</td>
<td>n.a.</td>
<td>4.619</td>
<td>-</td>
<td>98.535</td>
<td>n.c.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>4.520 -</td>
</tr>
<tr>
<td>Sn</td>
<td>0.810</td>
<td>5.103</td>
<td>-</td>
<td>132.904</td>
<td>n.c.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>4.993 -</td>
</tr>
<tr>
<td>Tb</td>
<td>0.880</td>
<td>5.292</td>
<td>-</td>
<td>148.171</td>
<td>n.c.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>5.220 -</td>
</tr>
<tr>
<td>Th</td>
<td>1.050</td>
<td>5.616</td>
<td>-</td>
<td>177.148</td>
<td>5.577</td>
<td>-</td>
<td>173.489</td>
<td>5.600 -</td>
</tr>
<tr>
<td>U</td>
<td>1.000</td>
<td>5.503</td>
<td>-</td>
<td>166.622</td>
<td>5.344</td>
<td>-</td>
<td>152.631</td>
<td>5.468 -</td>
</tr>
<tr>
<td>V</td>
<td>0.720</td>
<td>4.757</td>
<td>-</td>
<td>107.650</td>
<td>n.c.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>n.a. -</td>
</tr>
<tr>
<td>Zr</td>
<td>0.840</td>
<td>5.127</td>
<td>-</td>
<td>134.745</td>
<td>5.112</td>
<td>-</td>
<td>133.568</td>
<td>5.128 -</td>
</tr>
<tr>
<td>Ti</td>
<td>0.740</td>
<td>4.915</td>
<td>-</td>
<td>118.748</td>
<td>n.c.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>n.a. -</td>
</tr>
<tr>
<td>Li'</td>
<td>0.760</td>
<td>4.690</td>
<td>-</td>
<td>103.149</td>
<td>4.569</td>
<td>-</td>
<td>95.374</td>
<td>4.614 -</td>
</tr>
</tbody>
</table>


n.a. not available, n.c. not computed. `tetravalent six-fold coordination with oxygen. `trivalent six-fold coordination with oxygen. `pentavalent six-fold coordination with oxygen: lithium niobate structure (R3cR). `lattice vectors and angles converted from computed rhombohedral to hexagonal primitive cell values to ease comparison. `tetravalent eight-fold coordination with oxygen. `antifluorite structure where the anions adopt a face centered cubic arrangement with cations in the tetrahedral interstices.
Figure 5-4. Defect energies of tetravalent trace elements as function of ionic radius (Shannon 1976). All points are plotted with respect to the six-fold radius of the defect cation. Results from embedded cluster calculations are shown as white crosses that overlay the supercell points. Vasp_{E}-1 data points include an empirical correction for the ionization energy of the atoms while Vasp_{E}-2 values are based on computed ionization energies (see text for explanation).

Figure 5-5. Solution energies of tetravalent trace elements as function of ionic radius (Shannon 1976). All points are plotted with respect to the six-fold radius of the defect cation, except light blue crosses. In the latter case, the binary oxide energies are based on the cubic (Fm3m) crystal structure (eight-fold coordinated). Results from embedded cluster calculations are shown as white crosses that overlay the supercell points, and differ only marginally from computed supercell energies. Curves fitted to the solution energies constrain the parameters in equation (1) to $r_0=0.66$ Å, $E_0=598$ GPa for GULP ($R^2 = 0.976$) and $r_0=0.60$ Å, $E_0=507$ GPa for VASP ($R^2 = 0.651$) simulations respectively.
cation is equal to the binary-oxide environment of the corresponding substituting ion pairs (e.g. Purton et al. 1997a; van Westrenen et al. 2000).

Equation (3) becomes:

\[
\text{Ti}_2\text{O}_5(\text{solid}) + \text{M}^{4+}\text{O}_2(\text{melt}) \rightarrow \text{M}_n\text{Ti}_{i-n}\text{O}_2(\text{solid}) + \text{Ti}^{4+}_i\text{O}_2(\text{melt})
\] (5)

And the solution energy \(E_{\text{solution}}\) describing the full exchange reaction (5) can thus be given as:

\[
E_{\text{solution}} = [E_{\text{tot}}(\text{M}_n\text{Ti}_{i-n}\text{O}_2) - E_{\text{perfect}}(\text{Ti}_2\text{O}_5)] + [E_{\text{perfect}}(\text{TiO}_2) - E_{\text{perfect}}(\text{MO}_2)]
\] (6)

where the last two terms represent the relative difference in binary oxide energy instead of the relative energy of the ions in equation (4).

Figure 5-5 shows solution energies according to eq. 6, calculated with GULP and VASP. For the classical simulations, two different 'melt' local environments were considered: one that resembles octahedral coordination to oxygen (as in rutile) and one where the cations are eight-fold coordinated (as in the fluorite structure). The calculated lattice parameters and experimental fluorite structures are given in Table 5-5. Solution energies using the embedded cluster method are almost identical to results from the supercell approach with silicon showing the largest difference (1.3‰). Solution energies show a clear near-parabolic dependence on trace element radius, consistent with the lattice strain model of eq. 1. Nonlinear curve fitting (with a coefficient of determination \(R^2=0.976\)) is used to constrain the parameters in equation (1) resulting in an optimum radius \(r_0=0.66 \text{ Å}\) and an apparent Young’s modulus \(E=598 \text{ GPa}\).

Changing assumed local melt environments to resemble those in the fluorite structure, i.e. increasing the coordination number to oxygen to eight, causes solution energy changes. The incorporation in rutile of elements that exist in the fluorite structure (Zr, Sn, Hf, U and Th are shown here) is energetically less favourable, as their binary oxide lattice energies are more negative. Because the binary oxides represent a hypothetical melt-like environment, this indicates that when more oxygen is available (as in more depolymerised melts) the larger tetravalent elements become less favourably incorporated in rutile, consistent with the model of Schmidt et al. (2004).

Combining defect energies from DFT calculations with computed binary oxide instead of bare ion total energies as the elemental reference, shows incorporation behaviour similar to classically determined values. Solution energies show a similar curvature (\(E=507 \text{ GPa}\)) around an optimum radius \(r_0=0.60 \text{ Å}\) which more closely resembles that of the displaced host cation than the classically derived value. However, small cations such as Si are more favourably incorporated in rutile than predicted with GULP, whereas Sn, Hf and Zr are energetically less favourably incorporated. Tetravalent U and Pa are more easily accommodated whilst Th is energetically least favourable. DFT calculations that combine defect energies with binary oxides in the fluorite structure to yield solution energies show Zr incorporation in rutile is lowered by \(-13 \text{ kJ mol}^{-1}\) and Th and U energies are less favourable by \(-55\) and \(-58 \text{ kJ mol}^{-1}\) respectively.

Experimentally determined partition coefficients (Table 5-1) show that \(D_{\text{U}} > D_{\text{Th}}\) and \(D_{\text{Hf}} > D_{\text{Zr}}\) (Klemme et al. 2005). First principles solution energies based on six-fold coordination environments confirm these relative differences, where \(E_{\text{solution}}(\text{Th})\) is \(-163 \text{ kJ mol}^{-1}\) higher than
$E_{\text{solution}}(\text{U})$ and $E_{\text{solution}}(\text{Zr})$ is ~10 kJ mol$^{-1}$ higher than $E_{\text{solution}}(\text{Hf})$.

Atomic charges and volumes

To separate the effect of atomic charge and atomic size on defect and solution energies, we performed Bader charge analyses on the total electronic charge densities (the sum of core and valence charge densities) of optimized defective rutile supercells and binary oxides lattices. In molecular systems, the charge density typically reaches a minimum between atoms and this is a natural place to separate atoms from each other. With this in mind we resolve the charge density into regions belonging to a specific ion. Hence, atomic volumes and the total charge contained within them can readily be obtained (Henkelman et al. 2006; Tang et al. 2009).

Figure 5-6a-c show the terms contributing to incorporating isovalent trace elements in rutile as a function of their atomic charge. Lattice energies of the binary oxides are plotted in combination with atomic charges and volumes obtained from the pure oxide phases. Charges and volumes in combination with defect and solution energies are obtained from supercell charge densities. All substituting atomic charges are larger than that of the host cation. Defect and binary oxide energies show no clear trend with atomic charge. Atomic charges of cations in their pure binary oxide form (Figure 5-6b) are slightly lower in comparison to their atomic charges incorporated as defects in rutile. This is especially so for actinides, and the only exception is silicon, which exhibits a higher charge in a binary oxide environment. Figure 5-6c shows a linear increase in solution energy with increasing atomic charge.

Figure 5-6d-f show energetics and corresponding volumes associated with atoms in rutile (Figure 5-6d,f) and their respective binary oxides (Figure 5-6e). Cations whose spatial extent of the electronic charge density is smaller than that of Ti in rutile (7.6 Å$^3$) are associated with slightly negative (Ge, Si) and moderately positive (Zr, Hf, Sn) defect energies. Note also that if the volume is assumed to be spherical, the ionic radius of Ti becomes about ~1.22 Å, which is about twice as large as the ionic radius given by Shannon and co-workers (Shannon 1976). Elements that occupy a significantly larger volume than the host cation (Th, U, Pa) show large positive defect energies whereas their charges are comparable to those of, for example, Hf and Zr. In addition, the volumes of Th, U and Pa in rutile supercells are significantly reduced relative to the volumes of these atoms in their binary oxide structure (Figure 5-6e). The volume reduction or compression of the spatial extent of the electronic charge density upon incorporation in rutile results in a strong defect energy penalty. At the same time, their net charge increases with respect to the binary oxide atomic charge. A plot of the atomic volume versus solution energy (Figure 5-6f) yields an optimum volume ($V_0 = 7.5$ Å$^3$) very close to that of rutile (7.6 Å$^3$), where again Th is more unfavourably incorporated and U and Pa are more easily accommodated in rutile compared to predicted behaviour on the basis of equation 1. Atomic volumes of binary oxides of Th, Pa and U and to a lesser extent Zr, Hf and Sn are larger compared to their respective volumes in rutile. A linear relation exists between the spherical radius and six-fold ionic radii from Shannon (Figure 5-7), where $R_{\text{spherical}}(\text{Å}) = 1.11^*R_{\text{Shannon}} + 0.43$ ($R^2 = 0.89$). Even though the coordination environment remains six-fold, charges and radii are different in the elemental bulk phases from those when incorporated as defects in rutile.

None of the tetravalent defects has a charge equal to that of the host (titanium). This
Chapter 5

requires a readjustment of the electronic charge density in the region surrounding the defect. Figure 5-8 shows the charges on oxygen and titanium surrounding the defect. There is an increased electron density on the octahedrally coordinated oxygen atoms directly bonded to the defect atom (Figure 5-8a). The variation in defect atom volume in Figure 5-6d correlates with small defect-to-oxygen bond length variations. For example, the Ge-O$_1$ distance is around 0.03-0.05 Å smaller whereas Th-O$_1$ is approximately 0.23-0.27 Å larger than Ti-O$_1$. The increased electron density of nearest neighbour oxygens has a considerable and perhaps counterintuitive effect on titanium at larger distance from the defect site (Figure 5-8b). The nearest-neighbour titanium atoms (~2.96 Å from the defect) exhibit a slight electron density decrease whereas those further away (at ~3.60 Å) display an increased electron density. Isovalent defect substitution

Figure 5-6. Defect energies, binary oxide energies and solution energies as function of ionic charge (a-c) and volume (d-f) derived from the decomposition of the total electronic charge density into atomic contributions according to Bader partitioning (Henkelman et al. 2006; Tang et al. 2009). The atomic charges and volumes corresponding to the defect –and solution energies are from TiO$_2$ supercells, whereas those corresponding to binary oxide energies (b,e) are computed from charge densities of fully relaxed binary oxides (rutile structure). Defect energies are computed from total energies of the perfect and defective supercells modified by an empirical term to account for the relative atomic and ionization energies (eq. 4).
Computer modelling of rutile-liquid trace element partitioning

Figure 5-7. Octahedral ionic radii and computed atomic volume (left ordinate) and corresponding spherical radius (right ordinate) for tetravalent point defects in TiO$_2$ supercells and in their corresponding binary oxide (rutile structure). The radii in rutile are linearly related by $R_{\text{spherical}} (\text{Å}) = 1.11 \times r_{\text{Shannon}} + 0.43 (R^2 = 0.89)$.

Figure 5-8. Charges associated with host oxygen (a) and titanium (b) atoms with distance from the isovalent defect location (colour coded per element).
thus selectively reduces the charge on Ti surrounding the defect to ‘charge balance’ the reaction and minimise cation-cation repulsion. The mechanism through which the electron density on Ti increases selectively for non-nearest neighbours is determined by the redistribution of the electron density (polarisation) of oxygens surrounding the defect, as illustrated for Si-Ti substitution in Figure 5-9.

Figure 5-9. Part of the rutile supercell showing the defect (Si) and its surrounding environment (≤4 Å). The blue and red coloured blebs are isosurfaces of the valence charge density difference between the perfect and the defective supercell. Thus, blue shows higher charge surrounding for example a Si defect, consistent with Bader partitioning. Oxygens around the defect (6-fold coordination, only three shown for clarity) show some polarisation towards the defect site. The nearest titanium (2.96 Å) is not affected by this, whereas the titanium further away (3.57 Å) now “feels” a different oxygen electron density. Note the slight Ti-O bond length difference of the “right” (0.02 Å) relative to the “left” of the defect, resulting in a smaller effect on the nearest neighbour Ti charge.
Rutile – aqueous fluid trace element partitioning model

In processes that (re-)distribute elements between minerals and aqueous fluids, the binary oxide approach adopted for melts cannot be applied as binary oxides are a poor descriptor of the local environment of elements in fluids. A starting-point to account for element exchange between rutile and aqueous fluid is to assume a fixed hydration environment surrounding the cations in the fluid:

\[ \text{Ti}_2\text{O}_2^{(\text{solid})} + M^{n+} (\text{H}_2\text{O})_6^{(\text{aq})} \rightleftharpoons M^{n+} \text{Ti}_{1-\gamma}\text{O}_{2\gamma}^{(\text{solid})} + \text{Ti}^{4+}\text{O}_2^{(\text{aq})} \]  

(7)

Two approaches were adopted here to obtain relative hydration energies of the substituting ion-pairs. The first method employs molecular orbital calculations with Gaussian03W. Binding energies and hydration enthalpies were computed according to the thermodynamic cycle similar to van Sijl et al. (2009), on the basis of an assumed coordination of six first-hydration shell water molecules. The second method takes six-fold coordinated geometries obtained with the first method and computes optimized gas-phase total energies at the gamma-point using a 15 Å simulation box with VASP. Here, all parameters and PAW potentials are kept identical to the defect calculations. To account for charged systems, the number of electrons is supplied manually and a neutralizing background charge is assumed. We correct the calculated total energies for differences in ionization potential and compute contributions from dipole and quadrupole moments, as well as errors introduced by periodic boundary conditions on charged systems (Neugebauer and Scheffler 1992; Kresse and Joubert 1999).

The computed solution energies are plotted in Figure 5-10. The atomic volume reported is that of the defect in the rutile supercell derived from Bader charge density analysis as detailed above. Both methods yield comparable solution energies. Compared to rutile-melt solution energies, the energy variation between trace elements is much larger. Silicon, Ge and Sn occupy a relatively small volume and the hydration enthalpies accordingly become more negative relative to the hydration enthalpy of titanium. Hence, they preferentially partition into the aqueous fluid. The actinides Th, Pa and U occupy a larger volume relative to titanium, and are thus much less favourably accommodated in the fluid than they were in a melt-like environment. There is a 1:1 relation between the atomic volumes in the rutile supercells and the atomic volumes in the aqueous fluid except for Th, Pa and U (Figure 5-11). Similar to increased
atomic volumes found for binary-oxide lattices, these elements exhibit a much larger volume in the fluid compared to those in the rutile supercell, which may be due to the much more flexible hydration shell compared to the more rigid local environment in rutile.

**Incorporation of Nb and Ta**

Incorporation of pentavalent (Nb\(^{5+}\) or Ta\(^{5+}\)) atoms into rutile is charge balanced by inserting a second defect at an interatomic distance of 7.136 Å (Figure 5-3 on page 105). Equation (5) thus becomes:

\[
\text{Ti}_2\text{O}_5\text{(solid)} + \frac{1}{2}\text{M}_2\text{O}_5\text{(melt)} + \frac{1}{2}\text{M}_2\text{O}_3\text{(melt)} \rightleftharpoons \text{M}^{5+}\text{M}^{3+}\text{Ti}_{2}\text{O}_5\text{(solid)} + 2\text{TiO}_2\text{(melt)}
\]

Consequently, the defect energy becomes:

\[
E_{\text{defect}} = E_{\text{lat}}(\text{M}^{5+}\text{M}^{3+}\text{Ti}_{2}\text{O}_5) - E_{\text{perfect}}(\text{Ti}_2\text{O}_5) + 2E_{\text{Ti}^{4+}} - E_{\text{M}^{5+}} - E_{\text{M}^{3+}}
\]

and the solution energy involves the first two terms of equation (9) modified by a term describing the addition of two defects from a melt-like environment and the removal of two host cations:

\[
E_{\text{solution}} = E_{\text{defect}} + 2 \cdot E_{\text{perfect}}(\text{TiO}_2) - E_{\text{perfect}}(\frac{1}{2}\text{M}_2\text{O}_5) - E_{\text{perfect}}(\frac{1}{2}\text{M}_2\text{O}_3)
\]

Trivalent ion lattice energies \((E_{\text{perfect}}\text{M}_2\text{O}_3)\) were derived from total energies of optimised unit cells of corundum. To minimise computational expense, DFT optimisations were based on the rhombohedral primitive unit cell \((R-3cR)\) whereas GULP optimisations make use of the full hexagonal cell. The resulting lattice parameters and experimental structures are given in Table 5-5 on page 106. Monoclinic \(\zeta\)-Nb\(_2\)O\(_5\) (Ercit 1991) and \(\zeta\)-Ta\(_2\)O\(_5\) (Zibrov et al. 2000) have relatively large unit cells and are difficult to optimise. Therefore, six-fold coordinated pentavalent lattice energies are approximated by:

\[
E_{\text{defect}}(\frac{1}{2}\text{M}_2\text{O}_5) = E_{\text{lat}}(\text{LiM}^{5+}\text{O}_3) - \frac{1}{2} \cdot E_{\text{lat}}(\text{Li}_2\text{O})
\]

where the lattice energies of lithium-niobate and lithium-tantalate are derived from rhombohedral
Computer modelling of rutile-liquid trace element partitioning (R3cR) unit cells (Hsu et al. 1997) containing 10 atoms (Figure 5-12), and the lithium-oxide lattice energy is derived from the cubic antifluorite structure (Fm-3m).

**Classical potentials**

With the newly developed interatomic potentials, we were able to reproduce the volumes of LiNbO$_3$ and LiTaO$_3$ to within 1.2% of the experimentally derived values. Defect energies obtained with the new potentials taking Al, Cr, Fe, Sc, Y, Lu and La as compensating defects are consistently more negative for Ta than Nb by -157 kJ mol$^{-1}$ (Figure 5-13). With increasing radius, a linear increase in defect energy is observed, as for isovalent defect energies calculated with GULP. The difference in defect energy between ion-pairs in close proximity (3.569 Å) compared to those at larger interatomic separation (10.707 Å) is a measure of their collective binding energy, and may be positive or negative depending on whether the corresponding association energies are positive or negative. The binding energy (Figure 5-13) is larger for compensating trivalent defects with larger ionic radii. Up to Lu, the binding energy with Ta is larger than Nb. Opposite behaviour is seen for Y and La. It must be noted however that the binding energies are small and their magnitudes are at the limit of the precision of the method.

On the basis of defect energies alone, these potentials are able to reproduce experimental observations for rutile-melt systems indicating $D_{Ta} > D_{Nb}$ (Schmidt et al. 2004; Klemme et al. 2005; Bromiley and Redfern 2008). In contrast, taking into account a hypothetical 6-fold coordination in a melt-like environment yields solution energies (Figure 5-14) slightly favouring Nb over Ta by at most 5 kJ mol$^{-1}$. The optimum radius of trivalent ions compensated by Nb or Ta ranges between $r_0 = 0.789-0.791$ Å with an apparent Young’s modulus $E_x = 607-611$ GPa ($R^2 = 0.994$). The larger optimum radius can be rationalised by the lower charge of the compensating defect (3+) compared to that of the host cation (4+). Under the assumption of equal availability and absence of other charge-compensating defects (e.g. hydrogen) or defect clustering, elements with ionic radii close to those of Sc and Lu are more favourably incorporated in rutile than for example Al, Cr or Fe. An explanation for high abundances of Al, Cr and Fe observed in rutile from natural samples and experiments thus lies beyond their coupled substitution with Nb or Ta.

**Density functional theory**

Solution energies computed with VASP plotted in Figure 5-15 were based on maximally separated ion-pairs (corresponding to a distance of 10.707 Å in the unrelaxed structure). Except for ion-pairs involving Lu, Ta is slightly more favourably incorporated over Nb, in agreement with rutile-fluid partitioning experiments that show $D_{Ta} > D_{Nb}$. Note however that their difference is very small (between 3.0-6.5 kJ mol$^{-1}$) and is approximately at the limit of the precision of the DFT simulations. The solution energy of Al is reduced by approximately 100 kJ mol$^{-1}$ compared to values obtained with GULP. Hence the incorporation of Nb or Ta in combination with Al, Sc or Lu computed with VASP is energetically more favourable compared to GULP, whereas coupled incorporation with La is less favourable by ~75 kJ mol$^{-1}$.

Similar to what is found when comparing the incorporation of Si between classical and DFT simulations, the small size of Al results in easier accommodation in rutile according to
Figure 5-12. Hexagonal unit cell and primitive rhombohedral cell used to simulate the local environment of trivalent ($R\text{-}3cR\ \alpha\text{-Al}_2O_3$) and pentavalent ($R3cR\ LiNbO_3$) trace elements in a ‘melt-like’ environment.

Figure 5-13. Defect energies of $3\times3\times3$ supercells containing two point defects: a pentavalent ion (Nb or Ta) charge compensated by a trivalent ion (Al, Cr, Fe, Sc, Lu, Y, La) at an interatomic separation of 3.569 Å (white crosses) and 10.707 Å (solid symbols). The binding energies range between -1.42 and 5.44 kJ mol$^{-1}$, and are plotted in the top panel as function of trivalent ionic radius (6-fold).
DFT computations than expected on the basis of GULP energies. Depending on whether La is included, fits through the solution energies of trivalent-pentavalent ion pairs yield an optimum volume $V_0 = 6.80 - 6.88 \text{ Å}^3$. In contrast to findings from classical simulations that find a larger optimum radius for trivalent ions, DFT-based optimum volumes are smaller than the volume of Ti (7.6 Å$^3$) or the optimum volume found for isovalent defects (7.5 Å$^3$).

Binding energies have been computed for Al-Nb and Al-Ta ion-pairs and are between 16.1 and 14.9 kJ mol$^{-1}$, indicating ion clustering is less favourable. On the other hand, ion-pair separation cannot be too large, as charges would not readily compensate each other. Bader analysis of total electronic charge densities reveal the charge density on Ta in rutile is on average 5.9% larger (3.054) than on Nb (2.875). Conversely, the atomic volume of Nb (8.676 Å$^3$) is 2.9% larger than that of Ta (8.433 Å$^3$). This confirms earlier empirical estimates based on partitioning experiments that indicate the ionic radius of Nb is ~0.01 – 0.02 Å larger (0.65–0.66 Å) than that of Ta (0.64 Å) (Tiepolo et al. 2000). On the basis of our computed atomic volumes alone, we find ionic radii for Ta and Nb differ by only 0.012 Å (0.95%) and we propose the following revised radii: Nb (0.652 Å) and Ta (0.640 Å). However, we note that more significant differences in electronic charge density, not taken into account explicitly in the lattice strain model (eqs. 1 and 2), may dominate the observed effect of $D_{\text{Ta}} > D_{\text{Nb}}$ in rutile.

The effect of element exchange with a hypothetical aqueous fluid is investigated as described above for isovalent substitutions. We compute pentavalent / trivalent ion-pair solution energies using method 1, i.e. via computed hydration enthalpies of the species assuming six-fold coordination with water. The exceptions are Lu (8-fold) and La (9-fold), which are well known to display higher coordination numbers in aqueous fluids (Rizkalla and Choppin 1991; 1994). Two host cations are interchanged for Nb or Ta and a compensating trivalent ion. The results are plotted in Figure 5-16. Similar to isovalent rutile-aqueous fluid simulations, small trivalent cations are energetically favoured in the aqueous environment. The heat of gas-phase complexation of

![Figure 5-14](image)

**Figure 5-14.** Solution energies of trivalent/pentavalent ion-pairs as function of six-fold ionic radius of the trivalent defect (Shannon 1976) computed with GULP according to the interatomic potentials developed in this study. Curves fitted to the solution energies constrain the parameters in equation (1) to $r_0=0.789-0.791 \text{ Å}$ and $E_x=607-611 \text{ GPa (R}^2 = \text{ is 0.994).}
Figure 5-15. Computed solution energies of trivalent ions in relation to trivalent-ion volumes in the rutile supercell, charge compensated by Nb and Ta (same symbols as in Figure 5-14). The local ‘melt’ environment is approximated with octahedral coordinated Nb or Ta in Li(Nb,Ta)O$_3$ (simulations are based on a rhombohedral primitive cell). Volumes are derived from Bader analysis of the total charge densities obtained through VASP.

Figure 5-16. Solution energies of trivalent lanthanide ions together with Nb or Ta in a rutile supercell with respect to a simulated aqueous fluid (method 1). Points are plotted as function of atomic volume of the trivalent ion according to Bader partitioning of the charge density. Whereas Al and Sc are most likely six-fold coordinated to water, Lu and La are eight respectively nine-fold coordinated (Rizkalla and Choppin 1991; 1994).
water molecules to La and Lu (i.e. the total binding energy) is much lower compared to Al (by 27-38%) or Ti (by 57-64%) respectively. Hence, these elements are less favourably hydrated relative to the exchanged host cations. The energy difference between Nb and Ta is on average 427.8±3.6 kJ mol$^{-1}$ with the smaller cation (Ta) being more favourably incorporated in rutile, consistent with experiment (Xiong et al. 2005). The difference in solution energy between Nb and Ta is much larger than for the simulated melt-like environment, indicating fluids may more strongly fractionate Nb from Ta than melts.

Figure 5-17. Computed solution energies of pentavalent ions as function of atomic volume in the rutile supercell, charge compensated by the energetically most favourable trivalent cation (Sc). The local ‘melt’ environment is approximated with octahedral coordination of the pentavalent ion in Li(M$^{5+}$)O$_3$ (simulations are based on a rhombohedral primitive cell). Volumes are derived from Bader analysis of the total charge densities obtained through VASP.
Application to Th-Pa-U systematics

To illustrate the wealth of information obtained from the simulations described above, we look at Th-Pa-U energetics in the context of their incorporation in rutile relative to melts and fluids.

Uranium-Th isotope disequilibria provide important constraints on the timing and mass transfer processes in subduction zones (see for example Sigmarsson et al. 1998; Turner et al. 2003). Traditionally, two scenarios are considered to rationalise the relative abundance of these elements in subduction derived magmas:

1. Excess abundance of the long-lived parent isotope $^{238}\text{U}$ relative to the short-lived daughter isotope $^{230}\text{Th}$. This is thought to be due to dehydration reactions that preferentially mobilize U (and Ra) over Th. The reason for this is that actinides display a much larger range in oxidation states compared to for example lanthanides, and U is readily oxidised to U(VI) whereas tetravalent Th is not (Katz and Manning 1952). The solubility of U(IV) is higher than Th(IV) (Choppin and Wong 1998), hence U is more mobile in the presence of water (Janeczek 1999; Hazen et al. 2009).

2. Excess abundance of short-lived $^{230}\text{Th}$ compared to $^{238}\text{U}$. This may be due to partial melting with rutile in the residue, preferentially retaining U over Th (Sigmarsson et al. 1998). A possible alternative explanation involving breakdown of thorium-bearing minerals (e.g. monazite, allanite, thorianite, thorite, and zircon) has to the best of our knowledge not been investigated.

The observed wide range in U-Th-Ra disequilibria for different arcs is intimately linked with the varying amount of fluid component added to the ascending magma. Oxygen fugacity variations within the mantle wedge may also influence U-series disequilibria (Huang and Lundstrom 2007). Most arc lavas show excess $^{231}\text{Pa}$ over $^{235}\text{U}$. It is suggested that due to the low solubility of Pa in aqueous fluids (e.g. Brenan et al. 1994; Keppler 1996), $^{231}\text{Pa}$ excess provides a less ambiguous view of partial melting processes than inferred from U-Th-Ra disequilibria (Pickett and Murrell 1997; Bourdon et al. 1999; Turner et al. 2006; Huang and Lundstrom 2007). Furthermore, changes in the partition coefficients for Pa and U are thought to vary much less during magma ascent compared to U-Th partition coefficients (Huang and Lundstrom 2007).

Few experimental studies on $^{231}\text{Pa}$-$^{235}\text{U}$ partitioning systematics are available due to the difficulty of measuring exceedingly low Pa concentrations (Koornneef et al. 2010). Residual rutile could potentially retain Pa (Blundy and Wood 2003a) and thus potentially lower the $^{231}\text{Pa}$ to $^{235}\text{U}$ ratio (Dosseto et al. 2003). However, extrapolation of measured pentavalent partition coefficients to infer the value for $\text{Pa}^{5+}$ excludes rutile as a possible sink of Pa (Klemme et al. 2005). Alternatively, zircon has been proposed as a compatible mineral to host Pa, based on the behaviour of Nb$^{5+}$ as proxy for Pa$^{5+}$ (Blundy and Wood 2003a; Schmitt 2007).

Our simulations offer a unique perspective on these considerations by identifying several possible pitfalls of these empirical models:

1. The inferred chemical similarity between Pa and Nb. Maddock and co-workers (1949) concluded that aqueous solutions of Pa$^{5+}$ resemble those of zirconium more closely than those of tantalum. Bader analyses on computed charge densities show Pa$^{5+}$ in rutile has approximately a 7% higher charge compared to Ta and a 14% higher charge compared
to Nb. This translates into quite different atomic volumes of these elements. On the basis
of these observations, the assumption of chemical similarity between these elements is
precarious.

2. The inferred pentavalent oxidation state of Pa as opposed to tetravalent Pa. Elson and
co-workers (1950) have succeeded in unequivocally establishing the existence of a tetravalent
oxidation state by preparing and identifying PaCl₄ and PaO₂. In the same study these
authors prove the existence of Pa₂O₅ and a complete solid solution between PaO₂ and
Pa₂O₅. Figure 5-5 on page 108 shows Pa⁴⁺ is slightly more favourably incorporated in rutile
than U⁴⁺. The oxidation state of Pa may be similar to U in rutile. Taking into account the
slightly smaller radius of Pa relative to U, this implies a rutile-melt partition coefficient
slightly more compatible relative to U⁴⁺ (D values between 0.4 and 2.5 depending on
melt composition, Table 5-1 on page 94). Assuming pentavalent Pa incorporation in
rutile, we compute Pa is approximately twice more unfavourably incorporated in terms
of energy relative to Nb or Ta (Figure 5-17 on page 120). Together with results from V⁵⁺
incorporation, the four pentavalent ions define a curve centered around the optimum
atomic M⁵⁺ volume of 7.2 Å³, which is slightly smaller than the tetravalent volume of
7.5 Å³ as expected from its higher charge.

3. Accurate knowledge of the ionic radius of Pa (Shannon ionic radius is 0.78 Å in octahedral
coordination) is required to assess the precise location of Pa⁵⁺ on the experimental
pentavalent partitioning curve. Bader analysis on the rutile supercells in this study reveal
atomic volumes of Pa⁴⁺ (and Th, U) as defect are smaller compared to the volumes in the
simulated binary oxides by approximately 26% (see Figure 5-7 on page 112). In addition,
the defect atomic volume of Pa⁵⁺ is approximately 7.5% smaller than that of Pa⁴⁺.

4. Aqueous mobilization of Pa⁵⁺ analogous to ²³⁸U⁶⁺ is not entirely unlikely, because actinide
solubility in aqueous solutions depends on several factors such as the pH, oxidation state
(Eₚ), reaction with complexing agents (e.g., carbonate, phosphate, fluoride), sorption
to surfaces of minerals etc. (Choppin and Wong 1998). Comparing aqueous complexes
of pentavalent Nb, Ta and Pa we compute the hydration enthalpy of Pa is about 9% less
negative than that of U. Hence, in the absence of complexing agents, Pa will be
preferentially incorporated in rutile. This conclusion is supported by bond lengths
obtained for six-fold coordinated aqueous complexes of pentavalent Nb, Ta and Pa,
which show a similar environment for Nb and Ta in solution, but Pa-H₂O distances that
are 0.25 Å larger.

Summarising, using lattice strain model based curves to predict the behaviour of Pa in rutile
in the presence of melts or aqueous fluids critically depends on assumptions on (changes in)
oxidation state and ionic radii (shown to depend on host lattice). This is confirmed by our
molecular DFT simulations that show that tetravalent Pa behaves similar to U in rutile in the
presence of a hypothetical melt-like environment, whereas pentavalent Pa is approximately twice
less favourably incorporated compared to Nb or Ta. Pentavalent Pa is energetically strongly
preferred in rutile compared to aqueous fluids supporting the view that Pa is sensitive to partial
melting and less prone to be affected by fluid fluxing.
Conclusions

We demonstrate the application of classical and DFT molecular simulations to investigate trace element incorporation into rutile relative to melt- and aqueous fluid-like environments. Solution energies of tetravalent substitutions of titanium in TiO$_2$-rutile in combination with a hypothetical melt-like environment computed classically (GULP) show good agreement with DFT simulations (VASP). Both methods constrain the optimum ionic radius close to that of the anticipated value for Ti ($r_0 = 0.605$ Å), but the DFT derived radius (0.60 Å) more closely resembles that of the displaced host cation than the classically derived value (0.66 Å). Relative solution energy differences between elements qualitatively resemble measured partition coefficient trends that show $D_{U} > D_{Th}$ and $D_{Hf} > D_{Zr}$.

Bader partitioning analysis on the total electronic charge density of defect containing supercells shows a linear relation exists between solution energies of elements and their charge and a cubic dependence on atomic volume. Likening the obtained radius to six-fold ionic radii from Shannon, the following relation is obtained $R_{\text{spherical}}$ (Å) = $1.11*r_{\text{Shannon}} + 0.43$ ($R^2 = 0.89$). Charges and radii are different in the elemental bulk phases compared to the values for point defects in rutile. All tetravalent defects studied have a charge larger than that of the host (titanium), that is balanced by a mechanism involving polarisation of the octahedral oxygen atoms in combination with charge reduction of non-nearest neighbour titanium atoms.

Simulations combining ion exchange in rutile with hydration enthalpies and gas-phase total energies show, in contrast to rutile-melt solution energies, that small cations preferentially partition into the fluid while large cations are energetically more favourable in rutile. In addition, the variation between elements is much larger. Here too, elements in a simulated aqueous environment display a much larger volume than their respective atomic volumes in rutile.

The classical potentials developed in this study for Nb and Ta do not result in the observed preferential incorporation of Ta in rutile over Nb. Qualitatively, we show that trivalent elements may compensate the incorporation of pentavalent ions with an optimum trivalent ionic radius close to Sc and Lu rather than for example Al, Cr or Fe.

In contrast to this, DFT based optimum volumes are smaller than the volume of Ti (7.6 Å$^3$) or the optimum volume found for isovalent defects (7.5 Å$^3$). On the basis of our computed atomic volumes, we propose revised ionic radii for Ta and Nb are 0.640 Å and 0.652 Å respectively. Similar to results from classical simulations, DFT results show the difference between Nb and Ta solution energies is negligibly small. Comparing the energy difference between Nb and Ta in relation to a hypothetical aqueous fluid shows the smaller cation (Ta) is on average $427\pm4$ kJ mol$^{-1}$ more favourably incorporated in rutile than Nb, indicating fluids have the potential to fractionate Nb from Ta more than melts.