

Chapter 7

Conclusions and Outlook

Conclusions and outlook

In this thesis, I combined computer models of trace element complexation in subduction zone fluids with high-pressure, high-temperature mineral-fluid partitioning experiments to shed new light on the behaviour of key trace elements in subduction zone fluids.

The thermodynamic cycle that was developed in Chapter 1 provides insight into the relative hydration Gibbs free energies of rare earth element (REE)-water clusters embedded in a solvation model computed from a *first principles* quantum mechanical point of view. All REE hydration free energies computed using density functional theory (DFT) are negative at both ambient pressure-temperature conditions and the high pressures and temperatures characteristics of subduction zones, indicating thermodynamically favourable solvation by water. The hydration free energy is more negative for smaller complexes (heavy lanthanides) relative to larger complexes (light lanthanides) by ~ 361 kJ mol⁻¹. Aqueous complexation of REE with fluoride is energetically more favourable than with chloride by ~ 206 kJ mol⁻¹. REE-Cl and REE-F complexes are both energetically favoured with respect to REE-water clusters. The results indicate that fluid REE contents can be affected by the presence of fluoride or chloride, but that changes in REE-ratios are unlikely to occur.

The latter is consistent with experimental results (Chapter 6) that show heavy REE / light REE diopside-fluid partition coefficient ratios to be unaffected by the presence of 10 wt.% fluoride and chloride solutions. Embedded cluster calculation results suggest absolute REE concentrations are likely to be increased in solution due to the presence of complexing ligands. This is not observed in our experiments, which leads us to conclude that it is likely that for diopside-fluid REE partitioning, diopside exerts a dominating control on REE behaviour. The thermodynamic cycle and embedded cluster calculations allow for pressure and temperature variations to be included indirectly. Parameterised changes in temperature (e.g. dielectric constant) and density do not significantly affect REE-ratios.

Due to the nature of these *static* simulations, geometric parameters are optimised assuming a certain coordination environment (the local environment of the solvated ion) at the given PT conditions. Coordination number variations due to pressure and temperature are therefore only implicitly included. It is concluded that a better understanding of the detailed structure and dynamics of hydration shells and the effect of ions on the hydrogen bond network of liquid water under supercritical conditions is of critical importance.

This is the main objective of Chapter 2 and 3, where we report changes in coordination environment of the lightest high field strength element (HFSE) titanium in pure water as a function of temperature and water density relevant to subduction zone settings using *first principles* molecular dynamics (FPMD). Equilibrating the ambient condition initial geometry of the simulations by quenching from higher temperatures may drive the system into a metastable state, where the dynamics do not evolve fast enough to escape the local minimum without considerable computational effort. Using metadynamics to overcome this obstacle, we observe an unanticipated five-fold coordination of Ti(IV) is favoured under ambient conditions, with rapid interconversions between square pyramidal and trigonal bipyramidal structures. This is in marked contrast to the long-held view that Ti is six-fold coordinated, and demonstrates the

added value of (accelerated) dynamic over static simulations.

At supercritical conditions the Ti coordination number increases from five to six, adopting both octahedral and trigonal prismatic geometries, with Ti-O bond lengths in excellent agreement with static DFT molecular cluster calculations. At 1000 K, a water density increase from 0.9 – 1.3 g cm⁻³ (corresponding to a pressure increase from approximately 0.9-3.6 GPa) increases the number of first hydration shell water molecules from less than five to six. Thus for tetravalent titanium in solution, the effect of higher pressure, favouring larger coordination numbers, dominates the effect of an increase in temperature, which favours lower coordination.

Studies simulating ion hydration under comparable PT-conditions are rare. Nevertheless, we note strikingly similar coordination changes with density for titanium when compared to lithium, despite the very different Li-O and Ti-O bond strengths. Future simulations on the supercritical solvation behaviour of other tetravalent ions are required to assess whether the pattern that we observe for titanium and lithium is unique to these elements.

In addition to geometry changes, titanium-water complexes display marked modifications of their electronic structure with temperature and density (Chapter 3). The main two observations related to these modifications are the marked increase in first hydration shell water molecule dipole moments at ambient and supercritical conditions relative to the bulk water dipole moments. Also, at ambient conditions there is still a discernable effect of the central Ti ion on the dipole moments beyond the first hydration shell whereas this is absent at supercriticality.

At 1000 K and water densities from 0.6 – 1.5 g cm⁻³, corresponding to pressures of approximately 0.3 – 8 GPa, fluoride and chloride form aqueous complexes with titanium, i.e. hydrated TiF and TiCl (Chapter 4). Hydration enthalpy calculations show that complexation reactions of the type observed here will increase the solubility of Ti, qualitatively consistent with recent experimental data showing enhanced rutile solubility in the presence of Cl⁻ and F⁻ (e.g. Rapp *et al.* 2010). Although HFSE solvation is anticipated to be enhanced in the presence of these complexing agents, there may be a large dependence on the absolute halogen abundances and their preference for other cations in solution. The relation between halogen availability and HFSE mobility is sometimes linked to the relative stability of fluorapatite. Future studies that focus on the connection between (fluoro-)phosphate stability (e.g. apatite, monazite, xenotime) and nominally insoluble element mobility may provide further clues to this relation.

Despite the observed TiF and TiCl complex formation in our simulations, our experiments indicate the concentration of Ti in the fluid is not enhanced in either chloride or fluoride-rich aqueous solutions in the system diopside-fluid (Chapter 6). Observations also indicate that Zr and Hf are enriched in pure water and F-bearing solutions relative to diopside whereas complexation with chloride is much less favourable. We conclude from these experiments that complexing halogens in solution have the potential to significantly alter the relative compatibility of trace elements, and hence partition coefficient ratios can vary significantly depending on crystal- and fluid chemistry.

We also conclude that there appears to be a disagreement between the experimentally observed influence of halogens on diopside-fluid partitioning of some HFSE and energetically favourable formation of titanium complexation from *first principles* molecular dynamics. Resolution of this apparent disagreement requires additional experimentation as well as FPMD simulations on other HFSE in more complex, multi-component solutions. Also, simulations

should account for the competing effects between fluid and mineral. As an illustration of such more advanced atomic-scale computer models, we establish a fully quantum mechanical picture of rutile-melt and rutile-aqueous fluid HFSE partitioning relevant in particular to subduction zone settings (Chapter 5). Assuming similar hydration behaviour of HFSE to titanium, we compare Nb and Ta incorporation in rutile relative to a melt or aqueous fluid. We observe that the energetic differences between Nb and Ta are larger in the case of element exchange between rutile and aqueous fluids relative to melts. This is consistent with the notion that trace element partitioning behaviour strongly depends on local liquid environments as well as crystal chemistry.

Making use of Bader partitioning analysis of the total electronic charge density, we show that charges and radii of elements in their bulk oxide phases are different compared to values for elements as trace element defect in rutile. Even for isovalent element substitution reactions, the higher charge of the substituting element relative to Ti requires some form of charge compensation mechanism. In rutile, a mechanism involving polarisation of the octahedral oxygen atoms in combination with charge reduction of non-nearest neighbour titanium atoms accounts for charge differences. 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.