

Fluids in the Earth – Reconstructing their composition through space and time.

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Introduction

The abundance of water on Earth has a profound impact: aqueous fluids facilitate plate tectonics, control the redistribution of elements to make ore deposits and determine the availability of (trace) elements crucial to life (Fig 1A). Knowledge of their compositions is therefore essential. Unfortunately, direct fluid samples are rare, especially for deep in the Earth and for its earliest history. However, minerals with preserved compositions are readily available, sampling environments >200 km in depth and back to 4.2 billion years ago. Minerals record a fingerprint of the associated fluid by element exchange (Fig 1B) and this record can be read if we understand and can predict the partitioning of elements between minerals and fluid.

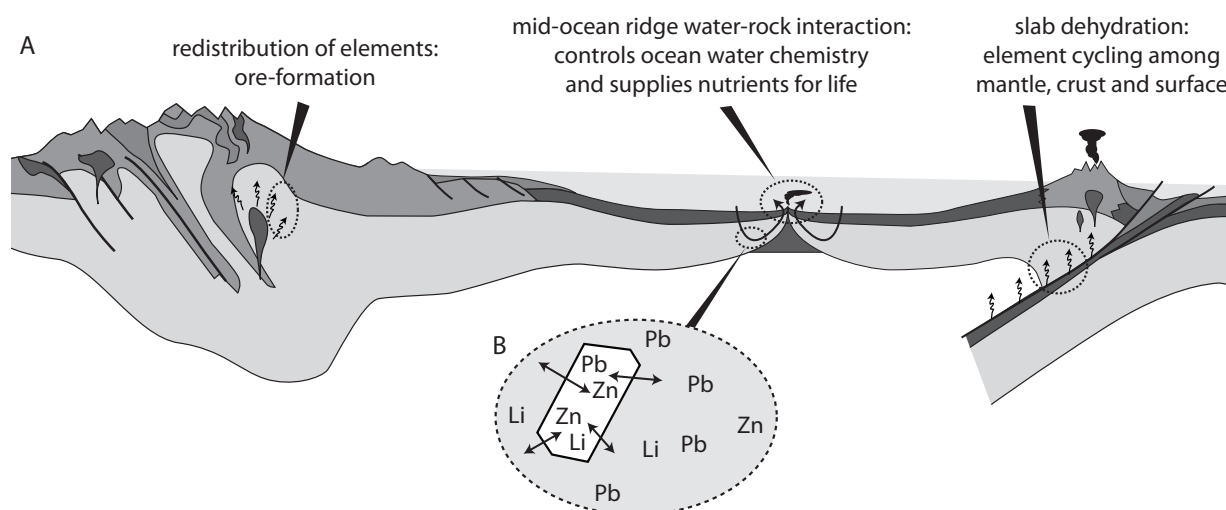


Figure 1. Fluids are the prime agent of element redistribution in and on the Earth, and as such control element cycling through subduction zones and the mid-ocean ridges, control ocean water chemistry, and concentrate elements into ores.

The goal of this project was to develop a method for reading this mineral record of fluid composition, with the hypothesis that the preference of an element to enter the mineral is controlled by how well it fits in the crystal structure in terms of its radius and charge, i.e. that it obeys Lattice Strain Theory.

Methods

To test the hypothesis, we experimentally determined the partitioning behaviour between minerals and aqueous fluids at elevated temperatures and pressures for a suite of 50 trace elements covering a wide range of radius and charge. We further conducted mineral-melt experiments at increasing levels of a dopant element to investigate partitioning behaviour at high concentrations. The experimental work was accompanied by Density Functional Theory computational simulations of the crystal structure of the mineral albite with changing pressure. These simulations predict the effect of pressure on partitioning by determining the adjustment of the lattice site size and elasticity as pressure increases. Albite was chosen, as it is a common mineral in subduction zone and mid-ocean ridge rocks, and ore deposits, and its structure is relatively well-understood.

Results

Our experimental results show that partition coefficients (D) vary systematically with the misfit of an element's radius and charge compared to the ideal crystal structure occupant, and this behaviour can be fit with Lattice Strain Theory (Fig 2A). This means that element uptake is indeed controlled by the mineral lattice properties as hypothesized. Adding a dopant at increasing concentrations leads to a sudden change in partitioning (Fig 2B) as a Henrian limit is encountered (i.e. when the trace elements are no longer at "infinite dilution"). Below this limit, a characteristic D -value describes the partitioning, and the mineral concentration can be directly translated to a trace element content in the fluid. In contrast, above this limit, the D -values depend on the dopant concentration, and the trace element content of the fluid is strongly over-estimated (Na) or under-estimated (La, Yb) when using the Henrian D -value. However, despite this change in absolute D -values, the

systematics with radius remain unchanged (Fig 2C), and element uptake can still be evaluated using Lattice Strain Theory. The validity of Lattice Strain Theory opens the possibility to predictive modelling of partitioning by constraining the sensitivity of the Lattice Strain parameters to pressure, temperature and mineral/fluid composition. We have explored this using Density Functional Theory structure optimisation simulations. Having learned this methodology during this project, I confirmed that it accurately predicts the changes in the crystal structure and elastic properties of albite with changing pressure. The modification of the crystal lattice leads to smaller and stiffer element sites at higher pressures, and hence a shift to preferred incorporation of smaller elements, and overall reduced trace element uptake.

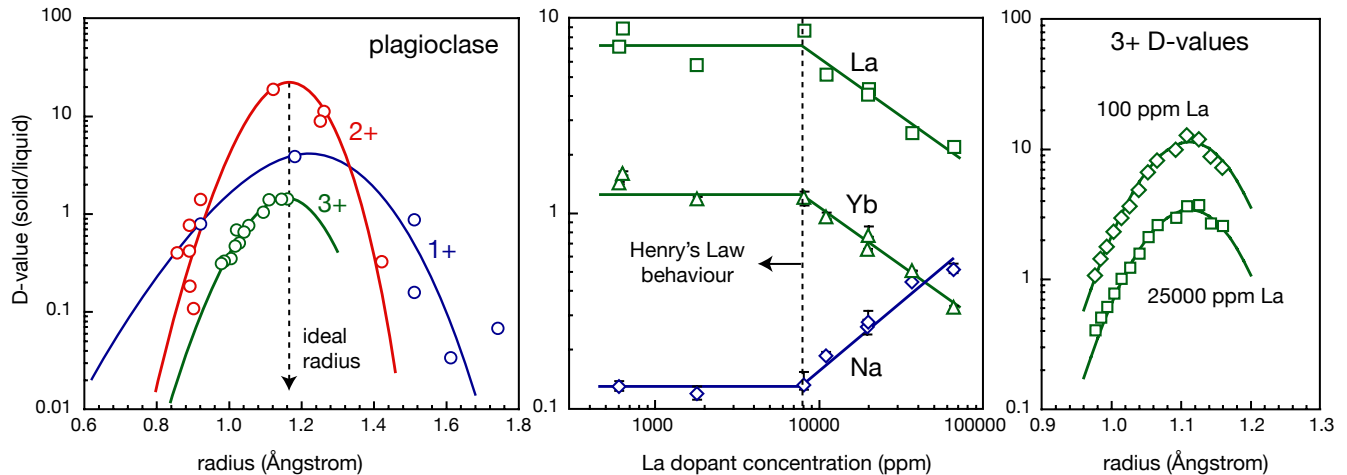


Figure 2. A) Experimentally determined D-values show excellent correspondence with LST fits (solid lines); B) At high concentrations, D-values become a function of dopant level, because they are no longer present at "infinite dilution". However, the systematics among elements of a given charge remain unchanged, as shown in C, with LST fits identical aside from absolute D-values.

We have used the mineral-based approach developed in this project to calculate the composition of fluids released in subduction zones by combining the trace element content of a tourmaline grain from the Tauern Window in the Austrian Alps with experimentally determined partition coefficients. The results not only confirmed that fluids are the source of the characteristic compositional signature in arc volcano lavas, but we also provided actual trace element concentrations in these fluids for depths up to 70 km. These concentrations are the key input required for quantitative modelling of element cycling between the crust and mantle at subduction zones. More recently, we managed to calculate the composition of ocean water at 3.2 billion years ago from altered oceanic crust preserved in the Tartoq Group of Southwest Greenland, and showed that the ocean water was remarkably similar in trace element composition compared to the modern day, except for an enrichment in Ni and Co. The Ni enrichment confirms earlier inferences from Banded Iron Formations and is important because Ni is a crucial nutrient for methanogenic organisms, which are regarded as limiting the build-up of oxygen in Earth's atmosphere during its earliest history.

Conclusions and Impact

The outcomes of this project have a major impact on our ability to determine the compositions of fluids in and on the Earth, providing a novel and powerful methodology. No other approach is able to access the same range of conditions or timescales, and because interaction between fluids and minerals is a universal process, the approach developed here is of general use. Not only will knowledge of fluid composition improve our fundamental understanding of the inner workings of the Earth, and constrain the cycling of elements through crust, mantle and surface, it will also provide essential input in modelling processes such as ore formation. In fact, the partition coefficients obtained in this project are for minerals and conditions that are directly applicable to ore formation, slab dehydration and interaction between crust and ocean water at the mid-ocean ridges. Moreover, exchange of elements between minerals and fluids is a fundamental process, not only in nature, but also in industrial processes. Knowledge of the composition of such fluids, when they cannot be accessed directly, allows for monitoring of industrial activities, as well as their optimisation, reducing costs and waste.

On a personal level, I have learned a new methodology; DFT simulations, which is a highly valuable methodology in my future research career, and I have had the opportunity to set up a collaborative, inter-disciplinary network to support this work. I have also greatly expanded my experimental expertise.