Reading the mineral record of fluid composition from element partitioning

Vincent J. van Hinsberg*, Artasches A. Migdisov, and Anthony E. Williams-Jones
Hydrothermal Geochemistry Group, Department of Earth and Planetary Sciences, McGill University, Montreal, Quebec H3A 2A7, Canada

ABSTRACT

Earth is the “blue planet,” with more than 70% of its surface covered in water and the equivalent of up to four oceans of water in its interior. This abundance of water has a profound impact on the processes that shape our planet as well as the development of the organisms that inhabit it. To understand this impact, it is necessary to know the properties and compositions of this fluid. At present, this information is largely unavailable, because direct samples of fluid are rare, especially for early Earth and Earth’s interior, and other estimators are semiquantitative, at best. Here we propose a different approach in which the composition of the fluid is reconstructed from that of minerals, based on the characteristic trace element partitioning between minerals and aqueous fluids. We show experimentally that this partitioning is systematic and obeys lattice-strain theory. It depends strongly on element complexation in the fluid, but this dependence is predictable and can be accommodated. Unlike fluids, minerals with preserved compositions are readily available in the geological record, and this approach therefore provides a powerful and widely applicable tool to reconstruct a quantitative record of fluid composition for the full range of Earth environments and for its earliest history.

INTRODUCTION

An understanding of the chemical behavior of volatiles, and aqueous fluids in particular, is key to interpreting the processes operating in Earth’s interior and on its surface, because of their profound impacts on the physical and chemical properties of Earth materials. Volatiles in the mantle allow plate tectonics to operate by lowering the strength of the upper mantle and facilitating melting (Mei and Kohlstedt, 2000; Gerya et al., 2008; Méard and Grove, 2008). In the crust, aqueous fluids are the main agents of element transport. However, this transport is highly selective, as the capacity to solvate individual elements is sensitive to the fluid properties, especially temperature and ligand activity (Kesler, 2005). The most obvious manifestation of this dependence is the selective enrichment of elements to form ore deposits. Element redistribution during water-rock interaction at mid-ocean ridges is also a key process determining ocean water chemistry (Komiya et al., 2008). It is likely that changes in ocean water chemistry over geological time have had an important impact on the evolution of life, because the viability of organic synthesis pathways crucially depends on the availability of specific trace elements for use as catalytic constituents in the associated enzymes (Anbar and Knoll, 2002; Russell et al., 2005; Komiya et al., 2008; Konhauser et al., 2009).

In all these environments, our understanding requires knowledge of the composition of the associated fluids. Whereas we have direct access to such fluids on Earth’s surface at the present time, and can determine their compositions directly, reliable fluid samples are exceedingly difficult to acquire for Earth’s interior and earlier stages of its history. Fluid inclusions in minerals are currently the main source of compositional information, but challenges in their analysis and nontrivial interpretation (Heinrich et al., 2003; Rickers et al., 2004) makes them an unsatisfactory data source for all except the major elements. Similarly, the metasomatic imprint of fluids on their host rocks (e.g., Spandler et al., 2003) yields only semiquantitative information, and forward thermodynamic modeling is severely limited by a lack of data. These methods, moreover, are suited mainly to determining the major element composition, whereas it is the trace element signature of the fluid that is the most sensitive indicator of processes and conditions.

Here we show that the composition of fluids, and their trace element content in particular, can be reconstructed from the mineral record. At equilibrium, elements partition characteristically between minerals and fluid, and minerals thereby record a chemical signature of the composition of the fluid (Fig. 1). When partition coefficients are known, it is therefore possible to reconstruct fluid composition from mineral chemistry. The availability of minerals with preserved compositions from deep within Earth (Spandler et al., 2003) and ages up to 4 Ga (Compston and Pidgeon, 1986) allows fluid compositions to be obtained from well into Earth’s interior and for most of its history. Furthermore, because minerals are our main source of information on pressure and temperature in and on Earth, as well as our main chronometers, their added capacity to provide information on fluid composition would make them a universal tool to gain insights into the processes that shape our planet and the changes therein over geological time.

The key requirement for reading the mineral record is precise partition coefficients for relevant pressure-temperature conditions and mineral and fluid chemistry. Notwithstanding experimental and analytical challenges, these data can be obtained from experiments (e.g., Keppler, 1996; Brenan et al., 1995; Ayers, 1998; Stalder et al., 1998). However, partitioning is highly sensitive to variations in physicochemical conditions, with coefficients changing up to three orders of magnitude and elements from compatible to incompatible (Stalder et al., 1998). This precludes extrapolation of partition coefficients beyond experimental conditions and, as obtaining coefficients for every plausible combination of physicochemical conditions is a practical impossibility, severely limits the applicability of this approach to obtain information on aqueous fluid composition at present.

In this paper, we present a new method for interpolating and extrapolating mineral-fluid partition coefficients among trace elements and to conditions beyond those of available experimental data, based on lattice-strain theory, which is used with great success to model partitioning between minerals and silicate melts (Blundy and Wood, 1994, 2003). Unlike mineral-melt partitioning, the speciation of elements in the aqueous fluid exerts a strong influence on their partitioning, and this has commonly been seen as an insurmountable barrier to using lattice-strain theory to evaluate fluid chemistry (e.g., Keppler, 1996; Brenan et al., 1995; Bau, 1996; Ayers,

*E-mail: VJ.vanhinsberg@gmx.net.

Figure 1. Conceptual drawing of the mineral-fluid element partitioning approach. As a mineral grows in an aqueous environment, its composition will reflect that of the surrounding fluid through characteristic partitioning of trace elements. After the mineral is separated from the fluid, it can preserve this information. Given partition coefficients for appropriate physical and chemical conditions, D(T, P, X), the fluid composition can be reconstructed.
PARTITIONING EXPERIMENTS

We have conducted partitioning experiments involving fluorite and Cl-, NO₃-, or SO₄-bearing aqueous solutions doped with trace concentrations of a wide range of elements (see the GSA Data Repository for details). These experiments produced a well-developed, fine-grained monomineralic crystalline precipitate of fluorite (Fig. 2) with a trace element signature similar to that of natural fluorite, including a strong preference for the rare earth elements (REEs) (Marshall et al., 1998; Hill et al., 2000). Good reproducibility among duplicates and excellent agreement between Ca concentrations in the final solutions and those determined from fluorite solubility (Richardson and Holland, 1979) show that fluorite composition reflects equilibrium (see the Data Repository for further details). Digested fluorite and reacted solutions were analyzed to obtain partition coefficients. There is good agreement between duplicate experiments (Fig. 3) as well as between directly measured partition coefficients and those obtained from mass balance with the starting solution.

When plotted against ionic radius (for the fluorite cation coordination number of 8), the partition coefficients show a systematic decrease away from the radius of Ca, the major cation in fluorite (Fig. 3). This systematic behavior follows lattice-strain theory as is evident from the good lattice-strain fits to the data. Lattice-strain theory quantifies the observation that elements that are similar in charge and radius will exchange for one another, whereas elements with large mismatch in these parameters will not (Blundy and Wood, 1994, 2003). A mineral will therefore selectively incorporate elements according to the elastic and electric characteristics of its lattice sites. A stiff lattice site cannot easily accommodate elements with deviating radii, and partition coefficients will therefore decrease sharply with increasing radius mismatch. Similarly, a high-capacitance site cannot readily dissipate excess charge and will therefore shun elements with large charge mismatch.

Partition coefficients for elements not determined experimentally can be read from the lattice-strain fit, because charges and radii of the elements are largely known (Shannon, 1976). This fit is described by three parameters (Fig. 3): an ideal radius, \( r_0 \), its associated characteristic partition coefficient, \( D_0 \), and a measure of the elastic properties of the lattice site, \( E \), which is related to the Young’s modulus.

Figure 2. The solid run product of the experiments consists of well-developed crystalline monomineralic fluorite as is evident in this binocular microscope image and XRD spectrum for a Cl-bearing experiment. Diffraction peaks characteristic of the highly refractory REE-fluorides are absent, as are peaks for Cs-fluoride.

Figure 3. Trace element partition coefficients for fluorite-fluid experiments conducted in Cl-, NO₃-, and SO₄-dominated aqueous solutions. Symbols show experimental data (in duplicate for Cl experiments) with associated uncertainty, and curves show the lattice-strain fit through these data. There is good agreement between the data and lattice-strain curves, indicating that the lattice-strain model provides an accurate description of the observed partitioning behavior. Three characteristic values determine this fit: (1) the ideal radius of the mineral lattice site, \( r_0 \), which is close to that of Ca in our experiments as would be expected for fluorite, (2) the partition coefficient for this ideal radius, \( D_0 \), and (3) a measure of the elastic properties of the lattice site, \( E \), which determines the width of the curve. Given these values, the partition coefficient for any element can be predicted from its charge and radius.

\(^1\)GSA Data Repository item 2010235, detailed methodology of the experiments, data handling and fitting, and thermodynamic modeling, as well as tables listing the compositions of the experimental solutions, partition coefficients between fluorite and aqueous solution, analytical detection limits, lattice-strain fit parameters and element radii and charges used in obtaining the lattice-strain fit, and calculated element speciation in the Cl-dominated experimental solution, is available online at www.geosociety.org/pubs/ft2010.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.
(Blundy and Wood, 2003). To extrapolate to conditions beyond the experimental data, only the dependence of these three parameters on the conditions needs to be known, rather than the dependence for each individual trace element. Moreover, this dependence can, in part, be independently constrained. For example, the change in lattice site dimensions and hence $r_0$ can be determined from structure analyses of minerals at elevated temperatures and pressures (e.g., Katsura et al., 2009), and changes in E can be predicted from the change in elastic modulus for the bulk mineral (Blundy and Wood, 2003) as determined experimentally or in molecular simulations (Li et al., 2006; Reichmann et al., 2008). Finally, the changes in D0 with changing conditions can be estimated from the changes in the mineral’s solubility. However, a base set of experimentally determined partition coefficients for the mineral-fluid system of interest remains necessary to establish a lattice-strain fit and act as a starting point for extrapolation.

**EFFECT OF SPECIATION ON PARTITIONING**

The distribution of elements between minerals and aqueous solutions is not controlled solely by the mineral lattice as is the fundamental tenet of lattice-strain theory, because the solution is not a passive reservoir in which all elements are equivalently available for incorporation in minerals. On the contrary, elements in aqueous solutions are distributed over a number of species, consisting of metal-ligand complexes enclosed in hydration shells, and this speciation varies substantially among the elements. For a given element, partitioning will take place between the mineral lattice site and every aqueous species containing that element, with an associated characteristic coefficient for each. With a change in speciation, the contribution of each species to bulk partitioning changes and hence the bulk partition coefficient that is measured. Consequently, differences in speciation among elements adversely affect the ability of lattice-strain theory to model partitioning. This effect can be observed in our data for Sb, which occurs dominantly as Sb(OH)$_3$ whereas most other 3+ elements are F-specified. Antimony consequently shows the strongest deviation from the 3+ lattice-strain fit (Fig. 3).

To incorporate speciation in a model of mineral-fluid partitioning therefore requires knowledge of the speciation of each element, which we have determined from thermodynamic modeling. This modeling shows that there is no significant correlation between partitioning and speciation for species involving the ligands Cl, NO$_3$, SO$_4$, and O/OH, nor for the free ion. Furthermore, the partitioning of elements in Cl, NO$_3$, and SO$_4$ solutions is remarkably similar (Fig. 4A). These observations lead us to conclude that partitioning of elements with fluorite is controlled dominantly by F-species. Indeed, the agreement between experimental data and the lattice-strain fit improves significantly, in particular for the 2+ elements, when only the fraction of each element residing in F-species is considered (Fig. 4B). Moreover, the recalculated partition coefficients for the 2+ elements exceed those for the 3+ elements, as the latter are dominated by F-species, whereas the former are not. This leads to an ideal charge for the fluorite cation site of 1.9 when fitted, rather than a value more than 3 for a fit of the original data (Fig. 4C). A value close to 2 is expected for this mineral and agrees with fluorite-melt partitioning data (Marshall et al., 1998) where speciation is much less of an issue. Given a measure of element speciation, it is therefore possible to account for its effects on partition coefficients and regain, or use, the underlying lattice-strain control. The application of this method requires information on the major element composition of the fluid, especially its ligand content, but this is available from other sources, e.g., fluid inclusions.

**CONCLUSIONS AND IMPLICATIONS**

The results of this study demonstrate that mineral-fluid partition coefficients among elements vary systematically in a manner that can be predicted from lattice-strain theory. Adherence to this theory allows partition coefficients to be determined from interpolation and extrapolation among elements of equal charge, and between different charges. It also allows partitioning to be described by a limited set of parameters, and only the dependence of these parameters on pressure, temperature, and mineral composition needs to be determined for partition coefficients to be extrapolated to conditions beyond those for which they have been evaluated experimentally. The speciation of elements in the fluid clearly impacts on partitioning, but this effect can be accommodated when speciation is known. However, even when speciation is not known, interpolation among elements of equal charge is still possible, because their speciation is commonly similar (cf. the good lattice-strain fit for noncorrected coefficients in Fig. 3). For example, when partitioning for a few of the REEs is known, coefficients for the other REEs can be determined by interpolation, even when there is no information on the aqueous fluid and its ligands, because the speciation of the REEs in aqueous fluids is similar.

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**Figure 4. A comparison of the lattice-strain curves for Cl, NO$_3$, and SO$_4$ experiments shows that these are identical within uncertainty (A). This independence of the partition coefficients from chloride, nitrate, and sulfate concentrations indicates that the species involved in element partitioning with fluorite do not include any of these ligands. As discussed in the main text, F-species control the partitioning, and when coefficients are corrected for the fraction of each element residing as F-species, the lattice-strain fit improves markedly (B). Furthermore, the ideal charge shifts to 1.9 (C), which agrees with that expected for the fluorite structure.**
The methodology presented in this paper allows partition coefficients to be determined for relevant physicochemical conditions and therefore provides the means to read the record of fluid chemistry stored in mineral compositions. Given the availability of marine mineral precipitates for most of Earth’s history, our results provide a method to reconstruct ocean water chemistry back in time to that of early Earth where life emerged, and explore the links between changes in ocean water chemistry and the evolution of marine organisms. Similarly, minerals from the subducting slab, transferred from deep within Earth by the actions of plate tectonics, allow the compositions of fluids released during subduction to be determined. This provides insights into the elements released during slab dehydration and helps to constrain the element fluxes to mantle and crust materials associated with subduction. Although we have focused predominantly on natural systems, the methodology is equally applicable to man-made environments. Mineral-fluid interaction is an important process in industry from wastewater treatment to preparation of drinking water and ore beneficiation. In any process where minerals form in the presence of a fluid, the composition of this fluid is recorded by minerals, and their analysis can unlock this record.

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