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Determination of trace element partition coefficients between water and minerals by high-pressure and high-temperature experiments: Leaching technique

Kenneth T. Koga

Laboratoire de Sciences de la Terre, UMR 5570 CNRS-ENS Lyon-UCB Lyon 1, 46 Allée d'Italie, F-69364 Lyon Cedex 7, France

Now at Laboratoire Magmas et Volcans, Université Blaise Pascal-OPGC, 5 Rue Kessler, F-63038 Clermont-Ferrand Cedex, France (k.koga@opgc.univ-bpclermont.fr)

Isabelle Daniel and Bruno Reynard

Laboratoire de Sciences de la Terre, UMR 5570 CNRS - ENS Lyon - UCB Lyon 1, 46 Allée d'Italie, F-69364 Lyon Cedex 7, France

[1] A refined approach for the experimental determination of fluid composition at elevated pressure and temperature conditions is developed. It effectively determines partition coefficients of trace elements between aqueous fluid and minerals. This approach is developed on top of many previously known technical achievements. However, it differs from the previous ones by the use of calibrated base and acid leaching of quenched samples to strip off the precipitates formed from the fluid during the quench. This permits the reconstruction of a fluid composition from an experimental charge that consists of a complete mixture of solid and fluid phases. This is a significant difference from the previous analogous studies, in which the fluid was separated from the solids all through the experiment. Mass balance calculations and error propagation assess the merits of the present method applied to a fluid-antigorite system.

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1. Introduction

[2] Determination of fluid compositions (fluid is used for H₂O or CO₂ solutions as opposed to silicate melt) at elevated temperature and pressure conditions has been an important objective of geochemical investigations. In particular, an accurate knowledge of the fluid composition in subduction zone provides further understanding

of magma production rate at arcs [e.g., *Stolper and Newman*, 1994], of fluid recycling through the subduction zone [e.g., *Tatsumi and Eggins*, 1995], and of transport rate of magma [e.g., *Condomines et al.*, 1988; *Gill et al.*, 1993, *Hawkesworth et al.*, 1991, 1993]. Fluid compositions are usually inferred, using thermodynamic and experimental partitioning data, from rocks that were once in equilibrium with these fluids.

For such studies, the required partition coefficients of elements between fluid and minerals are determined by petrologic/geochemical experiments in laboratory where the compositions of both mineral and fluid equilibrated at high pressure and temperature have to be determined.

[3] The determination of the equilibrium fluid composition in high-pressure, high-temperature experiments (e.g., >1 GPa, >300°C) poses a challenge for experimental petrologists, and the difficulty of these measurements has various origins. First, retention of water in a capsule is a challenge, especially if a large quantity of fluid is required for the experiment, because it is difficult to seal water inside the capsule and to prevent its collapse during pressurization. Also, hydrogen atoms can diffuse through a thin metal capsule at elevated temperature condition [e.g., *Chou et al.*, 1978]. Second, because of drastic changes of cation solubility and high cation diffusivities, fluids in high-pressure temperature experiments are not quenchable at room temperature-pressure conditions [e.g., *Lasaga*, 1998].

[4] Several technical solutions have been reported for conducting fluid bearing experiments. It has been shown that arc welding can seal a small quantity of water in a noble metal tube (e.g., approximately 50 mg in a tube of 5 mm diameter and 5 mm height [*Manning and Boettcher*, 1994]). Similarly, water can be introduced into a welded capsule using powders of compounds with structural hydroxyl molecules (e.g., brucite $\text{Mg}(\text{OH})_2$, talc $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) or hydrous glass [e.g., *Holloway and Wood*, 1988] that release water under the run conditions. The quantity of water introduced into the system is limited to 10% by weight (abbreviated as wt% hereafter), and many experiments are conducted with H_2O below 5 wt%. Finally, a pressure-seal technique has been developed that allows retention of large amounts of water up to nearly 90 wt% [*Ayers et al.*, 1992].

[5] With these technical difficulties, experimental determination of trace element partition coefficients between fluid and minerals have remained limited in number. *Brenan et al.* [1995a, 1995b, 1998] and *Ayers et al.* [1997] produced partition coefficient data using the above mentioned pressure-seal technique, in combination with mass balance calculations for fluid composition. *Keppeler* [1996] determined the fluid-silicate melt partition coefficients using large sample capsule (more than 100 mg of starting material [*Keppeler*

and *Wyllie*, 1991]) at a pressure of 0.2 GPa, in combination with a chemical leaching method to infer fluid composition. *Stalder et al.* [1998] and *Kessel et al.* [2004] recently reported high-pressure and -temperature fluid compositions that were inferred from laser ablation inductively coupled plasma mass-spectrometer (LA-ICPMS) analyses of the fluid and its quench precipitates trapped in pore spaces of fine diamond powder. Thus all these partitioning experiments rely on the successful developments of indirect techniques for measuring trace quantity elements in the fluid in equilibrium with minerals or melts at high-pressure temperature, or on mass balance calculations of fluid compositions.

[6] The issue of the reconstruction of fluid composition from quenched material is not new, and has evolved as new analytical techniques became available. Often, the quenched material of fluid were directly removed from the capsule and analyzed. For separating the quenched material of fluid from the solid, some studies used double capsule designs [e.g., *Schneider and Eggler*, 1986; *Manning and Boettcher*, 1994], and others used fluid permeable perforated membrane [*Brenan et al.*, 1998; *Ayers and Eggler*, 1995; *Ayers et al.*, 1997]. However, it was later argued that the presence of fluid and small temperature gradient in a sample capsule readily promotes compositional zoning [*Stalder and Ulmer*, 2001; *Schmidt and Ulmer*, 2004]. In our view, the possibility of compositional zoning discards any further experiment promoting mechanical segregation between fluid and solid. Therefore we aimed to determine the composition of both fluid and solid phases in high-pressure experiment in which phases are mixed.

[7] The previous studies represent significant achievements and provide essential data, yet the limitations and uncertainties associated with the reported experimental methods are not thoroughly evaluated. Here, we identify some of these limitations and propose an improved method that takes advantage of the various known procedures. In this method, fluid composition is reconstructed by leaching all quenched precipitates in the experimental samples, in its spirit an identical approach as *Keppeler* [1996]. While *Keppeler* [1996] conducted the experiments on a large quantity of material (100+ mg), we reduced the sample quantity to approximately 10 mg by adapting calibrated leaching procedure. Result for fluid composition in equilibrium with anti-

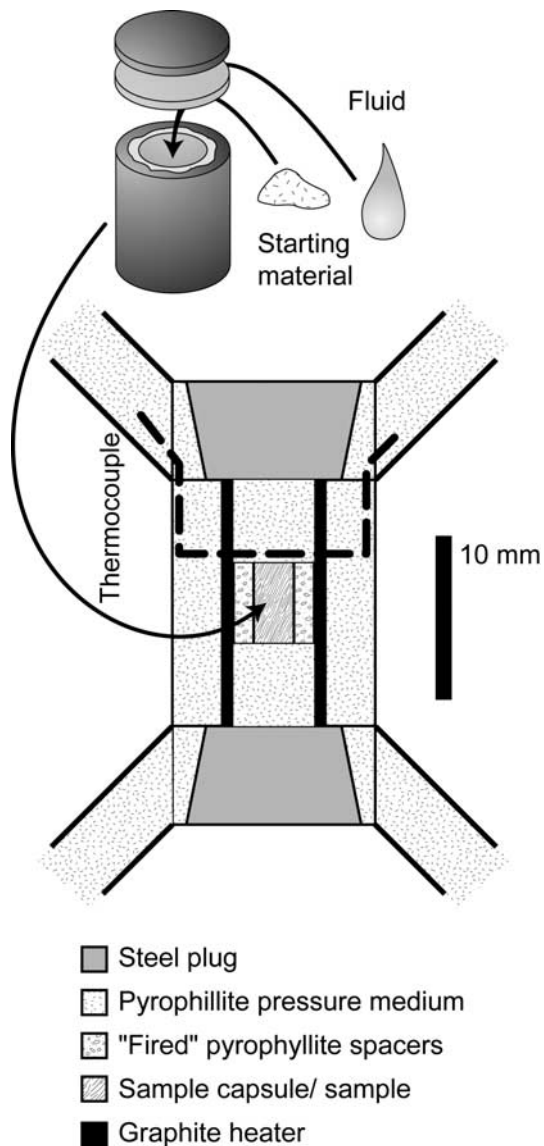


Figure 1. Illustrations of pressure-seal capsule and experiment assembly. Top illustration shows the capsule. The pressure-seal capsules are made of hard metal (Ta or Ni) lined with Au tube that is sealed at one end (shown as light gray part). Size of outer capsule is 3 mm diameter and 5 mm long; Au tube is 1.9 mm diameter with 0.3 mm wall thickness, 4 mm long. Au gasket is sandwiched between the capsule and a hard metal lid. The bottom is a scaled cross section of an assembly used for belt experiments.

gorite at high pressure and temperature are presented and also error propagation methods used to discuss the applicability of the approach. As an example, the proposed method is applied to a fluid-antigorite system doped with trace elements,

since this should represent fluid-mantle interactions in subduction zones.

2. Method

2.1. Starting Material

[8] The experiments were conducted in a system that mainly consists of $\text{MgO-FeO-SiO}_2\text{-H}_2\text{O}$. In order to promote the growth of antigorite, a small quantity of antigorite serpentinite powder from Cuba (sample Cu12 described by *Auzende et al.* [2002]) was mixed with forsterite ($\text{Mg}_{1.8}\text{Fe}_{0.2}\text{SiO}_4$), enstatite ($\text{Mg}_{1.7}\text{Fe}_{0.2}\text{Al}_{0.2}\text{Si}_{1.9}\text{O}_6$) (powders of hand picked crystals from a Kilbourn Hole nodule, New Mexico, USA) and with MgO and SiO_2 oxides. Mixing proportions were on dry weight: MgO 35.0 wt%, SiO_2 25.3 wt%, forsterite 21.3 wt%, orthopyroxene 14.5 wt%, and antigorite 3.9 wt% with $\pm 5\%$ relative uncertainty. This mixture results in 0.8 wt% Al_2O_3 and 3.3 wt% FeO as minor impurity.

[9] The selected trace element ICPMS standard solutions were mixed and diluted to 100 ppm by weight to form a doping agent (see below for sample doping procedure). Liquid water (Millipore[®] water) was also used in capsule. Quantities of trace elements and water in each run were determined by weighing their masses with an absolute uncertainty of ± 0.2 mg, yielding a relative uncertainty of $\pm 7\%$. Contribution of initial minerals to the trace element budget is less than 2% relative of the total, except for Mn, Co, and Ni (15%).

2.2. Experiments

[10] The pressure-seal double capsule method was adapted to retain water inside the capsule (Figure 1). The capsule construction and run procedures are detailed by *Ayers et al.* [1992]. A gold capsule of 12 mm^3 was employed, for conducting experiments at pressures up to 3 GPa or more. For loading the starting materials, first, using a syringe, the trace element solution was dropped in the capsule, and subsequently dried in order to eliminate the acid. Then, the powder mixture was added to the capsule. For every step, the capsule was weighed to determine the quantity of added materials. The capsule loaded with the powder was kept in drying oven at 80°C while assembling pressure-transmitting cell. When the assembly was nearly completed, a weighed quantity of liquid water was introduced in the cooled capsule. The capsule was tightly sealed with the gasket using a vice,

Table 1. Mass of Experimental Material^a

	Solid	Fluid	Total
Start	3.0	3.0	6.0
Recovered	3.3	2.4	5.7
Expected ^b	3.5	2.5	6.0

^a 2.4 GPa, 550°C, annealed for 38 hours. Unit in mg; uncertainty of weighing is ± 0.2 mg.

^b Expected solid and fluid masses are calculated using antigorite chemical formula, assuming the entire initial solid has converted to antigorite.

weighed, and immediately assembled to start experiments.

[11] A belt press [Hall, 1960] at University of Lyon 1 was used to reach pressure conditions of 2–4 GPa. The press was calibrated against the room temperature fixed-point metal transitions and high-temperature quartz to coesite reaction. Temperature was monitored with a chromel-alumel K-type thermocouple encased in a stainless steel sheath. If the thermocouples broke during compression, relationship between output power and temperature was used to obtain the desired temperature. Judging from several power-temperature relationships, the uncertainty of the run condition temperature was $\pm 40^\circ\text{C}$ at worst.

[12] The sample capsule was recovered from the assembly and immediately weighed to check for water loss. It turned out that capsule was often oxidized, leading to weight gain, or chipped during recovery resulting in significant weight loss. Despite successful run recoveries, weight differences of ± 4 mg were observed, higher than the introduced amount of water (Table 1). In order to refine the procedure for a posteriori measurement of retained water, we first peeled off the hard metal lid, then slowly abraded off the Au using a rotating cutter, until Au was removed 0.5 to 1 mm deep. Then, the capsule was weighed, before opening with a sharp needle. Upon piercing, fluid came out from the capsule, which was then carefully dried in an oven at 80°C for 12 h, before a new weighing. Weight difference was attributed to the quantity of water present in the capsule, at the end of the experiment. The capsule was then carefully opened to recover the powder, which mass was measured both by the direct quantity and mass difference of the emptied capsule. The difference between the two values never exceeded 0.1 mg. Closure of system was diagnosed when the total of fluid and powder masses were within 5% of the mass initially introduced (Table 1).

2.3. Dissolution of Quench Precipitates

[13] As a sample was quenched and dried, dissolved elements precipitated as oxide, amorphous material, and hydroxides. All of them were susceptible to the attack of base or acid. Following the procedure of clay mineral separation, we leached these precipitates from high-pressure minerals such as serpentine in the present study [Gilg *et al.*, 2004; Girard and Fouillac, 1995]. First, the extracted powder was mixed with up to 3 mL of NaOH (0.5 N) and stirred for 3 min, in order to leach such compounds as amorphous silica. The solution was centrifuged and clear liquid was carefully removed. Distilled water (2 ml) was added for rinsing; the wet powder was stirred, centrifuged and then the liquid was removed. Second, the rinsed powder was mixed with up to 3 mL HCl (1N). This step was aimed to attack remaining oxides precipitates. The mixture was stirred for 2 min then rinsed. Thirdly, the HCl leaching procedure was repeated with 5 min stirring. Each leached solution was kept in separate vials and mixed with rinsed solutions that immediately followed the leach. No solution was discarded during this procedure.

[14] Leached and rinsed powders were then dried, weighed, and completely dissolved by HF and HNO₃ following a commonly used rock digestion technique [e.g., Blichert-Toft *et al.*, 1997]. The mass difference between before and after the leaching was normally less than 10%. As the attack was completed, the solution was dried and dissolved with a 5 to 10 mL of HNO₃ solution (3 mol%) for ICPMS analysis.

2.4. Analysis of Powder and Quench Precipitates by ICPMS

[15] We have used a quadrupole ICPMS (Thermo Elemental X7 at ENS Lyon) to determine the concentration of elements in the leachates and attack solutions. In a standard procedure, the concentration of elements in the solution was diluted to meet a range of 1–50 ppb with 3% HCl or HNO₃ solution, which is an optimal concentration for ICPMS detection. During analyses, blank solution was monitored for every 3 to 5 analyses. When high blank were detected, the samples were reanalyzed.

[16] Prior to ICPMS measurements, the masses of prepared solutions were measured within an uncertainty of $\pm 0.05\%$, which is further considered as negligible. The measured concentration was then

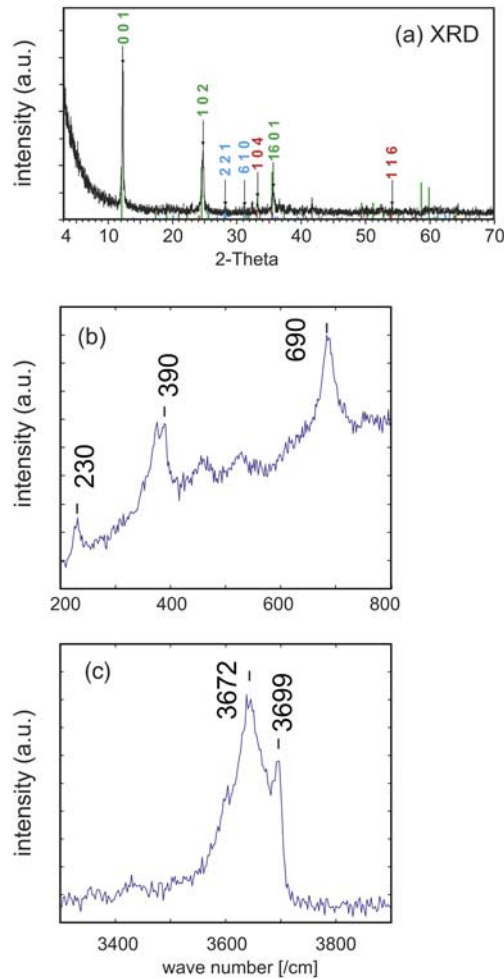


Figure 2. Characterization of run products by (a) X-ray diffraction (monochromatic ray at 1.541Å) with 2-theta degrees on a horizontal axis and arbitrary intensity on a vertical axis and (b and c) Raman spectroscopy. In Figure 2a, green tick lines show expected peak positions of antigorite. The observed peaks and these ticks are in good agreement. Blue ticks represent enstatite, and red is hematite. The indices are shown by the corresponding colors. The signal is dominated by antigorite and thus confirms the synthesis of antigorite. In (b) low-frequency and (c) high-frequency plots, spectra of Raman scatter are shown with wave number on a horizontal axis and arbitrary intensity on a vertical axis. The peak positions correspond to known antigorite spectra [Auzende *et al.*, 2004].

converted to the total mass of element present in each vial. The masses of an element in vials from three leaching steps were added to obtain the total mass of an element leached by the procedure. The total masses of elements were then divided by the mass of fluid (determined by drying) to calculate the concentration of elements in fluid in an exper-

iment, before the quench. The uncertainties are within $\pm 20\%$.

3. Results

3.1. Confirmation of Phases

[17] The presence of fluid in a capsule is confirmed by eye observation upon the piercing of the capsule. This observation and the absence of measurable water loss (Table 1, discussed above) give the evidence that fluid has been retained at high-pressure and -temperature conditions and recovered after quench. It should be noted that the amount of recovered fluid is less than the introduced amount. Proportionally, complete hydration of the starting solid material results in a +10 to +15% gain of the initial mass.

[18] The presence of antigorite was confirmed by Raman spectroscopy and X-ray diffraction. Both analyses were performed on the powder recovered after the leaching. Figure 2a shows the X-ray diffraction pattern of an experiment. The dominant phase is definitely antigorite. Minor phases, enstatite and hematite, are also present in the run products. However, the relative intensity of their most intense diffraction line, compared to that of antigorite, indicates that they constitute less than 5 wt% of the powder. The presence of antigorite as the most abundant mineral was also confirmed by Raman spectroscopy (Figures 2b and 2c). No accessory phases (e.g., zircon, rutile) were found in a quench material.

3.2. Stepwise Leaching

[19] The goal of leaching is to recover all the precipitates formed during quench. We have therefore tested the effectiveness of leaching on the quenched material, by monitoring sequentially the cations released into fluid at each step of leach (Figure 3). In Figure 3a, two leaching series are shown, and they illustrate the extent of leaching and the optimal cutoff time: (1) sequential leaching in a stirred NaOH solution, followed by repeated steps of 1 to 2 min leaching in a HCl solution (Figure 3a, solid diamond) and (2) sequential leaching in a stirred NaOH solution, followed by repeated steps of 1 to 2 min leaching in a HCl solution, and the final leaching by a 5 min ultrasonic wash in HCl (Figure 3a, open circle). The quantity of Mg leached out decreases monotonically during the progressive HCl wash over 6 min total. In contrast, a violent ultrasonic wash releases large quantity of Mg into solution

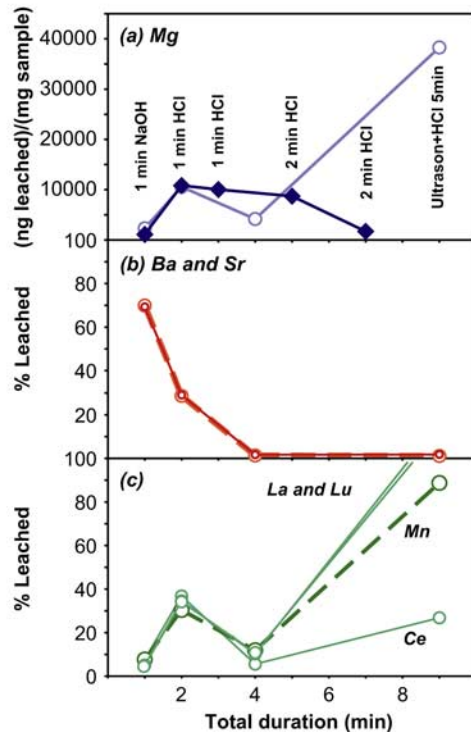


Figure 3. Abundance of elements mobilized by stepwise leaching shown as percent fraction of total budget in a system. (a) Abundance of Mg in leachates. The line with solid diamonds is one series of leaching without ultrasound wash, and the line with open circles is the other series with ultrasonic wash. (b) Ba and Sr show almost identical behavior (ultrasonic wash). Thick broken line is Ba, and solid thin line is Sr. (c) REE and Mn mobility is somewhat similar to Mg. They are readily mobilized by ultrasonic wash. “% leached” is the relative quantity of the mass of element leached and the mass of element in system. Some exceed 100% due to uncertainty in measurements.

suggesting that antigorite dissolved. We conclude that stepwise acid wash of approximately 6 min is optimal.

[20] The trace elements are also removed by the leaching. The precipitates of Ba and Sr are readily removed by NaOH leaching and HCl leaching (Figure 3b). Because they are incompatible elements, excess leaching (by HCl ultrasonic wash) does not further remove the elements. In contrast, Rare Earth Elements (REE) and Mn are removed somewhat like Mg, that is immobile against NaOH and mildly mobile with HCl. The release of large quantity of REE and Mn with an ultrasonic wash illustrates that elements in Figure 3c are more compatible than those of Figure 3b. Thus the

stepwise acid wash stopped at 6 min prevents the dissolution of elements compatible to solids.

3.3. Fluid Composition and Partition Coefficients

[21] The concentration of elements in the fluid is found by dividing the total masses with the mass of fluid present during experiments (Table 1), since total masses of elements removed by the leaching procedure are equal to the masses of elements presumably present in fluid during high-pressure temperature experiments. Using the measured masses of the fluid and solid in the experiment, the total quantity of element measured in experiments is calculated, and compared against total mass of element initially introduced with the doped solution. Propagating the respective uncertainties, with the largest contribution from the weighing procedure, a successful experiment leads to the recovery of elements within $100 \pm 15\%$ (Table 2). A majority of elements are successfully recovered.

[22] Some elements are not quantitatively recovered. For example, boron is completely lost due to its volatility, despite the initial dope. Similarly, Ag cannot be recovered, probably due to alloying with the Au capsule during experiments. However, we have no obvious explanation for the depletion of Co and Ga, their recovery is less than complete. Limited alloying of these elements with Au may explain the depletion.

[23] Partition coefficients of trace elements are calculated from the ratio of the equilibrium fluid concentrations obtained from the above method and the solid phase concentrations from the HF-HNO₃ attack. In our experiment, the solid is nearly 100% antigorite. Thus the partition coefficient represents that of antigorite and fluid at high-pressure and -temperature conditions. The propagation of error on solid and liquid compositions results in a general range from ± 20 to $\pm 30\%$ relative uncertainty for the partition coefficients (Table 2).

4. Discussion

4.1. Strengths and Weaknesses of the Method

[24] The experiments are conducted at high-pressure conditions under which the volume of the sample is limited to approximately 10 mg. It should be stressed that there is a trade off between the

Table 2. Results of ICPMS Measurements for an Experiment^a

	Mass Leached, ng	Conc. in Fluid, ppm	Conc. in Solid, ppm	Element Loss, ^b %	D (Solid/Fluid)
B	0	0	0.0	100	
Mn	225(7)	90(14)	112(44)	32(18)	
Co	176(6)	70(12)	52(6)	60(10)	
Ni	196(6)	78(13)	411(199)	14(8)	5.2(33)
Cu	395(13)	158(25)	155(9)	0(23)	1.0(2)
Ga	183(3)	73(12)	47(4)	61(10)	
Sr	791(7)	316(26)	2.5(24) ^c	11(8)	0.008(8)
Ag	0	0	0.0	100	
Cd	633(13)	254(34)	22(2)	21(18)	0.09(2)
Ba	709(14)	284(46)	90(7)	0(35)	0.32(8)
Pb	975(24)	390(63)	1.1(9) ^c	0(45)	0.003(3)
Bi	994(23)	397(64)	41(3)	0(47)	0.10(2)
Eu ^d	18.2(4)	7.3(8)	26(6)	19(8)	3.5(14)

^a2.4 GPa, 550°C, annealed for 38 hours.^b“Element loss” is the mass fraction (%) of element that is not recovered after the experiment.^cData obtained with high ICPMS blank. The numbers inside the parentheses are the uncertainties on the last digits of the value.^dEuropium result is taken from another experiment (2.8 GPa, 550°C, 89 hours). Initial mass of each element introduced in the system is 900 ng except for Eu (135 ng) and Ni (1900 ng).

volume of the sample and the size of the uncertainty. Each weighing process has a precision of ± 0.2 mg. If the weighed quantity is 2.0 mg, the uncertainty is 10%. Certainly, if the sample mass is larger, the relative uncertainty inversely diminishes. Therefore a sample mass of 10 mg is near the limit of the current procedure, and the results of 2 weighing procedures and 2 concentration measurements by ICP-MS gives a $\pm 30\%$ uncertainty on the partition coefficients.

[25] The leaching of the bulk experimental sample can extract the fluid composition from the sample charge that is a mixture of fluid and solid. As we have stressed in the introduction, the complete mixture of fluid and solid in a charge promotes the attainment of equilibrium. The draw back of the leaching is the possibility of leachate contamination by excess dissolution of solid. For example, if a large quantity of antigorite is dissolved in the leachate, the fluid composition and the calculated partition coefficient will not be accurate. Our results on three experiments conducted at the same temperature conditions show general constancy of partition coefficients over a range of 1.5 GPa (Table 3). While the range of variation of Ba partition coefficients spans over a factor of 2, the Bi partition coefficients vary over a factor of 4. Certainly some variations are greater than our propagated uncertainty. The mass of the leached residue is approximately 5–20% less than the mass of the solid before the leach. The mass reduction can occur during the manipulation of small quantity of powder. Assuming all the missing mass contributes to the leachate contamination, the par-

tion coefficients of incompatible elements would shift to approximately 10% greater values, and the partition coefficients of compatible elements ($D < 10$) may shift to approximately 50% lesser values. The absolute values of the partition coefficients of compatible elements are more sensitive to excess leaching. When the leaching method is applied, it is thus critical to calibrate the leaching procedure to the mineral of interest.

4.2. Comparisons With Other Experimental Techniques

[26] Experiments with large fluid fractions [Brenan *et al.*, 1995a, 1995b, 1998; Ayers *et al.*, 1997] rely upon high-quality measurements of trace element concentrations in minerals to determine the fluid composition by the mass balance calculation. This approach requires the demanding condition of a

Table 3. Representative Results at 550°C

P, GPa	2.4	3.3	3.9
Duration, hours	38	42	91
Fluid frac. ^a	0.41(8)	0.44(9)	0.29(6)
Ni	5.2(33)	3.3(9)	2.0(9)
Cu	1.0(2)	3.1(12)	1.2(9)
Sr	0.008(8) ^b	0.020(10)	0.017(8)
Cd	0.09(2)	0.08(2)	
Ba	0.32(8)	0.20(8)	0.49(10)
Pb	0.003(3) ^b	0.05(1)	0.03(1)
Bi	0.10(2)	0.08(2)	0.35(10)

^a“Fluid frac.” is a fraction of fluid in experiment expected during the run conditions.^bData obtained with high ICPMS blank.

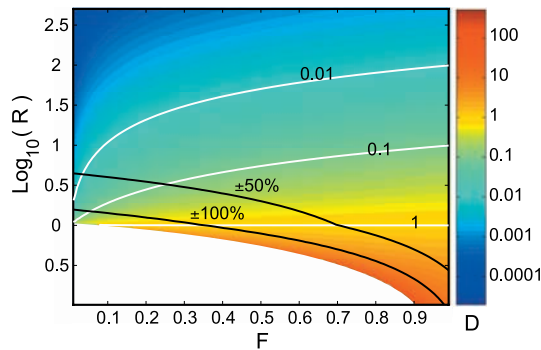


Figure 4. Projection of uncertainty on the contour of partition coefficient determined by two values. The mass balance calculation determines partition coefficient (D) of a system from two measured variables: fraction of fluid in a system (F) and the ratio of total concentration of element in a system over measured solid concentration (R). The formula is given as $D = \frac{F}{R+F-1}$. Partition coefficients are shown as color contour with white solid lines. Relative uncertainty of D, due to measurement uncertainty for R and F, is calculated and plotted as solid black lines. The relative uncertainty is less than the indicated value in region above a line. For example, $D = 1$ determined at fluid fraction of 0.6 has relative uncertainty from 50 to 100%. Here, the uncertainties of F and R are chosen as $\pm 10\%$ and $\pm 35\%$, respectively, which are typical published values.

closed system during experiments. Uncertainties of partition coefficients reported for experiments of *Brenan et al.* [1995a, 1995b, 1998] are approximately 30–50%. Analysis of error propagation shows that this approach is very effective in determining very small partition coefficients, such as those reported by *Brenan et al.* [1995a, 1995b, 1998]. However, owing to the mathematical form of the mass balance calculation, unreliable partition coefficients are obtained if elements are compatible (Figure 4). For example, the relative one-sigma uncertainty is $\pm 100\%$ for a partition coefficient of 1, when determined from an experiment with a fluid fraction of 0.3. This essentially prevents one to distinguish compatible from incompatible elements. In extreme cases, one cannot statistically differentiate partition coefficients of 100 from 10, because the more compatible the element, the more uncertain the value of the partition coefficient.

[27] *Ayers et al.* [1997] determined the abundance of trace elements in the fluid by separating the quench precipitates from minerals using a perforated membrane. This method allowed the determination of fluid composition especially for

elements that are compatible to minerals. Because a small quantity of fluid remains in the pore space of minerals and that cannot be included in the *Ayers et al.* [1997] analytical method, the measurement uncertainty for elements that are incompatible to minerals is significantly influenced by the estimates of fluid quantity in the mineral pores.

[28] The diamond aggregate technique isolates fluid from solid and allows direct LA-ICPMS measurements of the abundance of elements in the trapped fluid. This technique avoids the shortcoming of the mass balance calculation by measuring fluid composition. Although fluid composition is modified during quench, all quench products are expected to remain within the pores. Because the laser beam is larger than the pores, it ablates a heterogeneous material composed of quenched fluid and diamond aggregate. Therefore the measured values represent an average, but for determination of fluid composition, the results must be corrected for the mass of diamond ablated. The reported uncertainties for element concentrations in fluid are ± 30 to $\pm 40\%$ [*Stalder et al.*, 1998]. Recently, *Kessel et al.* [2004] demonstrate that a combination of a freezing stage, LA-ICPMS, and Cs internal standard phenomenally reduces the uncertainty of the measurements (± 0.7 to $\pm 2.5\%$). Our method lacks such state-of-the-art precision. However, it does not require the internal standard that must be absolutely incompatible to solids in the experiments. Our method is suited for experiments concerning serpentine, mica, or amphibole, because Cs cannot serve as an internal standard in these conditions.

[29] We stress the importance of this experimental approach particularly for moderately and highly compatible elements, although the excess leaching affects the accuracy. When the leaching is properly calibrated, it improves the uncertainty on the fluid composition, compared with that obtained by the mass balance method. It also gives an advantage to experiments that do not crystallize large crystals, such as antigorite. In such a case, chemical leaching of phases can efficiently isolate the solid part from the fluid precipitates. The application of this method to other mineral-fluid systems will involve (1) calibration of the strength of acid and (2) selection of elements which do not easily react with the surrounding capsule. For trace element partitioning experiments on the highly incompatible elements, we conclude that the mass balance technique [*Brenan et al.*, 1995a, 1995b, 1998; *Ayers et al.*, 1997] is better suited. Furthermore, the mass bal-

ance technique can be combined with the leaching technique to determine internally consistent partition coefficient.

[30] Increasing the quantity of material used in experiments can reduce the uncertainty associated with this procedure. We note that uncertainties on partition coefficients originate from measurements of mass and concentration in fluid and solid. The contribution of the solid to the uncertainty would be minimized if the composition of individual minerals could be measured by microanalytical technique, such as ion probe and LA-ICPMS. Moreover, combination of the present method with those microanalytical techniques would allow determining the multiple partition coefficients between fluid and the minerals present in a single equilibrium experiment.

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