#### FLUIDS IN THE CRUST

# Constraints on the mobilization of Zr in magmatic-hydrothermal processes in subduction zones from in situ fluid-melt partitioning experiments<sup>‡</sup>

### MARION LOUVEL<sup>1,\*</sup>, CARMEN SANCHEZ-VALLE<sup>1,†</sup>, WIM J. MALFAIT<sup>1</sup>, HERVE CARDON<sup>2</sup>, DENIS TESTEMALE<sup>3</sup> AND JEAN-LOUIS HAZEMANN<sup>3</sup>

<sup>1</sup>Institute for Goechemistry and Petrology, ETH Zurich, CH-8092, Zurich, Switzerland <sup>2</sup>Laboratoire de Géologie de Lyon, ENS Lyon, FR-69364, Lyon, France <sup>3</sup>Institut Néel, Département MCMF-Grenoble, FR-38042, Grenoble, France

#### ABSTRACT

The partitioning of Zr between high P-T aqueous fluids and melts has been investigated in situ in the haplogranite-H<sub>2</sub>O and haplogranite-(F)-H<sub>2</sub>O systems to assess the mobilization of high field strength elements (HFSE) in magmatic-hydrothermal processes in subduction zones. The partition coefficients  $D_{Tr}^{\ell m}$  were determined from Zr concentrations measured in situ by synchrotron X-ray fluorescence (SXRF) in both aqueous fluids and F-free or F-bearing hydrous haplogranite melts equilibrated in diamond-anvil cells at 575 to 800 °C and 0.3 to 2.4 GPa. This experimental approach eliminates the need for internal or external calibrations of the SXRF signal and/or post-mortem analysis of the melt phase, hence decreasing the total uncertainties on  $D_{Zr}^{Um}$  below 16%. Above 0.6 GPa, Zr partitions favorably into the hydrous silicate melt in both F-free and F-bearing systems, with  $D_{Zr}^{\ell m}$  that range between  $0.19 \pm 0.02$  and  $0.38 \pm 0.03$ . However, the relatively high  $D_{Zr}^{Um}$  values indicate that alkali-silica rich aqueous fluids generated by metamorphic devolatilization may contribute significantly to the recycling of HFSE in subduction zones. The efficient uptake of Zr (and likely other HFSE) by subduction zone fluids, regardless of their nature (aqueous fluid, hydrous melt, or supercritical fluid), supports the idea that the typical HFSE depletion recorded in arc magmas does not result from their incompatibility in water-rich slab-derived fluids but most probably originates from complex fluid-melt-rock interactions occurring at the slab interface and within the mantle wedge. At shallow crustal pressure conditions (800 °C and 0.3 GPa), Zr partitions reversely into the aqueous fluid in the presence of fluorine  $(D_{Zr}^{en} =$  $1.40 \pm 0.10$ ) as observed for Nb at similar conditions by Webster et al. (1989). The enrichment of the aqueous phase in HFSE (Zr, Nb) at shallow crustal conditions is likely related to the enhanced peralkalinity of low pressure, F-bearing aqueous fluid with temperature, that provides the favorable conditions for their mobilization via the formation of HFSE-O-Si/Na clusters. This mechanism may control the enrichment in HFSE (and plausibly other rare metals such as REE) in early magmatic fluids exsolved from granitic melts, leading to the formation of HFSE-enriched aggregates in shallow magmatic-hydrothermal environments (e.g., Strange Lake and Thor Lake Nechalacho deposit, Canada; Galineiro complex, Spain).

Keywords: Zirconium, HFSE, fluid-melt partition coefficients, SXRF, subduction zones, rare metal deposits

#### INTRODUCTION

It is widely accepted that volatile-rich fluids released from the subducting slab favor partial melting of the mantle wedge and drive arc magmatism (Hermann et al. 2006; Johnson and Plank 1999; Manning 2004; Schmidt and Poli 1998; Stern 2002). However, the link between the chemistry of subduction zone fluids (e.g., aqueous fluid, supercritical liquid, or slab melt) and the trace element signature of arc magmas remains poorly understood. Subduction-related volcanic rocks are characterized by a strong enrichment in large ion lithophile elements (LILE: Sr, Rb, Th, U...) and a depletion in high field strength elements (HFSE: Nb, Ta, Zr, Ti, Hf) compared to mid-ocean ridge basalts (Gill 1981; Hawkesworth et al. 1991). This signature is mainly controlled by the incompatible or compatible behavior of trace elements upon fluid/melt-rock interactions in the slab and/or the mantle wedge. For instance, the HFSE depletion has commonly been assigned to the low solubility of HFSE-bearing accessory phases, such as rutile or zircon, in H<sub>2</sub>O (Antignano and Manning 2008; Audetat and Keppler 2005; Tropper and Manning 2005) and their selective segregation in minerals from the slab or the mantle wedge such as Ti-clinohumite, olivine, pyroxenes,

<sup>\*</sup> Present address: Research School of Earth Sciences, ANU, AU-0200, Canberra, Australia. E-mail: marion.louvel@anu.edu.au † E-mail: carmen.sanchez@erdw.ethz.ch

<sup>‡</sup> Special collection papers can be found on GSW at http://ammin. geoscienceworld.org/site/misc/specialissuelist.xhtml.

garnet, or spinel (Brenan et al. 1994; Foley et al. 2000; Kelemen et al. 1990; Rudnick et al. 2000; Rubatto and Hermann 2003; Scambelluri and Philippot 2001; Spandler et al. 2007). This assignment supports a significant contribution of diluted aqueous fluids to mantle wedge metasomatism. Conversely, the relative HFSE-enrichment recorded in high-Nb basalts (HNB) or adakitic magmas in volcanic arcs such as Kamtchatcka, Cascades, or Lesser Antilles (Bouvier et al. 2010; Defant and Drummond 1993; Munker et al. 2004) has frequently been attributed to the contribution of hydrous slab melts to their primary source, in good agreement with the relatively high solubility and partitioning of HFSE in silicic melts (Dickinson and Hess 1985; Keppler 1993; Hermann and Rubatto 2009; Linnen and Keppler 1997; Linnen and Keppler 2002; Klimm et al. 2008). However, the occurrence of rutile or zircon-rich veins in UHP metamorphic rocks (Gao et al. 2007; Rubatto and Hermann 2003) indicate that high temperature aqueous fluids have the potential to mobilize and transport nominally insoluble HFSE in subduction zones. Experimental studies provide further evidences that the addition of Cl, F, and alkali-silicates can significantly enhance the solubility of HFSE-bearing phases in aqueous fluids (Antignano and Manning 2008; Hayden and Manning 2011; Manning et al. 2008; Rapp et al. 2010; Wilke et al. 2012), most probably via the formation of alkali-silicate complexes (Louvel et al. 2013; Wilke et al. 2012). The aqueous fluids produced by metamorphic devolatilization of the subducting slab can contain up to several wt% of dissolved Si, Na, and Cl (Scambelluri and Phillippot 2001; Manning 2004). Consequently, melting of the slab may not be required to tranfer HFSE to arc magma source regions. The efficient uptake of HFSE by aqueous fluids is also recorded in large crustal granitic complexes, where remobilization of HFSE by highly alkaline late-magmatic fluids was found to enhance the potential to form economical rare metal ore deposits (Zr, Nb, REE; Strange Lake and Thor Lake Nechalacho deposit, Canada; Galineiro complex, Spain; Agangi et al. 2010; Gysi and Williams-Jones 2013; Salvi and Williams-Jones 1996; Sheard et al. 2012).

The goal of this paper is to improve our understanding of the processes controlling the mobilization/segregation of HFSE in subduction zones and their hydrothermal enrichment in large granitic complexes in the shallow crust. This requires better constraints on the partitioning behavior of HFSE in complex fluid-melt-rock systems at relevant pressure and temperature conditions. Up to now, experimental studies of the distribution of HFSE are however mainly limited to investigations of HFSE partitioning between crystals and melts  $D^{c/m}$  (Green et al. 2000; Kelemen et al. 1990; Klemme et al. 2002, 2005; Klimm et al. 2008; Prowatke and Klemme 2005). Very few studies have determined crystal-fluid partitioning coefficients D<sup>c/f</sup> for HFSE at such conditions (Adam et al. 1997; Ayers et al. 1997; Kessel et al. 2005; Stalder et al. 1998), mostly due to challenges associated to the recovery and analysis of solute-rich fluid phases. In addition, investigations of fluid-melt partitioning of HFSE have been limited to the study of magmatic-hydrothermal processes in the crust (P < 0.3 GPa, Borodulin et al. 2009; Keppler 1996; London et al. 1988; Webster et al. 1989) without direct applications to assess the mobilization of HFSE from subducting slab. Measurements of aqueous fluid-melt partition coefficients  $D^{f/m}$  at high P-T conditions are advantageous because the equilibration times for melt-fluid systems are shortened compared to crystalfluid systems. Moreover, the  $D^{\ell m}$  values can be converted into  $D^{e/f}$  values using available  $D^{e/m}$  data according to the equation  $D^{e/f} = D^{e/m}/D^{\ell m}$ .

In this contribution, we present in situ experiments conducted to investigate the partition of Zr between aqueous fluids and silicate melts at P-T conditions relevant for subduction zones and crustal magmatic-hydrothermal settings. Fluid-melt partition coefficient of  $Zr(D_{Zr}^{f/m})$  were determined from in situ synchrotron X-ray fluorescence (SXRF) analysis of alkali silicate-bearing aqueous fluids and hydrous haplogranitic (F-free and F-bearing) melts equilibrated in hydrothermal diamond-anvil cells (HDAC; Bassett et al. 1993) at 575 to 800 °C and 0.3 to 2.4 GPa. The in situ characterization of both the aqueous fluid and hydrous melt phases overcomes the need for calibration of the absolute fluorescence signal, the use of internal standards or post-mortem analysis of the quenched hydrous melts, hence reducing total uncertainties in  $D_{Zr}^{f/m}$  below 16%. The investigated haplogranitic melts are peralkaline in composition and represent reasonable analogs for slab melts produced by the breakdown of alkali-rich phases (i.e., phengite, biotite, or amphiboles) during the hydrous melting of subducted pelite or MOR-basalts (Hermann and Spandler 2008; Prouteau et al. 2001), and for the composition of granitic bodies that lead to the formation of HFSE deposits in the upper crust (Salvi and Williams-Jones 1996; Montero et al. 1998). The results are used to discuss the role of aqueous phases in the transport and deposition of Zr, and by extension other HFSE, in subduction-related metamorphic and magmatic environments, from the subducting slab to the upper crust.

#### METHOD

#### In situ SXRF measurements in the HDAC

The partition of Zr between haplogranite melts and aqueous fluids was investigated as a function of pressure, temperature, and composition in high P-T experiments conducted in Bassett-type hydrothermal diamond-anvil cells (HDAC; Bassett et al. 1993). The HDAC were mounted with low fluorescence type Ia diamonds with a 600 or 700 µm diameter culet. The thickness of the diamond window on the detector side was reduced to 1.2 mm to decrease the detection limits of the SXRF analysis (Sanchez-Valle et al. 2004). The sample chamber was formed by a 300 µm hole drilled in a 250 µm thick rhenium gasket compressed between the two diamond anvils and externally heated with Mo wires wrapped around the WC seats supporting the diamond anvils. During heating, the cell was continuously flushed with a reducing gas (98% Ar-2% H mixture) to prevent the oxidation of the Mo heaters, the WC seats or the diamond anvils. Temperature was measured to  $\pm 2$  °C with K-type thermocouples attached on each diamond-anvil near the sample chamber. The temperature gradient between the thermocouples and the sample chamber was calibrated for each HDAC using the melting temperature at ambient pressure of sulfur (115.4 °C), sodium nitrate (308 °C) and sodium chloride (800.5 °C). The pressure in the sample chamber was monitored with a precision better than 10% from the variation of the lattice parameters of an Au internal pressure standard determined by angle-dispersive X-ray diffraction (Louvel et al. 2013) using the equation of state for Au of Jamieson et al. (1982).

The sample chamber was loaded with a piece of Zr-bearing haplogranite glass and a pellet of a mixture of Au + Al<sub>2</sub>O<sub>3</sub> powders used for pressure calibration (Louvel et al. 2013) and subsequently filled with Milli-Q water. Fluorine-free and fluorine-bearing haplogranite glasses, both doped with 4000 ppm Zr, were used in the experiments to determine the influence of F on the partition of Zr between aqueous fluids and melts (Table 1). The haplogranite glass samples are from the same batch used in a previous study of the speciation of Zr in subduction zone fluids and details about the synthesis and characterization are found in Louvel et al. (2013). The volumetric proportions of glass and aqueous fluid in the loading were adjusted by adding double-side polished glass pieces of known proportions to the sample chamber of known dimensions. Upon heating and compression, the haplogranite melt-aqueous fluid system displays the phase relations documented in previous studies (e.g., Bureau and Keppler 1999; Mibe et al. 2008; Shen and Keppler 1995). Depending on pressure conditions, hydrous melting of the haplogranite glass was observed at around 600–650 °C. The partitioning measurements were performed in the coexisting hydrous melt and aqueous fluid up to 800 °C (Table 2). A microphotograph of the sample chamber arrangement during the experiments can be found in Figure 1.

SXRF measurements were performed at the BM30b FAME beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France; Proux et al. 2005, 2006) together with the X-ray absorption spectroscopy (XAS) measurements previously reported in Louvel et al. (2013). Briefly, SXRF spectra were collected using a monochromatic beam of 18.05 keV focused down to  $10 \times 15$  $\mu m^2$  (FWMH VxH) by a set of Kirkpatrick-Baez mirrors. This configuration ensured a photon flux of ~109 photons/s at the Zr K-edge energy. The emitted fluorescence radiation ( $ZrK\alpha = 15.77$  keV) was collected in transmission at the rear-side of the cell using a Si drift detector set at 20° from the incident beam in the horizontal plane (Sanchez-Valle et al. 2003, 2004). This configuration enables collecting SXRF throughout the entire sample chamber and hence the in situ sampling of both the aqueous fluid and the hydrous melt at identical P-T conditions (Fig. 2.), with the advantage of avoiding post-mortem characterization of the quench melt (Bureau et al. 2007; Borchert et al. 2009). Angle-dispersive X-ray diffraction patterns ( $\lambda = 0.69654$  Å) were collected on the internal Au pressure calibrant before and after each SRXF analysis using a high-resolution CCD camera positioned behind the cell in transmission geometry.

After each heating step, the temperature was stabilized for about 30 min. The temporal evolution of the Zr concentration in the fluid and hydrous melt was monitored by repeated SXRF analysis in both phases until the intensity of the fluorescence signal (i.e., Zr concentration) was constant. Time series SXRF measurements revealed that equilibrium was typically achieved within less than 30 min after reaching the target P-T conditions, in agreement with previous reports (Borchert et al. 2009). 2D-SXRF concentration maps and transversal fluorescence scans were collected across the sample chamber to monitor the

distribution of Zr between the aqueous and melt phases (Fig. 1). SXRF analysis were only performed once the system reached a stable state where the melt globule was stationary and bridging both diamonds to ensure the sampling of pure fluid and melt phases without contamination of the signal from the coexisting phase (Fig. 2 and 3). A minimum of three fluorescence spectra were collected in several locations across the fluid and the melt phases with counting times of 30 s. The intensities of spectra collected in each phase at identical *P-T* conditions were constant within <5%, indicative of the homogeneity of the fluid and melt phases. All SXRF spectra were normalized to the incident beam intensity for the quantitative analysis. Characteristic normalized fluorescence spectra recorded in the aqueous fluid and silicate melt at high *P-T* are reported in Figure 3.

#### Determination of fluid-melt partition coefficients D<sub>Zr</sub><sup>fluid/melt</sup>

The integrated intensity of the X-ray fluorescence emission line of an element  $(I_i)$  and its concentration in the analyzed phase  $(C_i)$  are related through a complex expression that depends on element-related factors (fluorescence cross section), experiment-related factors (angle of detection, contribution of the different media traversed by the X-ray) and sample-related factors such as density or thickness (Cauzid et al. 2006; Sanchez-Valle et al. 2004; Sparks 1980). It can be reduced as:

$$I_i = I_0 \cdot t \cdot A_{\text{eff}} e^{-B} \cdot e^{-C} \cdot C_i \cdot \sigma_i \rho_s \cdot e^{-X}$$
(1)

where  $I_0$  is the intensity of the incoming beam; t is the counting time;  $A_{\text{eff}}$  accounts for the efficiency of the fluorescence detector at the energy of the emitted signal;  $\sigma_i$  is the fluorescence cross section of the element *i* at the incident energy  $E_0$  and  $\rho_s$  is the density of the sample. The parameters B, C, and X are correction factors taking into account the absorption coefficient, the density and the thickness of the different media (i.e., air, diamond, and sample) traversed by the X-rays and the geometry of the experimental setup. As the partition coefficient of Zr between the fluid and melt phase,  $D_{Z^n}^{om}$ , corresponds to the ratio between the concentrations of Zr in each phase, Equation 1 can be rearranged as

 TABLE 1.
 Chemical composition (in wt%) of the F-free and F-bearing haplogranite glasses used as starting materials as determined from electron microprobe analysis (EMPA)

	Synthesis conditions											
Composition	T (°C)	P (GPa)	SiO <sub>2</sub> <sup>a</sup>	$AI_2O_3^a$	Na <sub>2</sub> O <sup>a</sup>	$K_2O^a$	$ZrO_2^a$	F <sup>a</sup>	Total	$H_2O^b$	ASI	NBO/T <sup>d</sup>
Haplo4	1200	1.5	75.74	8.32	7.56	4.52	0.418	-	96.558	3	0.48	0.13
Haplo4-F	1200	1.5	76.34	8.04	5.77	4.1	0.389	1.89	96.529	3	0.57	0.09
» A					. Chamalana			/ far Na O	NO KO-			

<sup>a</sup> Average of 20 EMPA analyses performed on each glass composition. Standard deviations are <0.1 wt% for Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, and F; <0.4 wt% for SiO<sub>2</sub>; and <0.05 wt% for ZrO<sub>2</sub>.

<sup>b</sup> Nominal H<sub>2</sub>O concentration.

 $^{c}\mathrm{ASI}{=}\frac{\mathrm{Al}_{2}\mathrm{O}_{3}}{\mathrm{Na}_{2}\mathrm{O}{+}\mathrm{K}_{2}\mathrm{O}}$  in moles.

<sup>d</sup> NBOT/T =  $\frac{Na + K + 4Zr - Al}{Al + Si}$  in moles.

TABLE 2. Zirconium fluid-melt partition coefficient as a function of P-T conditions, fluid, and melt compositions and densities

	$X_{g}^{a}$	<i>Т</i> (°С)	P (GPa)⁵	H <sub>2</sub> O dissolved in melt <sup>c</sup>	$\underset{\text{density}^{d} \rho_{m}}{\text{Melt}}$	Transmission in melt T <sub>m</sub>	Silicates in fluid	$ \begin{array}{c} Fluid \\ density^{h}  \rho_{f} \end{array} $	Transmission in fluid T <sub>f</sub>	$I_{Zr}^{f}/I_{Zr}^{m}$	$D_{\rm Zr}^{\rm f/m}$
						Haplogr	anite-H <sub>2</sub> O				
Run 1	0.79	660	1.5	17.3 ±2.3	$2.14 \pm 0.02$	0.84 ±0.01	12.4 ±2.2 <sup>f</sup> –15.3 ±3.3 <sup>e</sup>	$1.18 \pm 0.02$	0.97 < 0.01	$0.24 \pm 0.02$	0.38 ±0.03
		745	0.7	6.4 ±0.7	$2.24 \pm 0.01$	0.81 < 0.01	4.9 ±1.1 <sup>e</sup>	0.91 ±0.04	0.98 < 0.01	$0.18 \pm 0.01$	0.37 ±0.02
Run 2	0.69	575	0.85	9.0 ±1.1	$2.22 \pm 0.01$	0.82 < 0.01	3.3 ±0.6 <sup>e</sup>	$1.00 \pm 0.03$	0.97 < 0.01	$0.10 \pm 0.01$	0.19 ±0.02
		675	1.4	15.6 ±2.1	$2.15 \pm 0.02$	$0.84\pm\!0.01$	$11.4 \pm 2.2^{\rm f} - 15.5 \pm 2.8^{\rm e}$	$1.15 \pm 0.02$	0.97 < 0.01	$0.12 \pm 0.01$	$0.20 \pm 0.02$
						Haplograr	nite-(F)-H <sub>2</sub> O				
Run 3	0.69	700	2.4	33.1 ±5.0	1.98 ±0.05	0.88 ±0.01	10.5 ±0.5 <sup>f</sup>	1.50 ±0.21	0.94 ±0.03	0.26 ±0.01	0.32 ±0.04
		800	0.3	3.0 ±0.2	2.26 < 0.01	0.80 < 0.01	1.1 ±0.2 <sup>e</sup> – 5 <sup>g</sup>	$0.58 \pm 0.03$	0.99 < 0.01	0.45 ±0.01	1.40 ±0.10

 $^{a}$  Initial glass fraction in the loading (wt  $\pm$ 0.02) calculated considering an uncertainty of 10% on volumetric proportions.

<sup>b</sup> Uncertainty on pressure is 10%.

<sup>c</sup>H<sub>2</sub>O solubility (in wt%) in the haplogranite melt calculated from the solubility data of Mysen and Wheeler (2000).

<sup>d</sup> Melt density (in g/cm<sup>3</sup>) calculated as a function of *P-T* conditions and melt composition according to Malfait et al. (2014).

e Silicate (SiO<sub>2</sub>, Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, and K<sub>2</sub>O) solubility (in wt%) in the aqueous fluid coexisting with haplogranite melt calculated from the albite solubility data of Anderson and Burnham (1983).

<sup>f</sup> Silicate solubility in the aqueous fluid estimated from Wohlers et al. (2011) for P > 1 GPa.

<sup>g</sup> Silicate solubility in the aqueous fluid in the presence of F, as estimated following Webster (1990).

<sup>h</sup> Fluid density (in g/cm<sup>3</sup>) calculated as a function of *P-T* conditions from the data of Mantegazzi et al. (2013) at *P* > 0.5 GPa and of Driesner and Heinrich (2007) at *P* < 0.5 GPa.



**FIGURE 1. (a)** Microphotograph of the compression chamber showing the hydrous haplogranite melt coexisting with the aqueous fluid at 700 °C and 2.4 GPa and 2D-SXRF map showing the distribution of Zr between the coexisting phases. (b) SXRF profiles collected at the same P-T conditions across the sample chamber following the trajectories 1 and 2. The plateau displayed by the fluorescence signal of the melt globule indicates that the melt globule bridges both diamonds and therefore the melt phase can be measured without contamination from the aqueous fluid. SXRF spectra were collected in both the hydrous melt and aqueous phases to determine the partitioning coefficient of Zr between the phases. (Color online.)



**FIGURE 2.** Schematic view of the beam path through the diamond anvils and the sample chamber for the SXRF analysis of the hydrous melt (**a**) and the aqueous fluid (**b**) at identical *P*-*T* condition.  $E_0$  and  $I_0$ , and  $E_X$  and  $I_X$  are, respectively, the energy and intensity of the incident X-ray beam and the X-ray fluorescence signal emitted by the sample.  $\beta$ represents the angle between the incident X-ray beam and the position of the detector for the collection of the fluorescence signal. (Color online.)

$$D_{Zr}^{f/m} = \frac{c_{Zr}^{f}}{c_{Zr}^{m}} = \frac{\frac{I_{Zr}^{f}}{\rho_{f} \cdot e^{-X_{f}}}}{\frac{I_{Zr}^{m}}{\rho_{m} \cdot e^{-X_{m}}}}$$
(2)

where all the terms that account for the experimental setup (e.g., geometry and presence of different media on the path from the sample to the detector) and normalized counting times cancel out as they are identical for the spectra collected in the fluid and melt phase at given *P*-*T* conditions. Therefore, the emitted signal only has to be corrected for the different density and X-ray transmission of the signal and melt phases. The terms  $e^{-x_i}$  represent the effective transmission of the signal through the fluid (f) or the melt (m) phases (hereafter referred to as  $T_{eff}^t$  and  $T_{eff}^m$ ) that depend on the composition, density, and thickness of each phase. Therefore,  $D_{Z_f}^{tm}$  is obtained from the experimental spectra as

$$D_{Zr}^{f/m} = \frac{I_{Zr}^{f}}{I_{Zr}^{m}} \cdot \frac{T_{eff}^{m}}{T_{eff}^{m}} \cdot \frac{\rho_{m}}{\rho_{f}}$$
(3)

where  $I^{f}$  and  $I^{m}$  are the integrated intensity of the normalized fluorescence line as determined after background removal using a standard peak-fitting routine included in Peakfit v4.12 software (SeaSolve Software-USA). The high quality of all collected spectra and the possibility of resolving the fluorescence line of Zr without overlapping with other emission lines reduce the errors in the integrated intensity ratios (Fig. 3), with standard deviations that typically do not exceed 10% (Table 2).  $\rho_{r}$  and  $\rho_{m}$  are the fluid and melt densities at the relevant pressures, temperatures, and phase compositions (Table 2).

### Fluid composition, absorption corrections, and associated uncertainty on $D_{Tr}^{Um}$

The composition of the aqueous fluid and coexisting hydrous silicate melt at high *P-T*, i.e., the amount of dissolved silicates (as total silicates including SiO<sub>2</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, and Al<sub>2</sub>O<sub>3</sub> oxides) in the fluid and the H<sub>2</sub>O content in the hydrous melt,



**FIGURE 3.**  $ZrK\alpha$  fluorescence line (15.77 keV) from normalized SXRF spectra collected in alkali-SiO<sub>2</sub> rich fluid (blue line) and watersaturated haplogranite melt (red line) equilibrated at 660 °C and 1.5 GPa (Run 1). The dashed lines represent the background subtracted from the spectra to determine the integrated intensity of the  $K\alpha$  fluorescence line of Zr in the fluid and melt,  $I_f$  and  $I_m$ , respectively. (Color online.)

could not be determined in situ in the present experiments due to the inaccessibility of their absorption edges for SXRF analysis in the diamond-anvil cell (e.g., Bassett et al. 2000; Sanchez-Valle 2013). Consequently, the equilibrium phase compositions and associated densities at high *P-T* were determined from available experimental data on related compositions and *P-T* conditions (e.g., Anderson and Burnham 1983; Driesner and Heinrich 2007; Malfait et al. 2014; Mantegazzi et al. 2013; Mysen and Wheeler 2000; Wohlers et al. 2011). The recourse to data on related compositions results in larger associated uncertainties in the derived partition coefficients that have been assessed taking into account additional experimental uncertainty on the pressure calibration (10%). The calculated compositions and densities for all investigated *P-T* conditions are reported in Table 2 together with the associated uncertainties.

The total amount of solutes dissolved in the aqueous fluid at each P-T condition was calculated by extrapolating data on the solubility of albite by Anderson and Burnham (1983) to our experimental P-T conditions and taking into account the retrograde solubility with pressure reported by Wohlers et al. (2011) at 600 °C. These calculations yield between  $1.1 \pm 0.2$  and  $15.5 \pm 2.8$  wt% silicates dissolved in the aqueous fluid phase at the investigated conditions (Table 2). At the higher pressure investigated (>1 GPa and 600 °C), a range of solute contents is proposed to account for uncertainties in the calculations due to the lack of solubility data at appropriate pressure conditions. The composition of the high-pressure hydrous melt is more difficult to assess. LA-ICMPS analyses conducted on the quench melt globules show that the hydrous melts equilibrated with the aqueous phase at high pressure (P > 1 GPa) are less peralkaline (Aluminum Saturation Index, ASI = 0.63-0.77) than the starting glass composition (ASI = 0.48-0.57) due to the preferential partitioning of Na and K into the fluid compared to Al (Anderson and Burnham 1983). The water contents of the haplogranite melts were calculated from the H2O solubility model for peralkaline aluminosilicate melts calibrated by Mysen and Wheeler (2000) from 1000 to 1300 °C and 0.8 to 2 GPa. Using the temperature dependence of Mysen and Wheeler's data for NS4A6 compositions (6 mol%  $Al_2O_3$ , NBO/T = 0.17), which closely relates to the haplogranite melt used here (Table 1), the amount of water dissolved in the melt ranges between  $3.0 \pm 0.2$ and  $33.1 \pm 5.0$  wt% at the experimental conditions (Table 2).

The aqueous fluid and hydrous melt compositions were then used to determine their density. The density of the aqueous fluid phase was approximated to that of a NaCl aqueous solution with equivalent concentration in dissolved silicates using the equation of state of Driesner and Heinrich (2007) and Mantegazzi et al. (2013) at pressure below and above 0.6 GPa, respectively. The density of hydrous melts with variable water contents was determined at high *P-T* conditions using the equation of state determined by Malfait et al. (2014) for high *P*-*T* haplogranite melts with similar composition. Additional calculations were also performed to take into account the possible deviation of fluid and melt density induced by (1) changes on fluid composition with increasing temperature from a highly peralkaline to a more peraluminous composition (Anderson and Burnham 1983; Manning et al. 2010) and (2) the effect of F on fluid composition and melt density (Dingwell et al. 1993; Webster 1990). Consequently, the density of the high *P*-*T* aqueous fluids and hydrous melt varies between  $0.58 \pm 0.03$  and  $1.50 \pm 0.21$  g/cm<sup>3</sup>, and  $1.98 \pm 0.05$  to  $2.26 \pm 0.01$  g/cm<sup>3</sup>, respectively (Table 2). The uncertainties on the  $\rho_m/\rho_r$  ratio are within 6%, except at 700 °C and 2.4 GPa, where the significantly larger uncertainty on the determination of the aqueous fluid composition translates into a maximum uncertainty of 15%.

The effective transmission through the fluid and melt,  $T_{eff}^{f}$  and  $T_{eff}^{m}$ , represents the probability that the incoming X-ray excites a sample volume at depth x and the probability that the fluorescence radiation emitted by the sample volume traverses the samples without being absorbed. The effective transmission is then calculated as the average of  $e^{-\mu_0 x^*} e^{-\mu_1 (d-x)}$  over the entire sample thickness.  $\mu_0$  and  $\mu_1$  are, respectively the absorption coefficient of the sample at the incident energy  $E_0$  (18.05 keV) and at the energy of the characteristic fluorescence emission (*Zr K*-edge = 15.77 keV) derived as a function of melt or fluid compositions and densities using the Hephaestus software (Ravel and Newville 2005). The sample thickness *d* was input as an average of the thickness of the sample chamber after each run (~200  $\mu$ m). It may be noticed that uncertainties associated to samples thickness have a minor effect on  $T_{eff}^{e}$  and  $T_{eff}^{e}$ , ownpared to other sources of uncertainty (i.e., fluid and melt composition and density). A variation of the sample thickness by 50  $\mu$ m, for instance, changes  $T_{eff}^{e}$  and  $T_{eff}^{e}$  to the sample thic and 4.4%, respectively, and the total uncertainty on the  $T_{eff}^{en}T_{eff}^{e}$  tatio remains within 4%.

Overall, the recourse to previous studies to constrain the composition, density, and effective transmission of the high P-T aqueous fluids and haplogranite melts translates into estimated uncertainties on the partition coefficients that do not exceed 16%. The relatively modest uncertainty on the partition coefficient validates the experimental approach that permits in situ sampling of both the aqueous fluid and the hydrous melt and overcomes the need for calibration of the absolute fluorescence signal, the use of an internal standard to calibrate Zr concentrations or to determine the Zr concentrations in *post-mortem* analysis of the quenched hydrous melts.

#### **RESULTS AND DISCUSSION**

The partition coefficients  $D_{Zr}^{@m}$  obtained from 575 to 800 °C and 0.3 to 2.4 GPa in Runs 1 to 3 are reported in Table 2. The evolution of  $D_{Zr}^{@m}$  in F-free and F-bearing systems are reported as a function of temperature and water density in Figure 4.

#### The haplogranite-H<sub>2</sub>O system

In the haplogranite-H<sub>2</sub>O system (Runs 1 and 2),  $D_{Z_{T}}^{f/m}$  ranges from 0.19  $\pm$  0.02 at 575 °C and 0.7 GPa to 0.38  $\pm$  0.03 at 745 °C and 1.5 GPa. There is however no significant effect of P-T conditions on Zr partition coefficients, with a near constant  $D_{Zr}^{f/m}$  within each separate run (Fig. 4). This may result from the relatively low amounts of silicates dissolved in the aqueous fluids within the investigated P-T range (<15 wt%) and from the progressive increase of the Al fraction in the fluid upon increasing pressure (Anderson and Burnham 1983; Wohlers et al. 2011) that hinder the formation of alkali-zirconosilicate complexes that are necessary to stabilize significant amounts of Zr in the aqueous fluids (Louvel et al. 2013; Wilke et al. 2012). Moreover, the  $D_{Zr}^{f/m}$  determined in Run 1 (X<sub>g</sub> = 0.79) are slightly larger than those determined in Run 2 ( $X_g = 0.69$ ) at similar P-T conditions, suggesting an increase of the partition coefficient with increasing initial glass fraction (Xg) in the system (Fig. 4, Table 2). Mysen and Armstrong (2002) reported the increase of the Na dissolved in the fluid and a shift of the melt chemistry toward a less peralkaline composition with increasing X<sub>2</sub> above 0.5-0.6 in non-buffered alkali-aluminosilicate systems. Such increase of the Na concentration in the fluid at expenses of the

melt phase that evolves toward a less peralkaline composition could contribute to the increase of  $D_{Zr}^{\ell m}$  by promoting the formation of alkali-zirconosilicate complexes Zr-O-Si/Na in the aqueous fluids (Wilke et al. 2012; Louvel et al. 2013) while decreasing the stability of Zr in the silicate melt (Linnen and Keppler 2002). These observations point toward a significant control of the fluid and melt composition and, particularly, of the alkalis to aluminum ratio [(Na+K)/Al] of each phase on Zr partitioning. This is consistent with a recent study reporting the decrease of zircon solubility with the addition of Al<sub>2</sub>O<sub>3</sub> to alkalisilica aqueous fluids (Wilke et al. 2012).

#### The haplogranite-F-H<sub>2</sub>O system

In the haplogranite-(F)- $H_2O$  system (Run 3), the partitioning of Zr is significantly affected by *P*-*T* conditions (Table 2 and Fig. 4). The partition coefficient determined at 700 °C and 2.4 GPa



**FIGURE 4.** Evolution of Zr partition coefficient  $D_{Zr}^{fm}$  as a function of temperature (**a**) and H<sub>2</sub>O density (**b**) for different initial glass fraction X<sub>g</sub> in the system. The reported uncertainties take into account the uncertainties on pressure (10%) and on the determination of fluid and melt composition and density. Water densities are calculated using the density relations for pure water of Wagner and Pruss (2002) up to 1 GPa and Mantegazzi et al. (2013) at higher pressures. (Color online.)

falls within the range of values derived for the F-free system ( $D_{Zr}^{f/m}$  $= 0.32 \pm 0.04$ ). This observation leads to the conclusion that neither the P-T conditions nor the presence of F significantly affect the partitioning of Zr between the fluid and melt at high-pressure conditions. We note however a dramatic increase of the  $D_{Zr}^{f/m}$  to  $1.40 \pm 0.10$  at 800 °C and 0.3 GPa, indicating that Zr partitions strongly in favor of the aqueous phase. Interestingly, Webster et al. (1989) observed a similar enrichment in Nb in aqueous fluids coexisting with F- (and Cl-) bearing metaluminous granitic melts at temperature above 850 °C at 0.2 GPa (Fig. 5). The reverse partitioning of HFSE (Zr and Nb) into the aqueous phase at high temperatures (T > 800 °C) observed in Webster's and our study involving peralkaline compositions contrast with the behavior reported at lower temperatures in a similar pressure range, where  $D_{\text{Zr Nb}}^{\text{f/m}}$  remains lower than 1 (London et al. 1988; Webster et al. 1989). We note however that the Nb partition coefficients by Borodulin et al. (2009) at 0.1 GPa are 1-2 orders of magnitude smaller ( $D_{Nb}^{f/m} = 0.001 - 0.02$ ) than the results from London et al. (1988) and Webster et al. (1989) even at temperatures above 800 °C. The extremely low  $D_{Nb}^{f/m}$  values of Borodulin et al. (2009) may be likely associated to an underestimation of Nb in analysis of recovered fluids by ICP-MS or ICP-AES analysis. Combined with the data of London et al. (1988), our experimental results display a similar trend than the Nb data of Webster et al. (1989), with an increase of  $D_{Zr}^{f/m}$  above 1 as temperature increases from 650 to 800 °C at  $P \le 0.3$  GPa (Fig. 5). A direct comparison



**FIGURE 5.** Effect of temperature on the partition coefficients of Zr and Nb between aqueous fluid and haplogranitic melt in F-bearing systems at pressures below 0.3 GPa. The black arrows highlight the change on Zr and Nb partitioning with increasing temperature at 0.2–0.3 GPa. (Color online.)

between the available data sets may appear unwarranted due to differences in the melt composition (peralkaline vs. metaluminous), water contents, and degree of polymerization. However, while the peralkalinity index of the melt is expected to affect the absolute value of the partition coefficients (Borodulin et al. 2009), the observed trend with temperature is likely to be maintained. Our data further suggest that the addition of chlorine is not necessary to favor Zr (or HFSE) partitioning toward the aqueous fluid as suggested by Webster et al. (1989). We emphasize that the observations reported above are based on relatively few Zr and Nb fluid/melt partitioning data and that systematic studies of the effect of fluid and melt composition of the partitioning will be required before more robust conclusions can be drawn.

The large effect of temperature on Zr and Nb partitioning in F-bearing fluid/melt systems at low pressures (Fig. 5) raises questions regarding the mechanisms controlling HFSE incorporation in aqueous fluids in F-bearing systems. The formation of HFSE-F complexes is primarily quoted to explain the enhanced solubility of HFSE in F-bearing fluids or melts (Keppler 1993; Migdisov et al. 2011; Rapp et al. 2010) and could plausibly account for the preferential partitioning of HFSE toward the aqueous fluids observed in Webster et al. (1989) and our study. Although molecular dynamic (MD) simulations suggest the formation of hydrated TiF species in Ti-bearing high P-T aqueous fluids (van Sijl 2011), spectroscopic studies have not yet provided conclusive evidences for HFSE-F complexation in silicate melts or alkali-silica rich aqueous fluids (Farges 1996; Louvel et al. 2013). Nevertheless, the low F content in our experimental fluids (ca. 0.4 wt% F), resulting from the preferential partitioning of F into the hydrous melt (Webster 1990), suggests that HFSE-F complexation is not extensive in the fluid and may not be sufficient to explain the favorable partitioning of Zr into the fluid at low pressure and high temperature. Alternatively, the partitioning of Zr and Nb into the aqueous fluid at low pressure-high temperature could be associated to an increase in the peralkalinity of the fluid with temperature. Anderson and Burnham (1983) showed that low pressure (<0.4 GPa) aqueous fluids in equilibrium with albite progressively evolve toward more peralkaline compositions with increasing temperature. This result, together with the increased capacity of F-bearing fluids to dissolved higher amounts of silicate species (Si, Na, and Al) than pure H<sub>2</sub>O (Webster 1990), indicates that the experimental fluid phase at 800 °C and 0.3 GPa will be enriched in dissolved silicates and highly peralkaline. As a result, the composition of the coexisting hydrous haplogranite melt will be significantly less peralkaline compared to the experiments conducted at higher pressure. Such modification of the fluid and melt compositions could both decrease the solubility of HFSE in the silicate melt (Dickinson and Hess 1985; Linnen and Keppler 1997, 2002) and favor the formation of alkali-zirconosilicate complexes similar to those observed in Si, Na-rich fluids and hydrous melts (Louvel et al. 2013) in the aqueous phase, hence promoting the partitioning of HFSE into the fluid.

It is interesting to note that higher temperatures are apparently necessary to favor Nb partition into the low-pressure fluids, although both elements display similar partitioning trends upon increasing temperature (Fig. 5). Because Zr and Nb diplay similarities in their coordination environment in both diluted aqueous fluids and hydrous silicate melts (Louvel et al. 2013; Mayanovic et al. 2007), the stronger affinity of Zr for the aqueous fluid may thus denote an influence of the ionic charge on the solubility mechanism. It is thus plausible that the formation of the 6-coordinated alkali-niobiosilicate NbO<sub>6</sub>-Si/Na clusters, which favor the incorporation of Nb<sup>5+</sup> in the aqueous fluid, requires higher solute concentrations than necessary to stabilize alkali-zirconosilicate ZrO<sub>6</sub>-Si/Na clusters.

#### **GEOCHEMICAL IMPLICATIONS**

#### Mobilization of HFSE in subduction zones

The fluid-melt partition coefficients for Zr determined in this study at P-T conditions relevant for the release of aqueous fluids and hydrous melts from the subducting slab ( $T > 500 \text{ }^{\circ}\text{C}$ and P > 1 GPa, Hermann et al. 2006; Manning 2004; Schmidt and Poli 1998; Spandler and Hermann; 2008) are systematically higher than 0.1, both in F-free and F-bearing systems. Although Zr preferentially partitions into hydrous silicate melts at these conditions, the relatively high  $D_{Zr}^{f/m}$  values provide evidence for the incorporation of non-negligible amounts of this nominally insoluble element into the aqueous fluid phase. These results hence support that not only slab melts but also water-rich phases containing dissolved alkali-silicate species as those produced by metamorphic dehydration reactions may be important vectors for the transfer of Zr from the slab to the mantle wedge. A quantitative estimate of the uptake of Zr by dehydration fluids would require Zr partition coefficients between typical slab minerals (i.e., garnet, pyroxenes or amphiboles) and the aqueous fluid phase that remain scarce and limited to temperatures above 1200 °C (Ayers et al. 1997; Kessel et al. 2005; Stalder et al. 1998). Moreover, the aqueous fluid-melt partitioning coefficients in this study were determined at temperatures below the range where crystal-melt partitioning  $D_{Zr}^{c/m}$  data are available, hence limiting the indirect evaluation of crystal-fluid partition coefficients  $D_{Tr}^{c/f}$  $(D_{Zr}^{c/f} = D_{Zr}^{c/m}/D_{Zr}^{f/m})$ . Nevertheless, mineral-melt partition coefficients reported for various silicic melts between 1 and 4 GPa at temperatures below 1200 °C are systematically smaller than 0.1 for orthopyroxenes, close to 0.1 for clinopyroxenes, and greater than 0.1 for garnet (Adam and Green 2006; Green et al. 2000; Huang et al. 2006). Thus, Zr may preferentially partition from the fluid phase into garnet and probably clinopyroxenes, but not into orthopyroxenes. Such qualitative behavior of Zr during fluid-rock interactions and the affinities are consistent with available  $D_{7r}^{c/f}$  reported by experiments conducted at higher P-T conditions (Ayers et al. 1997; Kessel et al. 2005; Stalder et al. 1998) and will control the segregation of Zr into refractory phases in the slab.

Similarities between the solubility behavior of columbite  $(MnNb_2O_6)$ , rutile  $(TiO_2)$ , and zircon  $(ZrSiO_4)$  in silicate melts and aqueous fluids (Dickinson and Hess 1985; Linnen and Keppler 1997; Linnen and Keppler 2002; Manning et al. 2008) suggest that Ti and Nb should also be efficiently mobilized by the slab flux, regardless of its nature (aqueous fluid, hydrous melt, or supercritical liquid). The picture that emerges from these series of experimental studies is that melting of the slab is not necessary to mobilize HFSE in subduction zones and that aqueous fluids may contribute significantly to their recycling in subduction

zones. Thus, the typical HFSE depletion recorded in most arc magmas may arise from fluid-rock interactions during fluid migration through the slab interface and mantle wedge, rather than from HFSE low solubility in slab-derived aqueous phases. Fluid reactions with mantle wedge peridotite may indeed trigger the precipitation of the slab-derived solutes (Manning 2004; Hack and Thompson 2011) and favor HFSE segregation into refractory mineral phases (e.g., garnet, rutile, or clinopyroxene; Hermann and Spandler 2008; Hermann and Rubatto 2009; Johnson and Plank 1999; Kessel et al. 2005; Klemme et al. 2002, 2005). While dehydration-hydration processes could remobilize HFSE in the mantle wedge, it is likely that the hydrated peridotites adjacent to the top of the slab are ultimately recycled down to the transition zone with the subducting slab (Schmidt and Poli 1998), further preventing HFSE from reaching the source of arc magmas. The HFSE enrichment recorded in high-Nb basalts (HNB) or adakitic magmas (Aguillon-Robles et al. 2001; Defant and Drummond 1993; Munker et al. 2004) may thus arise from a combination of particular slab composition, subduction zone geometry and geothermal gradients that enable particular flow paths and/or significantly larger production of slab-derived fluids that could progressively consume the HFSE-bearing phases and ultimately lead to the recycling of HFSE up to the volcanic arc.

## HFSE enrichment in shallow magmatic-hydrothermal environments

In large crustal granitic complexes, the intrusion of alkaline halogen-rich magmatic bodies can lead to the formation of rare metals (Zr, Nb, REE) ore deposits (e.g., Strange Lake and Thor Lake Nechalacho deposit, Canada; Galineiro complex, Spain). The formation of HFSE-rich aggregates has often been considered as the result of the incompatible behavior of HFSE during fractional crystallization (Boily and Williams-Jones 1994). However, petrological and geochemical field observations, as well as numerical studies of fluid reaction paths indicate that the exsolution of highly alkaline late-magmatic fluids from crystallizing F-rich intrusions at  $T \le 600$  °C enhance the remobilization of HFSE and the potential to form economical rare metal ore deposits (Agangi et al. 2010; Gysi and Williams-Jones 2013; Montero et al. 1998; Salvi and Williams-Jones 1996; Schaltegger 2007; Sheard et al. 2012). The  $D^{f/m}$  larger than 1 reported in this study for Zr and previously for Nb (Webster et al. 1989) at low pressures and temperatures above 800 °C in related chemical systems suggests that similar processes could also occur at higher temperature in the earlier stages of the magmatic evolution. The exsolution of high-temperature alkaline fluids at pressures below 0.4 GPa have thus the potential to extract HFSE from F-rich granitic melt and may play a significant role in the formation of rare metal ore deposits. Although such deposits have not been described in subduction-related environment, the occurrence of HFSE-bearing accessory phases in volcanic vesicles at Lewotolo volcano (Indonesia), or the record of noticeable HFSE scavenging at the Los Azufres geothermal field (Mexico) provide evidences for the volatile-induced transport of HFSE in volcanic arcs (de Hoog and van Bergen 2000; Torres-Alvarado et al. 2007). The potential mobilization and redistribution of HFSE by high temperature–low pressure (T > 700-800 °C; 0.05 < P< 0.3 GPa) fluids and vapors in volcanic arcs could have critical implications for the geochemical interpretation of the trace element signature of arc magmas and requires further detailed experimental investigations.

#### **ACKNOWLEDGMENTS**

We thank O. Proux for assistance during the synchrotron experiments and M. Wälle for help with the LA-ICMPS analyses in quenched melts. A.B. Thompson and C. Manning are acknowledged for helpful comments on a preliminary version of the manuscript. D. Foustoukos is acknowledged for efficient editorial handling. The ESRF is acknowledged for provision of beamtime for these experiments. This work was supported by the Swiss National Science Foundation through grants SNF 200021-120575 and SNF 200020-132208 to C.S.V.

#### **REFERENCES CITED**

- Adam, J., and Green, T.H. (2006) Trace element partitioning between mica- and amphibole-bearing garnet lherzolite and hydrous basanitic melt: 1. Experimental results and the investigation of controls on partitioning behaviour. Contributions to Mineralogy and Petrology, 152, 1–17.
- Adam, J., Green, T.H., Sie, S.H., and Ryan, C.G. (1997) Trace element partitioning between aqueous fluids, silicate melts and minerals. European Journal of Mineralogy, 9, 569–584.
- Agangi, A., Kamenetsky, V.S., and McPhie, J. (2010) The role of fluorine in the concentration and transport of lithophile trace elements in felsic magmas: Insights from the Gawler Range Volcanics, South Australia. Chemical Geology, 273, 314–325.
- Aguillon-Robles, A., Calmus, T., Benoit, M., Bellon, H., Maury, R.O., Cotten, J., Bourgois, J., and Michaud, F. (2001) Late miocene adakites and Nb-enriched basalts from Vizcaino Peninsula, Mexico: Indicators of East Pacific Rise subduction below Southern Baja California? Geology, 29, 531–534.
- Anderson, G.M., and Burnham, C.W. (1983) Feldspar solubility and the transport of aluminum under metamorphic conditions. American Journal of Science, 283, 283–297.
- Antignano, A., and Manning, C.E. (2008) Rutile solubility in H<sub>2</sub>O, H<sub>2</sub>O-SiO<sub>2</sub>, and H<sub>2</sub>O-NaAlSi<sub>3</sub>O<sub>8</sub> fluids at 0.7–2.0 GPa and 700–1000 °C: Implications for mobility of nominally insoluble elements. Chemical Geology, 255, 283–293.
- Audetat, A., and Keppler, H. (2005) Solubility of rutile in subduction zone fluids, as determined by experiments in the hydrothermal diamond anvil cell. Earth and Planetary Science Letters, 232, 393–402.
- Ayers, J.C., Dittmer, S.K., and Layne, G.D. (1997) Partitioning of elements between peridotite and H<sub>2</sub>O at 2.0–3.0 GPa and 900–1000 °C, and application to models of subduction zone processes. Earth and Planetary Science Letters, 150, 381–398.
- Bassett, W.A., Shen, A.H., Bucknum, M., and Chou, I.M. (1993) A New Diamond-Anvil Cell for Hydrothermal Studies to 2.5 GPa and from –190 °C to 1200 °C. Review of Scientific Instruments, 64, 2340–2345.
- Bassett, W.A., Anderson, A.J., Mayanovic, R.A., and Chou, I.M. (2000) Hydrothermal diamond anvil cell for XAFS studies of first-row transition elements in aqueous solution up to supercritical conditions. Chemical Geology, 167, 3–10.
- Borchert, M., Wilke, M., Schmidt, C., and Rickers, K. (2009) Partitioning and equilibration of Rb and Sr between silicate melts and aqueous fluids. Chemical Geology, 259, 39–47.
- Borodulin, G.P., Chevychelov, V.Y., and Zaraysky, G.P. (2009) Experimental study of partitioning of tantalum, niobium, manganese, and fluorine between aqueous fluoride fluid and granitic and alkaline melts. Doklady Earth Sciences, 427, 868–873.
- Boily, M., and Williams-Jones, A.E. (1994) The role of magmatic and hydrothermal processes in the chemical evolution of the Strange Lake plutonic complex, Quebec-Labrador. Contributions to Mineralogy and Petrology, 118, 33–47.
- Bouvier, A-S., Deloule, E., and Metrich, A. (2010) Fluid inputs to magma sources of St. Vincent and Grenada (Lesser Antilles): New insights from trace elements in olivine-hosted melt inclusions. Journal of Petrology, 51, 1597–1615.
- Brenan, J.M., Shaw, H.F., Phinney, D.L., and Ryerson, F.J. (1994) Rutile-aqueous fluid partitioning of Nb, Ta, Hf, Zr, U and Th—Implications for High-Field Strength Element depletion in island-arc basalts. Earth and Planetary Science Letters, 128, 327–339.
- Bureau, H., and Keppler, H. (1999) Complete miscibility between silicate melts and hydrous fluids in the upper mantle: experimental evidence and geochemical implications. Earth and Planetary Science Letters, 165, 187–196.
- Bureau, H., Menez, B., Malavergnes, V., Somogyi, A., Simionovici, A., Massare, D., Khodja, H., Daudin, L., Gallien, J.-P., Shaw, C., and Bonnin-Mosbah, M. (2007) In situ mapping of high-pressure fluids using hydrothermal diamond anvil cells. High Pressure Research, 27, 235–247.
- Cauzid, J., Philippot, P., Somogyi, A., Menez, B., Simionovici, A., and Bleuet, P. (2006) Standardless quantification of single fluid inclusions using synchrotron radiation induced X-ray fluorescence. Chemical Geology, 227, 165–183.
- de Hoog, J.C.M., and van Bergen, M.J. (2000) Volatile-induced transport of HFSE, REE, Th and U in arc magmas: evidence from zirconolite-bearing vesicles in

potassic lavas of Lewotolo volcano (Indonesia). Contributions to Mineralogy and Petrology, 139, 485–502.

- Defant, M.J., and Drummond, M.S. (1993) Mount St-Helens: Potential example of the partial melting of the subducted lithosphere in a volcanic arc. Geology, 21, 547–550.
- Dickinson, J.E., and Hess, P.C. (1985) Rutile solubility and Titanium coordination in silicate melts. Geochimica et Cosmochimica Acta, 49, 2289–2296.
- Dingwell, D.B., Knoche, R., and Webb, S.L. (1993) The effect of F on the density of haplogranite melt. American Mineralogist, 78, 325–330.
- Driesner, T., and Heinrich, C.A. (2007) The system H<sub>2</sub>O-NaCl. Part I: Correlation formulae for phase relations in temperature-pressure-composition space from 0 to 1000 degrees °C, 0 to 5000 bar, and 0 to 1 X-NaCl. Geochimica et Cosmochimica Acta, 71, 4880–4901.
- Farges, F. (1996) Does Zr-F "complexation" occur in magmas? Chemical Geology, 127, 253–268.
- Foley, S.F., Barth, M.G., and Jenner, G.A. (2000) Rutile/melt partition coefficients for trace elements and an assessment of the influence of rutile on the trace element characteristics of subduction zone magmas. Geochimica et Cosmochimica Acta, 64, 933–938.
- Gao, J., John, T., Klemd, R., and Xiong, X.M. (2007) Mobilization of Ti-Nb-Ta during subduction: Evidence from rutile-bearing dehydration segregations and veins hosted in eclogite, Tianshan, NW China. Geochimica et Cosmochimica Acta, 71, 4974–4996.
- Gill, J.B. (1981) Orogenic Andesites and Plate Tectonics, p. 390. Springer-Verlag, Berlin.
- Green, T.H., Blundy, J.D., Adam., J., and Yaxley, G.M. (2000) SIMS determination of trace element partition coefficients between garnet, clinopyroxene and hydrous basaltic liquids at 2–7.5 GPa and 1080–1200 °C. Lithos 53, 165–187.
- Gysi, A.P., and Williams-Jones, A.E. (2013) Hydrothermal mobilization of pegmatite-hosted REE and Zr at Strange Lake, Canada: A reaction path model. Geochimica et Cosmochimica Acta, 122, 324–352.
- Hack, A.C., and Thompson, A.B. (2011) Density and viscosity of hydrous magmas and related fluids and their role in subduction zone processes. Journal of Petrology, 52, 1333–1362.
- Hawkesworth, C.J., Hergt, J.M., Ellam, R.M., and McDermott, F. (1991) Element fluxes associated with subduction-related magmatism. Philosophical Transactions of the Royal Society of London Series a–Mathematical Physical and Engineering Sciences, 335, 393–405.
- Hayden, L.A., and Manning, C.E. (2011) Rutile solubility in supercritical NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O fluids. Chemical Geology, 284, 74–81.
- Hermann, J., and Rubatto, D. (2009) Accessory phase control on the trace element signature of sediment melts in subduction zones. Chemical Geology, 265, 512–526.
- Hermann, J., and Spandler, C. (2008) Sediment melts at sub-arc depths: an experimental study. Journal of Petrology, 49, 717–740.
- Hermann, J., Spandler, C., Hack, A., and Korsakov, A.V. (2006) Aqueous fluids and hydrous melts in high-pressure and ultra-high pressure rocks: Implications for element transfer in subduction zones. Lithos, 92, 399–417.
- Huang, F., Lundstrom, C.C., and McDonough, W.F. (2006) Effect of melt structure on trace-element partitioning between clinopyroxene and silicic, alkaline, aluminous melts. American Mineralogist, 91, 1385–1400.
- Jamieson, J.C., Fritz, J.N., and Manghnani, M.H. (1982) Pressure measurement at high temperature in X-ray diffraction studies: gold as a primary standard. In S. Akimoto and M.H. Manghnani, Eds., High-Pressure Research in Geophysics, p. 27–48. Center for Academic Publishing, Tokyo.
- Johnson, M.C., and Plank, T. (1999) Dehydration and melting experiments constrain the fate of subducted sediments. Geochemistry, Geophysics, Geosystems, 1, 1–26.
- Kelemen, P.B., Johnson, K.T.M., Kinzler, R.J., and Irving, A.J. (1990) High Field Strength Element depletions in acr basalts due to mantle-magma interactions. Nature, 345, 521–524.
- Keppler, H. (1993) Influence of fluorine on the enrichment of high-field strength trace-elements in granitic-rocks. Contributions to Mineralogy and Petrology, 114, 479–488.
- (1996) Constraints from partitioning experiments on the composition of subduction-zone fluids. Nature, 380, 237–240.
- Kessel, R., Schmidt, M.W., Ulmer, P., and Pettke, T. (2005) Trace element signature of subduction-zone fluids, melts and supercritical liquids at 120-180 km depth. Nature, 437, 724–727.
- Klemme, S., Blundy, J.D., and Wood, B.J. (2002) Experimental constraints on major and trace element partitioning during partial melting of eclogite. Geochimica et Cosmochimica Acta, 66, 3109–3023.
- Klemme, S., Prowatke, S., Hametner, K., and Gunther, D. (2005) Partitioning of trace elements between rutile and silicate melts: Implications for subduction zones. Geochimica et Cosmochimica Acta, 69, 2361–2371.
- Klimm, K., Blundy, J.D., and Green, H. (2008) Trace element partitioning and accessory phase saturation during H<sub>2</sub>O-saturated melting of basalt with implications for subduction zone chemical fluxes. Journal or Petrology, 49, 523–553.
- Linnen, R.L., and Keppler, H. (1997) Columbite solubility in granitic melts: conse-

quences for the enrichment and fractionation of Nb and Ta in the Earth's crust. Contributions to Mineralogy and Petrology, 128, 213–227.

- (2002) Melt composition control of Zr/Hf fractionation in magmatic processes. Geochimica et Cosmochimica Acta, 66, 3293–3301.
- London, D., Hervig, R.L., and Morgan, G.B. (1988) Melt-vapor solubilities and elemental partitioning in peraluminous granite-pegmatite systems—Experimental results with Macusani glass at 200 MPa. Contributions to Mineralogy and Petrology, 99, 360–373.
- Louvel, M., Sanchez-Valle, C., Malfait, W.J., Testemale, D., and Hazemann, J-L. (2013) Zr complexation in high pressure fluids and implications for the mobilization of HFSE in subduction zones. Geochimica et Cosmochimica Acta, 104, 281–299.
- Malfait, W.J., Seifert, R., Petitgirard, S., Perrillat, J-P., Mezouar, M., Ota, T., Nakamura, E., Lerch, P., and Sanchez-Valle, C. (2014) Supervolcano eruptions driven by melt buoyancy in large silicic magma chambers. Nature Geosciences, 7, 122–125.
- Manning, C.E. (2004) The chemistry of subduction-zone fluids. Earth and Planetary Science Letters, 223, 1–16.
- Manning, C.E., Wilke, M., Schmidt, C., and Cauzid, J. (2008) Rutile solubility in albite-H<sub>2</sub>O and Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub>-H<sub>2</sub>O at high temperatures and pressures by in-situ synchrotron radiation micro-XRF. Earth and Planetary Science Letters, 272, 730–737.
- Manning, C.E., Antignano, A., and Lin, H.A. (2010) Premelting polymerization of crustal and mantle fluids, as indicated by the solubility of albite plus paragonite plus quartz in H<sub>2</sub>O at 1 GPa and 350–620 °C. Earth and Planetary Science Letters, 292, 325–336.
- Mantegazzi, D., Sanchez-Valle, C., and Driesner, T. (2013) Thermodynamic properties of aqueous NaCl solutions to 1073K and 4.5 GPa, and implications for dehydration reaction in subducting slabs. Geochimica et Cosmochimica Acta, 121, 263–290.
- Mayanovic, R. A., Anderson, A.J., Bassett, W.A., and Chou, I-M. (2007) Synchrotron X-ray spectroscopy of Eu/HNO<sub>3</sub> aqueous solutions at high temperatures and pressure and Nb-bearing silicate melt phases coexisting with hydrothermal fluids using a modified hydrothermal diamond anvil cell and rail assembly. Review of Scientific Instruments 78, 053904, 9 p.
- Mibe, K., Chou, I-M., and Bassett, W.A. (2008) In situ Raman spectroscopic investigation of the structure of subduction-zone fluids. Journal of Geophysical Research 11, B04208, 8 p.
- Migdisov, A.A., Williams-Jones, A.E., van Hinsberg, V., and Salvi, S. (2011) An experimental study of the solubility of baddeleyite (ZrO<sub>2</sub>) in fluoride-bearing solutions at elevated temperature. Geochimica et Cosmochimica Acta, 75, 7426–7434.
- Montero, P., Floor, P., and Corretge, G. (1998) The accumulation of rare-earth and high-field-strength elements in peralkaline granitic rocks: The Galineiro orthogneissic complex, Northwestern Spain. The Canadian Mineralogist, 36, 683–700.
- Munker, C., Worner, G., Yogodzinski, G., and Churikova, T. (2004) Behaviour of high field strength elements in subduction zones: constraints from Kamchatka-Aleutian arc lavas. Earth and Planetary Science Letters, 224, 275–293.
- Mysen, B.O., and Armstrong, L. (2002) Solubility behavior of alkali aluminosilicate components in aqueous fluids and silicate melts at high pressure and temperature. Geochimica et Cosmochimica Acta, 66, 2287–2297.
- Mysen, B.O., and Wheeler, K. (2000) Solubility behavior of water in haploandesitic melts at high pressure and high temperature. American Mineralogist, 85, 1128–1142.
- Prouteau, G., Scaillet, B., Pichavant, M., and Maury, R. (2001) Evidence for mantle metasomatism by hydrous silicic melts derived from subducted oceanic crust. Nature, 410, 197–200.
- Proux, O., Biquard, X., Lahera, E., Menthonnex, J.J., Prat, A., Ulrich, O., Soldo, Y., Trevisson, P., Kapoujyan, G., Perroux, G., and others. (2005) FAME: A new beamline for X-ray absorption investigations of very diluted systems of environmental, material and biological interests. Physica Scripta T, 115, 970–973.
- Proux, O., Nassif, V., Prat, A., Ulrich, O., Lahera, E., Biquard, X., Menthonnex, J.J., and Hazemann, J.-L. (2006) Feedback system of a liquid-nitrogen-cooled double-crystal monochromator: design and performances. Journal of Synchrotron Radiation, 13, 59–68.
- Rapp, J.F., Klemme, S., Butler, I.B., and Harley, S.L. (2010) Extremely high solubility of rutile in chloride and fluoride-bearing metamorphic fluids: An experimental investigation. Geology, 38, 323–326.
- Ravel, B., and Newville, M. (2005) ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. Journal of Synchrotron Radiation 12, 537–541.
- Rubatto, D., and Hermann, J. (2003) Zircon formation during fluid circulation in eclogites (Monviso, Western Alps): Implications for Zr and Hf budget in subduction zones. Geochimica et Cosmochimica Acta, 67, 2173–2187.
- Rudnick, R.L., Barth, M., Horn, I., and McDonough, W.F. (2000) Rutile-bearing refractory eclogites: Missing link between continents and depleted mantle. Science, 287, 278–281.
- Salvi, S., and Williams-Jones, A.E. (1996) The role of hydrothermal processes in

concentrating high-field strength elements in the Strange Lake peralkaline complex, northeastern Canada. Geochimica et Cosmochimica Acta, 60, 1917–1932.

- Sanchez-Valle, C. (2013) Structure and thermodynamics of subduction zone fluids from spectroscopic studies. Reviews in Mineralogy and Geochemistry, 76, 265–309.
- Sanchez-Valle, C., Martinez, I., Daniel, I., Philippot, P., Bohic, S., and Simionovici, A. (2003) Dissolution of strontianite at high P-T conditions: An in-situ synchrotron X-ray fluorescence study. American Mineralogist, 88, 978–985.
- Sanchez-Valle, C., Daniel, I., Martinez, I., Simionovici, A., and Reynard, B. (2004) Progress in quantitative elemental analyses in high P-T fluids using synchrotron X-ray fluorescence (SXRF). Journal of Physics: Condensed Matter, 16, S1197–S1206.
- Scambelluri, M., and Philippot, P. (2001) Deep fluids in subduction zones. Lithos, 55, 213–227.
- Schaltegger, U. (2007) Hydrothermal zircon. Elements, 3, 51-79.
- Schmidt, M.W., and Poli, S. (1998) Experimentally based water budgets for dehydrating slabs and consequences for arc magma generation. Earth and Planetary Science Letters, 163, 361–379.
- Sheard, E.R., Williams-Jones, A.E., Heiligmann, M., Pederson, C., and Trueman, D.L. (2012) Controls on the concentration of zirconium, niobium, and the rare earth elements in the Thor Lake Rare Metal Deposit, Northwest Territories, Canada. Economic Geology, 107, 81–104.
- Shen, A., and Keppler, H. (1995) Infrared spectroscopy of hydrous silicate melts to 1000 °C and 10 kbar: Direct observation of H<sub>2</sub>O speciation in a diamond-anvil cell. American Mineralogist, 80, 1335–1338.
- Spandler, C., Mavrogenes, J., and Hermann, J. (2007) Experimental constraints on element mobility from subducted sediments using high-P synthetic fluid/ melt inclusions. Chemical Geology, 239, 228–249.
- Sparks, R.S.J. (1980) X-ray Fluorescence Microprobe for Chemical Analysis. Synchrotron Radiation Research, p. 754. Plenum Press, New York.
- Stalder, R., Foley, S.F., Brey, G.P., and Horn, I. (1998) Mineral aqueous fluid partitioning of trace elements at 900–1200 °C and 3.0–5.7 GPa: New experimental data for garnet, clinopyroxene, and rutile, and implications for mantle metasomatism. Geochimica et Cosmochimica Acta, 62, 1781–1801.
- Stern, R.J. (2002) Subduction zones. Reviews of Geophysics, 40(4), 3-138.

- Torres-Alvarado, I.S., Pandarinath, K., Verma, S.P., and Dulski, P. (2007) Mineralogical and geochemical effects due to hydrothermal alteration in the Los Azufres geothermal field, Mexico. Revista Mexicana de Ciencias Geologicas, 24, 15–24.
- Tropper, P., and Manning, C.E. (2005) Very low solubility of rutile in H<sub>2</sub>O at high pressure and temperature, and its implications for Ti mobility in subduction zones. American Mineralogist, 90, 502–505.
- van Sijl, J. (2011) Trace elements in high pressure and temperature fluids in subduction zones. VU University Amsterdam.
- Wagner, W., and Pruss, A. (2002) The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. Journal of Physical and Chemical Reference Data, 31(2), 387–535.
- Webster, J.D. (1990) Partitioning of F between H<sub>2</sub>O and CO<sub>2</sub> fluids and topaz rhyolite melt—Implications for mineralizing magmatic-hydrothermal fluids in F-rich granitic systems. Contributions to Mineralogy and Petrology, 104, 424–438.
- Webster, J.D., Holloway, J.R., and Hervig, R.L. (1989) Partitioning of lithophile trace-elements between H<sub>2</sub>O and H<sub>2</sub>O+CO<sub>2</sub> fluids and topaz rhyolite melt. Economic Geology, 84, 116–134.
- Wilke, M., Schmidt, C., Dubrail, J., Appel, K., Borchert, M., Kvashnina, K., and Manning, C.E. (2012) Zircon solubility and zirconium complexation in H<sub>2</sub>O+Na<sub>2</sub>O+SiO<sub>2</sub>±Al<sub>2</sub>O<sub>3</sub> fluids at high pressure and temperature. Earth and Planetary Science Letters, 349–350, 15–25.
- Wohlers, A., Manning, C.E., and Thompson, A.B. (2011) Experimental investigation of the solubility of albite and jadeite in H<sub>2</sub>O, with paragonite plus quartz at 500 and 600 °C, and 1–2.25 GPa. Geochimica et Cosmochimica Acta, 75, 2924–2939.

MANUSCRIPT RECEIVED NOVEMBER 2, 2013

MANUSCRIPT ACCEPTED FEBRUARY 22, 2014

MANUSCRIPT HANDLED BY DIONYSIS FOUSTOUKOS