Rutile solubility in NaF-NaCl-KCl-bearing aqueous fluids at 0.5-2.79 GPa and 250-650°C

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Abstract

The complex nature of trace element mobility in subduction zone environments is thought to be primarily controlled by fluid-rock interactions, episodic behavior of fluids released, mineral assemblages, and element partitioning during phase transformations and mineral breakdown throughout the transition from hydrated basalt to blueschist to eclogite. Quantitative data that constrain the partitioning of trace elements between fluid(s) and mineral(s) are required in order to model trace element mobility during prograde and retrograde metamorphic fluid evolution in subduction environments. The stability of rutile has been proposed to control the mobility of HFSE during subduction, accounting for the observed depletion of Nb and Ta in arc magmas. Recent experimental studies demonstrate that the solubility of rutile in aqueous fluids at temperatures >700°C and pressures <2 GPa increases by several orders of magnitude relative to pure H₂O as the concentrations of ligands (e.g., F and Cl) in the fluid increase. Considering that prograde devolatilization in arcs begins at ~300°C, there is a need for quantitative constraints on rutile solubility and the partitioning of HFSE between rutile and aqueous fluid over a wider range of temperature and pressure than is currently available. In this study, new experimental data are presented that quantify the solubility of rutile in aqueous fluids from 0.5 to 2.79 GPa and 250 to 650°C. Rutile solubility was determined by using synchrotron x-ray fluorescence to measure the concentration of Zr in an aqueous fluid saturated with a Zr-bearing rutile

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crystal within a hydrothermal diamond anvil cell. At the PT conditions of the experiments, published diffusion data indicate that Zr is effectively immobile ($\log D_{\text{Zr}} \sim 10^{-25} \text{ m}^2/\text{s}$ at 650°C and $\sim 10^{-30} \text{ m}^2/\text{s}$ at 250°C) with diffusion length-scales of $< 0.2 \mu\text{m}$ in rutile for our run durations (< 10 hrs). Hence, the Zr/Ti ratio of the starting rutile, which was quantified, does not change during the experiment, and the measured concentration of Zr in the fluid was used to calculate the concentration of Ti (i.e., the solubility of rutile) in the fluid. The salts NaF-, NaCl-, and KCl- were systematically added to the aqueous fluid, and the relative effects of fluid composition, pressure, and temperature on rutile solubility were quantified. The results indicate that fluid composition exerts the greatest control on rutile solubility in aqueous fluid, consistent with previous studies, and that increasing temperature has a positive, albeit less pronounced, effect. The solubility of Zr-rutile in aqueous fluid increases with the addition of halides in the following order: 2 wt% NaF $<$ 30 wt% KCl $<$ 30 wt% NaCl $<$ 3 wt% NaF $<$ (10 wt% NaCl + 2 wt% NaF) $<$ 4 wt% NaF. The solubility of rutile in the fluid increases with the 2nd to 3rd power of the Cl^- concentration, and the 3rd to 4th power of the F^- concentration. These new data are consistent with observations from field studies of exhumed terranes that indicate that rutile is soluble in complex aqueous fluids, and that fluid composition is the primary control on rutile solubility and HFSE mobility.

1 INTRODUCTION

Rutile is a ubiquitous accessory phase in amphibolites and eclogites where it can be the major repository of high-field-strength elements (HFSE) (Meinhold 2010; Zack et al. 2002a), and is generally accepted as playing a role in the HFSE-depletion that is characteristic of arc magmas (Saunders et al., 1980; Green, 1981; Brophy and Marsh, 1986; Ryerson and Watson, 1987). The formula of rutile is TiO_2 , with possible substitutions for Ti^{4+} by Nb^{5+} , Ta^{5+} , Zr^{4+} , Hf^{4+} , Cr^{3+} and Fe^{3+} . Experimental data for the partitioning of HFSE between rutile and silicate melts indicate that rutile favors incorporation of HFSE in the order $\text{Ta} > \text{Nb} > \text{Hf} > \text{Zr}$ (Foley et al., 2000, 2002; Klemme et al., 2005). Rutile is generally

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thought to be chemically inert with respect to aqueous fluids evolved during prograde metamorphism, evinced by experimental data that demonstrate that the solubility of rutile in pure water is very low (Audétat and Keppler, 2005; Tropper and Manning, 2005). However, there is a growing body of evidence from natural systems (Zack et al., 2002a, b; Manning, 2004; Chen and Li, 2008; Gao et al., 2007, 2010; Luvizotto and Zack, 2009; John et al., 2011; Spandler et al., 2011) and experimental studies (Antignano and Manning, 2008; Manning et al., 2008; Rapp et al., 2010; Hayden and Manning, 2011; Tanis et al., 2015) that rutile is increasingly more soluble in halogen-bearing (e.g., F, Cl) aqueous fluids evolved during prograde metamorphism in subduction zone environments. Slab-derived fluids are not pure H₂O, but rather contain significant amounts of dissolved alkalis (Na, K), halogens and aluminosilicate components (Si, Al) (Manning, 2004). For example, Fu et al. (2001) investigated the compositions of fluid inclusions in exhumed rocks from Shuanghe, Dabie Shan, China, and reported that the salinity of the fluid inclusions, which were trapped during prograde metamorphic devolatilization, ranges from almost pure water to brines that contain up to 30 wt% NaCl equivalent. In light of the observations that halogens increase rutile solubility in aqueous fluids, and that fluids in subduction zone environments vary from dilute to highly saline, there is a critical need to constrain the partitioning of HFSE between rutile and aqueous fluid(s), as well as the solubility of rutile, as a function of fluid composition at pressure-temperature conditions appropriate for subduction zone environments. In this study, new experimental data are presented that quantify the solubility of Zr-bearing rutile based on the concentration of Zr in NaF-, NaCl-, and KCl-bearing aqueous fluids at pressures of 0.5 to 2.79 GPa and temperatures of 250 to 650°C. The effect of fluid composition, pressure, and temperature on rutile solubility is studied. The data constrain rutile solubility and provide a limit on Zr mobility.

2 EXPERIMENTAL METHODS

2.1 Rutile Synthesis and Characterization

Synthetic Zr-doped rutile (Zr-TiO₂) crystals were prepared following the method described in Hanchar et al. (2001). High-purity TiO₂ and ZrO₂ were mixed to achieve 5 wt% ZrO₂ in the rutile crystals in an HNO₃-cleaned agate mortar and pestle under absolute ethanol and allowed to dry. Once dried, the powders were mixed under absolute ethanol with the fluxing agents Li₂MoO₄ and MoO₃ in the following proportions: 83.7 mol% MoO₃, 10 mol% Li₂MoO₄, 6 mol% TiO₂, and 0.28 mol% ZrO₂, then allowed to dry. The mixture was then transferred to a clean Pt crucible with a tightly fitted Pt lid. The crucible was lowered into the “hot spot” of a preheated (1200°C) Deltech MoSi₂ vertical tube furnace and held at constant temperature for seven days, permitting the flux to evaporate in air. Using a type S control thermocouple, the temperature in the hot spot was measured to be stable within $\pm 1^\circ\text{C}$. When rutile saturation was reached, the rutile crystals began to grow in the residual flux. Upon completion of the synthesis, no residual flux remained in the crucible. The crystals were removed from the Pt crucible with tweezers and cleaned in concentrated HNO₃. Powder x-ray diffraction was performed to ensure that the rutile structure was obtained and not the TiO₂ polymorphs brookite or anatase.

Each starting crystal was imaged by using back-scattered electrons (BSE), and most of the starting crystals displayed slight zoning (Figure 1). The concentrations of Zr, Ti, and Mo were quantified in the starting crystals by using a Cameca SX100 electron probe microanalyzer (EPMA). A beam current of 50 nA (calibration and analysis) and an accelerating voltage of 15 kV were used. The analyzed crystals that were used are: LIF for Ti and LPET for Zr and Mo. Counting times (30 s at the peak) yielded detection limits for Zr, Ti, and Mo of approximately 580, 290 and 465 ppm, respectively. Standard ZAF techniques were used for the matrix corrections. The standards used included pure natural rutile (TiO₂), zircon (ZrSiO₄) and pure Mo metal. An EMPA line traverse, using a 5 μm focused beam with analyses

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spaced every 25 μm , was performed across the length of each crystal to evaluate chemical homogeneity. All totals summed to $100 \pm 1\%$. The concentrations of TiO_2 and ZrO_2 in the rutile crystal chosen for the experiments were 95.74 ± 0.35 and 4.49 ± 0.08 wt%, respectively, and the concentration of Mo, sourced from the flux, was ≤ 0.36 wt%. No other elements were detected. The concentration of ZrO_2 in the starting rutile is elevated relative to natural rutile, for which the highest reported ZrO_2 concentration is 2.98 wt% (Kalfoun et al., 2002). Our experimental technique, described below, requires high enough Zr concentrations in the starting rutile in order to have sufficient Zr contents in the aqueous fluid to be measured at experimental conditions. All starting crystals used in experiments contained less than 15% variability in the measured Zr concentration.

2.2 Experiments

A hydrothermal diamond anvil cell (HDAC, Bassett et al., 1993) was used in this study and was equipped with two opposing 800 μm culet diamonds. Molybdenum wires, coiled around a tungsten carbide seat that supported each diamond anvil, provided resistive heating. Two K-type (NiCr-NiAl) thermocouples, one on each diamond, were used to measure temperature. The HDAC was heated resistively by using variable transformers that facilitated flexible heating rates and allowed temperature to be maintained within $\pm 5^\circ\text{C}$. The melting point or phase transition of NaNO_3 , CsCl , and NaCl were used to calibrate the temperature of the HDAC up to 800°C . The measured temperatures were $\sim 0.85\%$ lower than the reported melting point or phase transition of NaNO_3 , CsCl , and NaCl (Kerrigan, 2011). A 1% H_2 -Ar gas mixture flowed constantly through the HDAC during the measurements to prevent corrosion of the diamonds and the heaters.

A rhenium gasket was pre-indented to a thickness of ~ 120 μm and then a hole of 600 μm diameter was drilled. The hole was filled with Au powder, compressed until the Au turned into a metallic solid and then a second 200-400 μm diameter hole was drilled. A single irregularly shaped Zr-

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rutile crystal measuring approximately 40x40x20 μm , as determined by using an optical microscope, was loaded into the sample chamber for each experimental run. Deionized H_2O containing either 2, 3, 4 wt% NaF, or 30 wt% NaCl, or 30 wt% KCl, or mixed 10 wt% NaCl + 2 wt % NaF, was then added by using a micro syringe. The HDAC was immediately sealed and pressurized to ~ 0.5 GPa.

The synchrotron x-ray fluorescence (SXRF) experiments were executed at undulator beamline 16-IDD (HPCAT) at the Advanced Photon Source (APS) synchrotron facility at Argonne National Laboratory. The incident beam energy was 27 keV. The beam was focused to a spot size of 25x50 μm full-width at half maximum (FWHM) by using a pair of Kirkpatrick-Baez mirrors. A 100 μm round pinhole was used before the HDAC to reduce the tails of the incident beam, which contained a flux of 1.14×10^{12} photons/s. The incident beam was directed into the sample chamber through the diamonds of the HDAC. The fluorescence from the sample was collected in a 170° backscattering geometry by using a Vortex-EX silicon drift detector that was positioned 0.8 m from the sample. To reduce the background, a pair of large collimating slits were placed before the detector. The energy channels of the multi-channel analyzer were calibrated with ^{55}Fe , ^{57}Co , and ^{109}Cd radioactive sources. The position and aperture of the detector was optimized by using the SXRF peak of pure Zr metal.

Before the experimental run started, the Zr-rutile crystal position was determined visually by using an online optical microscope. The pressure was increased to the starting pressure and then the temperature was increases at a steady rate of $5^\circ\text{C}/\text{min}$, until the desired temperature was reached. Fluorescence spectra (Figure 2a) were collected until the Zr peak area, at a given pressure and temperature condition became time-invariant (Figure 2b), which was interpreted to reflect the attainment of steady-state conditions. This took approximately 40-60 minutes at each given pressure-temperature point. The time to reach steady state is consistent with observations at similar temperatures reported in other studies. The time to reach steady state is consistent with observations at similar temperatures

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reported in other studies (Sanchez-Valle et al., 2003; Manning et al., 2008; Schmidt et al., 2007 ; Tanis et al., 2012 ; Wilke et al., 2012; Bernini et al., 2013; Tanis et al., 2015). For example, Wilke et al. (2012) measured the solubilities of rutile and baddeleyite in aqueous fluid in a HDAC and reported attainment of steady-state conditions in 15 – 30 minutes.

Once steady-state conditions were achieved, SXRF data were collected by using a 2D mapping technique at each unique PT point (Figure 2c). The HDAC was positioned in direct line of the SXRF detector to maximize the Zr count rate. Then the HDAC was moved in steps of 25 μm in the horizontal (x) and vertical (y) directions and XRF spectra, and the incoming and outgoing beam intensities were collected and recorded in 30 s intervals at each x-y position (Louvel et al., 2014; Tanis et al., 2015). A SXRF map of the empty HDAC (0 ppm Zr) and the same HDAC containing standard solutions of 600, and 1000 ppm Zr were also collected before each experimental run and used to build a calibration curve to determine the Zr concentration of experimental fluids, similar to the process described in Tanis et al. (2012) and shown in Figure 3. After collecting SXRF data at a unique PT point, the temperature was then increased to the next temperature point, and the pressure and SXRF data collection procedure was repeated.

During heating and cooling, there is some relaxation of the HDAC. This causes deformation of the Re-Au gasket sample chamber and results in a slight change in pressure. This change was observed and therefore pressure was measured before and after each sequence of fluorescence data were collected and the average pressure is reported. Pressure was monitored throughout the run by collecting XRD patterns of the Au gasket liner by a MAR 165 CCD detector placed in the forward scattering direction. The XRD patterns were integrated and corrected for geometric distortions by using Fit2D (Hammersley, 1997). A NIST standard CeO_2 pattern was collected and used for the XRD calibration. Gold pressure was determined by using the method of Dorogokupets and Dewaele (2007). The experimental run

conditions and results are reported in Table 1.

The concentration of Zr in the fluid was determined by integrating and then averaging the normalized Zr peak area from each (x, y) step significantly (50-75 μm) away from the Zr-rutile crystal. The fluorescence spectra from the standard solutions and high P-T experiments were corrected for absorption in the fluid using the fluid composition and density, then normalized to transmitted beam flux and time following the methods described in described in Sanchez-Valle et al. (2003), Schmidt et al. (2007), Manning et al. (2008), and Louvel et al. (2014). The density of the aqueous fluid was calculated after the experiment based on the experimental pressure and temperature of the run conditions by using the EOS of NaCl-H₂O fluids from Mantegazzi et al. (2013). There are no published high temperature-high pressure EOS for NaF- or KCl- bearing aqueous fluids; therefore, the EOS of NaCl- H₂O fluids were used as a proxy for the NaF- and KCl bearing fluids. A density of 2, 3, 4, and 30 wt% NaCl was used for 2, 3, 4 wt% NaF and 30 wt% KCl- bearing fluids, respectively. The density of 12 wt% NaCl was used for the mixed fluid containing 10 wt% NaCl + 2 wt% NaF (Mantegazzi et al., 2013). The background was determined by using the edges of the (x, y) scan where the beam hits the Re part of the gasket. The background values were consistent with the values from the map of the empty HDAC (i.e., at 0 ppm Zr). The background was subtracted from the normalized integrated Zr fluorescence peak. Uncertainties for the Zr concentration of the fluids measured in the SXRF experiments were calculated based on the statistical deviation across the sample chamber (10-15%). Zirconium concentrations at run conditions also include propagating the fitting errors from the standard calibration. Due to the iterative nature of the SXRF experimental technique and the small size of the crystal, recovering and analyzing the rutile crystal from each unique pressure-temperature condition was not possible.

3 RESULTS

3.1 Zr concentrations in aqueous fluid

The experimentally determined Zr concentrations in aqueous fluids containing 2, 3 and 4 wt% NaF, 30 wt% NaCl, 30 wt% KCl and the combined 10 wt% NaCl + 2 wt% NaF fluid are provided in Table 1. Zirconium concentrations in the fluid as a function of (a) temperature, (b) pressure and (c) density are presented in Figure 4. Lines in Figure 4a are trend lines and are not statistical best fits.

The data indicate a positive, albeit weak, temperature dependence (Figure 4a) for the concentration of Zr in each aqueous fluid. The concentrations of Zr in 2 wt% NaF-bearing aqueous fluid at 0.5-2.25 GPa increased from 25 ppm at 250°C to 50 ppm at 650°C. The concentration of Zr in a 3 wt% NaF-bearing aqueous fluid increases from 215 ppm at 300°C to 350 ppm at 500°C. The Zr concentration of the 4 wt% NaF-bearing fluid increases from 590 ppm at 300°C and 1.65 GPa to 665 ppm at 500°C and 2.27 GPa. Zirconium concentrations in 30 wt% NaCl-bearing aqueous fluid at 1.95-2.79 GPa increase from 110 ppm at 300°C to 140 ppm at 510°C. Zirconium concentrations in 30 wt% KCl-bearing aqueous fluid at 0.65-0.89 GPa increase from 58 ppm at 300°C to 75 ppm at 500°C. Zirconium concentrations in aqueous fluid containing both 10 wt% NaCl + 2 wt% NaF at 1.89-2.69 GPa increase from 285 ppm at 300°C to 360 ppm at 600°C. The increase in Zr concentrations of the fluid observed in this study is expected and consistent with previous studies (e.g., Audétat and Keppler, 2005; Antignano and Manning, 2008).

There also appears to be a slight increase in the concentration of Zr with pressure in all of the aqueous fluids (Figure 4b); however, much of this increase is attributed to the fact that the pressure in the HDAC increases as temperature increases. This is best illustrated by examining the results from the 3 wt% NaF-bearing aqueous solution. The data indicate that the concentration of Zr in the fluid changes from 215 to 350 ppm as temperature increases from 300 to 510°C, while pressure remains relatively constant (e.g., 2.34 to 2.37 GPa). Similarly, the concentration of Zr in aqueous fluid appears to be

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independent of fluid density (Figure 4c). The densities for each fluid composition are similar for each temperature-pressure step, except in the fluids containing 3 wt% NaF, where there appears to be a slight negative density dependence.

Fluid composition is the most significant factor affecting the concentration of Zr in the fluid at all P-T conditions (Figures 5 and 6). The addition of 4 wt% NaF to the fluid increases the Zr concentration (590-665 ppm) of the fluid by up to one order of magnitude relative to a 2 wt% NaF- (25-50 ppm), 30 wt% NaCl- (110-140 ppm) and 30 wt% KCl- (58-75 ppm) bearing fluid, and ca. two times more than the addition of 3 wt% NaF (215-350 ppm) and the combined fluid 10 wt% NaCl + 2 wt% NaF (285-360 ppm). The abundances of Zr and NaF in the fluid are positively correlated, as demonstrated by the linear fits illustrated in Figure 5 and listed in Table 2. These linear fits can only be used for interpolation between 2.0 to 4.0 wt% NaF because they do not satisfy the natural constraint that the solubility must be ≥ 0 when NaF concentration is ≥ 0 . For example, if extrapolated to NaF concentration < 2.0 wt%, physically meaningless negative solubility would be obtained. These fits were used to calculate NaF equivalent concentrations for the 30 wt% NaCl, 30 wt% KCl and combined 10 wt% NaCl + 2 wt% NaF aqueous solution. The addition of 30 wt% NaCl is equivalent to the addition of ~ 2.3 wt% NaF (Figure 5, triangles), which indicates that F has a much greater effect on Zr concentrations of the fluid than Cl. The addition of 30 wt% KCl is equivalent to the addition of ~ 2.1 wt% NaF (Figure 5, circles). The combined effect of 10 wt% NaCl + 2 wt% NaF has the same effect as adding ~ 3 wt% NaF (Figure 5, diamonds).

3.2 Rutile solubility in aqueous fluid

Titanium concentrations in aqueous fluid cannot be directly measured by our in situ method because the XRF peak for Ti is at about 5 keV, which is not possible to detect with the geometry of the experimental HDAC cell and SXRF detector. The measured Zr concentrations in aqueous fluid reported

above allow the concentration of Ti in the experimental aqueous fluids to be calculated by assuming congruent dissolution of the starting Zr-rutile crystal (Table 1, Figure 6). The reported diffusion coefficient of Zr in rutile is of the order 10^{-18} to 10^{-23} m²/s at 800°C (Sasaki et al., 1985; Cherniak et al., 2007; Marschall et al., 2014) and much lower in our 250-650°C experiments. Over the timescales of our experiments ($t < 10$ hrs) the diffusion distance of Zr in rutile would be less than 0.2 µm. Therefore, it can be assumed that the Zr:Ti ratio of the rutile did not change during the experiments. Because the rutile crystal in our experiments contains 97 mol% TiO₂, using Raoult's law, solubility of pure rutile (TiO₂) for comparison with literature data was calculated by dividing the Zr-rutile solubility values by 0.97 (Table 1).

In detail, the data indicate: (1) 30 wt% of KCl has a smaller effect than 30 wt% of NaCl on increasing Ti solubility. This is understandable assuming the increased solubility is due to the formation of Ti-Cl complexes because 30 wt% KCl is equivalent to 4.0 mol/kg of Cl⁻ whereas 30 wt% NaCl is equivalent to 5.1 mol/kg of Cl⁻; and (2) the effect of 30 wt% KCl or 30 wt% NaCl is equivalent to the effect of 2-3 wt% NaF. That is, fluoride is much more effective in increasing rutile solubility than chloride.

4 DISCUSSION

4.1 A comparison with literature data

Rutile solubilities from this work are generally consistent with and extend the literature data (Audétat and Keppler, 2005; Tropper and Manning, 2005; Antignano and Manning, 2008; Rapp et al., 2010) to lower temperatures and a wider range of fluid compositions. The data indicate an increase in rutile solubility in the fluid with increasing NaCl content (from 10 to 30 wt% NaCl, Figure 5, triangles). The data do not demonstrate a distinct difference in Ti concentration between the fluids containing 3 and

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4 wt% NaF (this study) and 10 wt% NaF (Rapp et al., 2010); however, it must be noted that the 10 wt% NaF data from Rapp et al. (2010) span almost an order of magnitude.

The data presented in the current study is compared to the data from previously published studies in Figure 6. All data demonstrate that increasing the concentration of halogens in aqueous fluid strongly increases rutile solubility in the fluid over a wide range of pressure and temperature. A quantitative comparison is not possible because our experimental temperatures are lower than data in published studies. Furthermore, rutile solubility data are highly scattered and hence cannot be modeled or extrapolated reliably. For example, five studies reported rutile solubility in pure H₂O fluid (Ayers and Watson, 1993; Tropper and Manning, 2005; Audétat and Keppler, 2005; Antignano and Manning, 2008, and Rapp et al., 2010) that differ by more than 3 orders of magnitude in concentration, with Audétat and Keppler (2005) reporting the lowest solubility, and Ayers and Watson (1993) reporting the highest solubility. The majority of the published data were produced by using the mass-loss technique, which, as discussed by Audétat and Keppler (2005), is notoriously difficult in accurately determining mineral solubilities. However, Manning et al. (2008) and Manning and Antignano (2008) reasoned that the low rutile solubility values reported by Audétat and Keppler (2005) are likely an artefact of their method of determination of rutile solubility, which was to visually determine complete loss of a rutile crystal in aqueous fluid in a HDAC. The large uncertainty and the large and systematic inter-laboratory differences preclude the development of a solubility model even though a large number of solubility data are available. Thus, the primary focus of the discussion is on using the data presented here to develop relations between rutile solubility and dissolved halogen concentrations. Our method of using Zr-bearing rutile and SXRF to measure in situ the Zr concentration at various temperatures and pressures to investigate rutile solubility provides an alternative method to the mass loss method.

4.2 Ti dissolution mechanism

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As mentioned previously, published rutile solubility data in aqueous solutions are highly scattered with a large inter-laboratory systematic difference. Because of this, it is difficult to combine our data with literature data to quantify how rutile solubility depends on various dissolved species concentrations. In this section, we use our data to determine the dependence of Ti solubility on the fluid composition and evaluate the dissolution mechanism.

The solubilities of SiO_2 and TiO_2 in aqueous fluid, measured experimentally at 800 – 1200 °C and 1.0 to 2.93 GPa, were considered by Ayers and Watson (1993) to be dominantly controlled by increasing temperature. However, several studies have demonstrated experimentally that the influence of temperature on mineral solubility is small compared to the effects of fluid composition, especially the alkali halide concentration (Knauss et al., 2001; Rapp et al., 2010; and Wu and Konga, 2013). For example, Knauss et al. (2001) demonstrated that over the neutral pH range, where the species $\text{Ti}(\text{OH})_4(\text{aq})$ is expected to dominate, the temperature dependence is very small at 100 – 300 °C. Rapp et al. (2010) demonstrated that the influence of F and Cl on the solubility of TiO_2 in aqueous fluid at 800 and 1000 °C and 0.5 GPa, is more pronounced than the influence of temperature variations, and that TiO_2 is more soluble in 10 wt% NaF aqueous solution than in 10 wt% NaCl aqueous solution (Figure 6). The results of Wu and Konga (2013) indicate that F (at less than 0.7 wt%) slightly increases SiO_2 solubility in aqueous fluid at 1 GPa and 770-947 °C and promotes incongruent dissolution of hornblende. Our results are consistent with these studies, and demonstrate that fluid composition has the strongest effect, and temperature effects are small in the temperature range investigated (e.g., 250-650°C; Figure 4a and 5).

Ti^{4+} and Zr^{4+} have the same charge and similar ionic radii (e.g., 74.5 pm for Ti^{4+} and 86 pm for Zr^{4+} in octahedral sites). Therefore, the speciation between Ti or Zr with Cl, F, and OH should also be similar. The review of Pokrovski et al. (2013) showed that the most common metal-OH speciation for

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304 typical hydrothermal fluids at temperatures $\leq 500^\circ\text{C}$ is the same for Zr and Ti (e.g., $\text{Zr}(\text{OH})_4^\circ$, $\text{Ti}(\text{OH})_4^\circ$).
305 The Raman data of Griffith and Wickins (1967) also demonstrated that the dominant species present in
306 Cl- and F-bearing acidic solutions is the same for Ti and Zr (e.g., $[(\text{Ti,Zr})\text{F}_6]^{2-}$ and $[(\text{Ti,Zr})\text{Cl}_6]^{2-}$).
307 Therefore, the speciation and complexation data for Zr can be applied to Ti and vice versa.

308 Very few experimental studies have investigated complexation of Cl and F with Zr and Ti.
309 Louvel et al. (2013) reported that x-ray absorption spectroscopic (XAS) measurements and ab initio x-
310 ray absorption near edge spectroscopic (XANES) calculations for dilute (e.g., 2.5 wt% HCl) Cl-bearing
311 aqueous fluids did not provide evidence for extensive Zr-Cl complexation up to 420°C . They reported
312 that Zr speciation is dominated by 8-fold-coordinated $[\text{Zr}(\text{H}_2\text{O})_8]^{4+}$ hydrated complexes. The results of
313 Louvel et al. (2013) may explain the low Zr concentrations (e.g., 113-141 ppm) in the 30 wt% NaCl
314 aqueous fluid. Jahn and Wilke (2014) performed ab initio molecular dynamics simulations for Zr and Hf
315 speciation in aqueous fluids at 1 GPa and 727°C and reported that Zr and Hf are dissolved in aqueous
316 fluid predominantly in octahedral coordination. Their results indicate that each Zr is surrounded by six
317 nearest neighbor anions (O or Cl) and that the coordination number decreases towards a pure water
318 solvent. These models suggest that complexation between HFSE could occur at higher concentrations of
319 Cl.

320 The rapid increase of rutile solubility with NaF concentration in the aqueous fluid suggests
321 complexation of F with Ti in the aqueous fluid. Assuming that Ti in pure H_2O fluid is dissolved as
322 $\text{Ti}(\text{OH})_4^\circ$ (fluid), the complex reactions can be written as follows:

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328 Alternatively, Reactions (2a) to (2d) can also be written as:

333 As F concentration and F/Ti ratio in the fluid increase, more Ti would be complexed with F. The above
334 reactions would strongly increase pH. In addition, other species and reactions are possible, e.g.,

337 The above reactions would reduce pH. The general species and reactions in the aqueous fluid may be
338 written as follows:

340 Limiting the coordination number to be no more than 6, then m may vary from 0 to 6 and n may vary
341 from 0 to $6-m$, where a negative $(4-n)$ value means that OH^- appears on the left hand side of Reaction
342 (5).

343 The total dissolved Ti in mol/kg in the NaF-H₂O fluid may be expressed as:

345 where brackets mean mole concentration (mol/kg). In the above expression, $[\text{TiF}(\text{OH})_3^\circ]$ is proportional
346 to $[\text{F}^-]$, $[\text{TiF}_2(\text{OH})_2^\circ]$ to $[\text{F}^-]^2$, $[\text{TiF}_3(\text{OH})^\circ]$ to $[\text{F}^-]^3$, and $[\text{TiF}_4^\circ]$ to $[\text{F}^-]^4$.

347 To quantify the effect of F on rutile solubility, it is necessary to know rutile solubility in pure
348 H₂O fluid. As can be seen from Figure 6, the concentration of Ti in a rutile-saturated pure H₂O fluid is
349 scattered and is low. For example, if the data from Antignano and Manning (2008) are used, the Ti

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concentration in pure H₂O would be of the order ≤ 1 ppm at temperature $\leq 500^\circ\text{C}$. Hence, compared to > 400 ppm Ti in NaF solutions, the concentration of $\text{Ti}(\text{OH})_4^\circ$ can be ignored for approximate treatment here. (In the future when rutile solubility in pure H₂O is better constrained, it can be incorporated in our treatment.) Figure 7a plots pure rutile solubility versus NaF concentration. When the data in Figure 7a are fitted by a power function with rutile solubility in pure H₂O assumed to be zero, rutile solubility is found to be roughly proportional to 3.6th to 3.8th power of NaF concentration at different temperatures, suggesting that the dominant dissolved Ti species contain 3 to 4 F, such as $\text{TiF}_3(\text{OH})^\circ$, $\text{TiF}_3(\text{OH})_2^-$, $\text{TiF}_3(\text{OH})_3^{2-}$, TiF_4° , TiF_4OH^- , and $\text{TiF}_4(\text{OH})_2^{2-}$. This treatment is semi-quantitative and the fits are not perfect, either due to data uncertainty or a need to construct a sophisticated thermodynamic model; however, the limited data would not be able to constrain such a model.

The effect of Cl^- on the concentration of Ti at rutile saturation can be examined similarly. Assuming Na^+ and K^+ do not play a role in Ti solubility (this needs to be verified by future experiments), rutile solubility data in both KCl and NaCl solutions can be combined by using the molar Cl^- concentration (mol/kg). Using the limited data in this work, Figure 7b indicates that rutile solubility increases with the 2.5th to 2.8th power of Cl^- concentration in the fluid at $300\text{--}500^\circ\text{C}$, suggesting that the dominant dissolved Ti species in the fluid contain 2 to 3 Cl, such as $\text{TiCl}_3(\text{OH})^\circ$, $\text{TiCl}_3(\text{OH})_2^-$, $\text{TiCl}_3(\text{OH})_3^{2-}$, $\text{TiCl}_2(\text{OH})_2^\circ$, $\text{TiCl}_2(\text{OH})_3^-$ and $\text{TiCl}_2(\text{OH})_4^{2-}$.

When both NaCl and NaF are present in the fluid, Ti solubility is greater than the simple addition of the individual effect by NaCl and NaF. This might be related to the formation of new species containing both F and Cl, such as $\text{TiF}_m\text{Cl}_p(\text{OH})_n^{-(m+n+p-4)}$ in NaCl-KCl-H₂O fluids:

Not enough data are available to quantify the effects of these species.

The new data presented here for the solubility of rutile based on the concentration of Zr in Zr-rutile-saturated aqueous fluid demonstrate that the effect of fluid composition, specifically the halogen ion concentration, is the dominant control on the solubility of rutile in aqueous fluid (e.g., Figures 4 and 5). In addition, the new data demonstrate that halogen-bearing aqueous fluids have the capacity to hold high Zr and Ti concentration. These results are consistent with published studies of HFSE-mineral solubility in complex, halogen-bearing aqueous fluids (Rapp et al., 2010; Louvel et al., 2013; Wu and Koga, 2013), and together evince the important roles for dissolved Cl- and F-salts to moderate HFSE compatibility in geologic fluids (Figure 5 and 6). The stronger ability of F-bearing fluids to dissolve and transport HFSE (e.g., Ti: Rapp et al., 2010; Nb: Tanis et al., 2015), relative to Cl-bearing fluids is most likely related to the local coordination of HFSE in the presence of each halogen.

Finally, it is important to note that Reactions 1 – 5 and 7 indicate that solubility of rutile affects and is affected by the pH of the fluid, similar to the solubility of many other minerals. Due to the many possible species of $\text{TiF}_m(\text{OH})_n^{4-m-n}$, limited data, and the inability to directly measure the concentrations of the individual species, it is not possible yet to construct a model to assess the effect of pH on rutile solubility and vice versa. Fluids evolved during prograde metamorphism of serpentinite in subduction zone environments will interact with high-pressure rocks such as eclogite as the fluid(s) migrates from the slab through metasedimentary eclogite into the mantle wedge, and mineral assemblages such as jadeite-paragonite-quartz in the slab, or talc-olivine in the mantle wedge, buffer pH, with near-neutral values of pH of, e.g., 4 – 6 at 500 °C and 1.8 GPa (Manning et al., 2010). Thus, in subduction zone environments, the ability of F- and Cl-bearing aqueous fluids to dissolve and transport Ti and, by analogy other high field strength elements, may be limited by the pH buffering capacity of the stable mineral assemblage. The data in the current study and those from the literature (Figure 6) indicate that a subduction zone halide-rich aqueous fluid is able to maintain high concentrations of dissolved titanium

during ascent because the temperature of the fluid increases during ascent through the subducting plate (Kelemen and Manning, 2015) and the weak permittivity (i.e., low dielectric constant) of water at high temperatures promotes the stability of associated Ti-F and Ti-Cl complexes (Pan et al., 2012; Williams-Jones and Migdisov, 2014). If an ascending Ti-bearing fluid experiences an irreversible pH decrease during water – silicate rock (i.e., eclogite) interaction (e.g., Sverjensky and Huang, 2015), this may cause rutile precipitation. Thus, the solubility of rutile in high-pressure metamorphic environments is likely to be a complex function of the concentration of alkali halides in the aqueous fluid and the pH buffering capacity of the rock matrix, and the total amount of rutile dissolution would depend on the water/rock ratio, and the spatial and temporal scales for subduction zone fluid flow. The efficiency of Ti-F and Ti-Cl complex transport is most likely maximized in channelized fluid-flow events where fluid-rock interaction is minimized relative to porous flow (e.g., John et al., 2012). A comprehensive model that incorporates all of these parameters is required to explain the variability of the HFSE signature among different subduction zone environments.

CONCLUSIONS

The data presented here indicate that fluid composition exerts the strongest control on rutile solubility in aqueous fluid at pressure-temperature conditions appropriate for fluid evolution in subduction zone environments. The data not only confirm the high solubility of rutile in chloride and especially fluoride solutions, but also show quantitatively that the solubility of rutile in aqueous fluid increases with the 2nd to 3rd power of Cl⁻ concentration, and 3rd to 4th power of the F⁻ concentration. The data demonstrate that halogen-rich aqueous fluids can dissolve, transport, and precipitate significant quantities of HFSE, as evinced by the presence of rutile-bearing veins in blueschist and eclogite in exhumed terranes in subduction zones. However, the results presented here indicate that the ubiquitous

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419 HFSE depletion in arc magmas likely implies that the fluids in that environment generally have low F
420 concentrations.

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6 REFERENCES

- Abramson, E.H., and Brown, J.M. (2004) Equation of state of water based on speeds of sound measured in the diamond-anvil cell. *Geochimica et Cosmochimica Acta*, **68**, 1827–1835.
- Antignano, A., and Manning, C.E. (2008) Rutile solubility in H₂O, H₂O–SiO₂, and H₂O–NaAlSi₃O₈ fluids at 0.7–2.0 GPa and 700–1000 °C: Implications for mobility of nominally insoluble element. *Chemical Geology*, **255**, 283–293.
- Audétat, 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.

REVISION 1

- 444 Ayers, J.C., and Watson, E.B. (1993) Rutile solubility and mobility in supercritical aqueous fluids.
445 *Contributions to Mineralogy and Petrology*, 114, 321-330.
- 446 Bassett, W.A., Shen, A.H., Bucknum, M., and Chou, I.-M. (1993) A new diamond anvil cell for
447 hydrothermal studies to 2.5 GPa and from 190 to 1200 °C. *Reviews of Scientific Instruments*, **64**,
448 2340-2345.
- 449 Beinlich, A., Klemd, R., John, T., Gao, J. (2010) Trace-element mobilization during Ca-metasomatism
450 along a major fluid conduit: Eclogization of blueschist as a consequence of fluid-rock interaction.
451 *Geochimica et Cosmochimica Acta*, **74**, 1892-1922.
- 452 Bernini, D., Audétat, A., Dolejš, D., and Keppler, H. (2013) Zircon solubility in aqueous fluids at high
453 temperatures and pressures. *Geochimica et Cosmochimica Acta*, **119**, 178-187.
- 454 Brenan, J.M., Shaw, H.F., Phinney, D.L., and Ryerson, F.J. (1994) Rutile-aqueous fluid partitioning of
455 Nb, Ta, Hf, Zr, U and Th: implications for high field strength element depletions in island-arc
456 basalts. *Earth and Planetary Science Letters*, **128**, 327-339.
- 457 Brophy, J.G., and Marsh, B.D. (1986) On the Origin of High-Alumina Arc Basalt and the Mechanics of
458 Melt Extraction. *Journal of Petrology*, **27**, 763-789.
- 459 Chen, Z., and Li, Q. (2008) Zr-in-rutile thermometry in eclogite at Jinheqiao in the Dabie orogen and its
460 geochemical implications. *Chinese Science Bulletin*, **53**, 768-776.
- 461 Cherniak, D.J., Manchester, J., and Watson, E.B. (2007) Zr and Hf diffusion in rutile. *Earth and*
462 *Planetary Science Letters*, **261**, 267-279.
- 463 Dorogokupets, P.I., and Dewaele, A. (2007) Equation of state of MgO, Au, Pt, NaCl-B1 and NaCl-B2:
464 Internally consistent high-temperature pressure scales. *High Pressure Research*, **27**, 431-446.
- 465 Ferry, J.M., and Watson, E.B. (2007) New thermodynamic models and revised calibrations for the Ti-in-
466 zircon and Zr-in-rutile thermometers. *Contributions to Mineralogy and Petrology*, 154, 429-437.

REVISION 1

- 467 Foley, S.F., Barth, M.G., and Jenner, G.A. (2000) Rutile/melt partition coefficients for trace elements
468 and an assessment of the influence of rutile on the trace element characteristics of subduction zone
469 magmas. *Geochimica et Cosmochimica Acta*, **64**, 933-938.
- 470 Foley, S.F., Tiepolo, M., and Vannucci, R. (2002) Growth of early continental crust controlled by
471 melting of amphibolite in subduction zones. *Nature*, **417**, 837-840.
- 472 Fu, B., Touret, J.L.R., and Zheng, Y.-F. (2001) Fluid Inclusions in coesite-bearing eclogites and jadeite
473 quartzite at Shuanghe, Dabie Shan (China). *Journal of metamorphic Geology*, **19**, 531-547.
- 474 Gao, J., John, T., Klemm, R., and Xiong, X. (2007) Mobilization of Ti–Nb–Ta during subduction:
475 Evidence from rutile-bearing dehydration segregations and veins hosted in eclogite, Tianshan, NW
476 China. *Geochimica et Cosmochimica Acta*, **71**, 4974-4996.
- 477 Gao, C., Liu, Y., Zong, K., Hu, Z., and Gao, S. (2010) Microgeochemistry of rutile and zircon in
478 eclogites from the CCSD main hole: Implications for the fluid activity and thermo-history of the
479 UHP metamorphism. *Lithos*, **115**, 51-64.
- 480 Guo, S., Ye, K., Chen, Y., Liu, J., Mao, Q., and Ma, Y. (2012) Fluid–rock interaction and element
481 mobilization in UHP metabasalt: Constraints from an omphacite–epidote vein and host eclogites in
482 the Dabie orogeny. *Lithos*, **136-139**, 145-167.
- 483 Green T.H. (1981) Experimental evidence for the role of accessory phases in magma genesis. *Journal of*
484 *Volcanology and Geothermal Research*, **10**, 405-422.
- 485 Hammersley, A.P. (1997) FIT2D: An Introduction and Overview. *ESRF Internal Report*,
486 ESRF97HA02T.
- 487 Hanchar, J.M., Finch, R.J., Hoskin, P.W.O, Watson, E.B., Cherniak, D.J., and Mariano, A.N. (2001)
488 Rare earth elements in synthetic zircon: Part 1. Synthesis, and rare earth element and phosphorus
489 doping. *American Mineralogist*, **86**, 667-680.

REVISION 1

- 490 Hayden, L.A., and Manning, C.E. (2011) Rutile solubility in supercritical NaAlSi₃O₈-H₂O fluids.
491 *Chemical Geology*, **284**, 74-81.
- 492 Henk, A., Franz, L., Teufel, S., and Oncken, O. (1997) Magmatic underplating, extension, and crustal
493 reequilibration: insights from a cross-section through the Ivrea Zone and Strona-Ceneri Zone,
494 northern Italy. *Journal of Geology*, **105** (3), 367–377.
- 495 Hofman, A.E., Baker, M.B., and Eiler, J.M. (2013) An experimental study of Ti and Zr partitioning
496 among zircon, rutile and granitic melt. *Contributions to Mineralogy and Petrology*, **166**, 235-253.
- 497 Jahn, S., and Wilke, M. (2014) Zr and Hf speciation in aqueous fluids at high P and T. Goldschmidt
498 Abstract.
- 499 Jenner, G.A., Foley, S.F., Jackson, S.E., Green, T.H., Fryer, B.J., and Longerich, H.P. (1994)
500 Determination of partition coefficients for trace elements in high pressure-temperature experimental
501 run products by laser ablation microprobe-inductively coupled plasma-mass spectrometry (LAM-
502 ICP-MS). *Geochemica et Cosmochimica Acta*, **58**, 5099-5103.
- 503 John, T., Scherer, E.E., Haase, K., Schenk, V. (2004) Trace element fractionation during fluid-induced
504 eclogitization in a subducting slab: trace element and Lu–Hf–Sm–Nd isotope systematics. *Earth and*
505 *Planetary Science Letters*, **227**, 441-456.
- 506 John, T., Klemd, R., Gao, J., and Garbe-Schönberg (2008) Trace-element mobilization in slabs due to
507 non steady-state fluid-rock interaction: Constraints from and eclogite-facies transport vein in
508 blueschists (Tianshan, China). *Lithos*, **103**, 1-24.
- 509 John, T., Scambelluri, Frische, M., Barnes, J.D., and Bach, W. (2011) Dehydration of subducting
510 serpentinite: Implications for halogen mobility in subduction zones and the deep halogen cycle.
511 *Earth and Planetary Science Letters*, **308**, 65-76.
- 512 John, T., Gussone, N., Podladchikov, Y.Y., Bebout, G.E., Dohmen, R., Halama, R., Klemd, R., Magna,

REVISION 1

- 513 T., and Seitz, H-M. (2012) Volcanic arcs fed by rapid pulsed fluid flow through subducting slabs.
514 *Nature Geoscience*, **5**, 489-492.
- 515 Kelemen, P.B., and Manning, C.E. (2015) Reevaluating carbon fluxes in subduction zones, what goes
516 down, mostly comes up. *Proceedings of the National Academy of Sciences*, **30**, 112.
- 517 Kerrigan, R.J. (2011) Reaction Rates and textural development of hydrolysis reactions in the system
518 MgO-SiO₂-H₂O. Dissertation, University of Maryland.
- 519 Klemme, S., Prowatke, S., Hametner, K., and Günther, D. (2005) Partitioning of trace elements between
520 rutile and silicate melts: Implications for subduction zones. *Geochimica et Cosmochimica Acta*, **69**,
521 2361-2371.
- 522 Konrad-Schmolke, M., Zack, T., O'Brien, P.J., and Barth, M. (2011) Fluid migration above a subducted
523 slab — Thermodynamic and trace element modelling of fluid–rock interaction in partially
524 overprinted eclogite-facies rocks (Sesia Zone, Western Alps). *Earth and Planetary Science Letters*,
525 **311**, 287-298.
- 526 Knauss, K.G., Dibley, M.J., Bourcier, W.L., and Shaw, H.F. (2004) Ti(IV) hydrolysis constants derived
527 from rutile solubility measurements made from 100 to 300°C. *Applied Geochemistry*, **9-10**, 1115-
528 1128.
- 529 Louvel, M., Sanchez-Valle, C., Malfait, W.J., Testemale, D., and Hazemann, J-L. (2013) Zr
530 Complexation in high pressure fluids and silicate melts and implications for mobilization of HFSE in
531 subduction zones. *Geochimica et Cosmochimica Acta*, **104**, 281-299.
- 532 Luvizotto, G.L., and Zack, T. (2009) Nb and Zr behavior in rutile during high-grade metamorphism and
533 retrogression: An example from the Ivrea-Verbano Zone. *Chemical Geology*, **261**, 303-317.
- 534 Manning, C.E. (2004) The chemistry of subduction-zone fluids. *Earth and Planetary Science Letters*,
535 **223**, 1-16.

REVISION 1

- 536 Manning, C.E., Kavner, A., Chopelas, A. (2010) On the relative roles of carbonate and molecular CO₂
537 in subduction zones: implications for Earth's deep carbon cycle. *American Geophysical Union, Fall*
538 *Meeting*, abstract #U23B-05.
- 539 Manning, C.E., Wilke, M., Schmidt, C., and Cauzid, J. (2008) Rutile solubility in albite-H₂O and
540 Na₂Si₃O₇-H₂O at high temperatures and pressures by in-situ synchrotron radiation micro-XRF. *Earth*
541 *and Planetary Science Letters*, **272**, 730-737.
- 542 Mantegazzi, E., Sanchez-Valle, C., and Driesner, T. (2013) Thermodynamic properties of aqueous NaCl
543 solutions to 1073 K and 4.5 GPa, and implications for dehydration reactions in subducting slabs.
544 *Geochimica et Cosmochimica Acta*, **121**, 263-290.
- 545 Meinhold, G. (2010) Rutile and its application in earth sciences. *Earth-Science Reviews*, **102**, 1-28.
- 546 Migdisov, A.A., Williams-Jones, A.E., van Hinsberg, V., and Salvi, A. (2011) An experimental study of
547 the solubility of baddeleyite (ZrO₂) in fluoride-bearing solutions at elevated temperatures.
548 *Geochimica et Cosmochimica Acta*, **75**, 7426-7434.
- 549 Pan, D., Spanu, L., Harrison, B., Sverjensky, D.A., and Galli, G. (2012) Dielectric properties of water
550 under extreme conditions of transport or carbonates in the deep Earth. *Proceedings of the National*
551 *Academy of Sciences*, **110** (17), 6646-6650.
- 552 Pollard, P.J., Pichavant, M., and Charoy, B. (1987) Contrasting evolution of fluorine-and boron-rich tin
553 systems. *Mineralium Deposita*, **22**, 315-321.
- 554 Rapp, J.R., Klemme, S., Butler, I.B., and Harley, S.L. (2010) Extremely high solubility of rutile in
555 chloride and fluoride-bearing metamorphic fluids: An experimental investigation. *Geology*, **38**, 323.
- 556 Ryerson, F.J., and Watson, E.B. (1987) Rutile saturation in magmas: implications for Ti Nb Ta depletion
557 in island-arc basalts. *Earth and Planetary Science Letters*, **86**, 225-239.
- 558 Salvi, S., and Williams-Jones, A.E. (1996) The role of hydrothermal processes in concentrating high-

REVISION 1

- 559 field strength elements in the Strange Lake peralkaline complex, northeastern Canada. *Geochimica*
560 *et Cosmochimica Acta*, **60**, 1917-1932.
- 561 Sanchez-Valle, C., Martinez, I., Daniel, I., Philippot, P., Bohic, S., and Simionovici, A. (2003)
562 Dissolution of strontianite at high *P-T* conditions: An in situ synchrotron X-ray fluorescence study.
563 *American Mineralogist*, **88**, 978–985.
- 564 Sasaki, J., Peterson, N.L., Hoshino, K. (1985) Tracer impurity diffusion in single-crystal rutile (TiO_{2-x}).
565 *Journal of Physics and Chemistry of Solids*, **46**, 1267-1283.
- 566 Saunders A.D., Tarney J., and Weaver S.D. (1980) Transverse geochemical variations across the
567 Antarctic Peninsula: implications for the genesis of calc-alkaline magmas. *Earth and Planetary*
568 *Science Letters*, **46**, 344-360.
- 569 Schmidt, C., Rickers, K., Bilderback, D.H., and Huang, R. (2007) In situ synchrotron radiation XRF
570 study of REE phosphate dissolution in aqueous fluids to 800 °C. *Lithos*, **95**, 87-102.
- 571 Shervais, J.W., and Jean, M.M. (2012) Inside the subduction factory: Modeling fluid mobile element
572 enrichment in the mantle wedge above a subduction zone. *Geochimica et Cosmochimica Acta*, **95**,
573 270-285.
- 574 Spandler, C., Pettke, T., and Rubatto, D. (2011) Internal and External Fluid Sources for Eclogite-facies
575 Veins in the Monviso Meta-ophiolite, Western Alps: Implications for Fluid Flow in Subduction
576 Zones. *Journal of Petrology*, **52**, 1207-1236.
- 577 Stalder, R., Foley, S.F., Brey, G.P., and Horn, I. (1998) Mineral-aqueous fluid partitioning of trace
578 elements at 900-1200 °C and 3.0-5.7 GPa: New experimental data for garnet, clinopyroxene, and
579 rutile, and implications for mantle metasomatism. *Geochimica et Cosmochimica Acta*, **62**, 1781-
580 1801.
- 581 [Sverjensky, D.A., and Huang, F. \(2015\) Diamond formation due to a pH drop during fluid-rock](#)

- 582 interactions. *Nature Communications*, **6**, 8702.
- 583 Tanis, E.A., Simon, A.C., Tschauner, O., Chow, P., Xiao, Y., Shen, G., Hanchar, J.M., and Frank, M.
- 584 (2012) Solubility of xenotime in a 2 M HCl aqueous fluid from 1.2 to 2.6 GPa and 300 to 500 °C.
- 585 *American Mineralogist*, **97**, 1708–1713.
- 586 Tanis, E.A., Simon, A.C., Tschauner, O., Chow, P., Xiao, Y., Burnley, P., Cline, C.J., Hanchar, J.M.,
- 587 Pettke, T., Shen, G., and Zhao, Y. (2015) The mobility of Nb in rutile-saturated NaCl- and NaF-
- 588 bearing aqueous fluids from 1-6.5 GPa and 300-800 °C. *American Mineralogist*.
- 589 Tomkins, H.S., Powell, R., and Ellis, D.J. (2007) The pressure dependence of the zirconium-in-rutile
- 590 thermometer. *Journal of metamorphic geology*, **25**, 703-713.
- 591 Tropper, P., and Manning, C.E. (2005) Very low solubility of rutile in H₂O at high pressure and
- 592 temperature, and its implications for Ti mobility in subduction zones. *American Mineralogist*, **90**,
- 593 502-50.
- 594 Watson, E. B., Wark, D.A., and Thomas, J.B. (2006) Crystallization thermometers for zircon and rutile.
- 595 *Contributions to Mineralogy and Petrology*, **151**, 413-433.
- 596 Wilke, M., Schmidt, C., Dubrill, J., Appel, K., Borchert, M., Kvashnina, K., and Manning, C.E. (2012)
- 597 Zircon solubility and zirconium complexation in H₂O+Na₂O+SiO₂±Al₂O₃ fluids at high pressure and
- 598 temperature. *Earth and Planetary Science Letters*, **349-350**, 15-25.
- 599 Williams-Jones, A.E., and Migdisov, A.A. (2014) Experimental constraints on the transport and
- 600 deposition of metals in ore-forming hydrothermal solutions. *Journal of Economic Geology Special*
- 601 *Publication*, **18**, 77-97.
- 602 Wu, J., and Koga, K. (2013) Fluorine partitioning between hydrous minerals and aqueous fluid and 1
- 603 GPa and 770-947°C: A new constraint on slab flux. *Geochimica et Cosmochimica Acta*, **119**, 77-92.
- 604 Zack, T., Kronz, A., Foley, S.F., and Rivers, T. (2002a) Trace element abundances in rutiles from

REVISION 1

605 eclogites and associated garnet mica schists. *Chemical Geology*, **184**, 97–122.

606 Zack, T., Foley, S.F., and Rivers, T. (2002b) Equilibrium and disequilibrium trace element partitioning
607 in hydrous eclogites (Trescolmen, Central Alps). *Journal of Petrology*, **43**, 1947–1974.

608 Zack, T., Moraes, R., and Kronz, A. (2004) Temperature dependence of Zr in rutile: empirical calibration
609 of a rutile thermometer. *Contributions to Mineralogy and Petrology*, **148**, 471–488.

610 Zack, T., John, T., (2007) An evaluation of reactive fluid flow and trace element mobility in subducting
611 slabs. *Chemical Geology*, **239**, 199–216.

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7 FIGURE CAPTIONS

Figure 1: (Top) Back-scattered electron (BSE) image of a rutile crystal with less than 15% variation in Zr concentration. (Bottom) BSE image of non-homogeneous rutile crystal that contained large variations in Zr concentrations as an example of crystals that were not considered for experiments.

Figure 2: a) A raw synchrotron x-ray fluorescence (SXRF) spectrum of the 1000 ppm Zr standard solution. The Zr peak was sufficiently distinct from the Compton scattering signal (~20 – 27 keV) arising from diamond, which justified a local linear background fit. All peaks other than Zr are generated by excitation by scattered radiation of other parts of the HDAC. b) The integrated peak area from the sum of each 3-D scan (~70 min intervals) for 30 wt% NaCl at 300 °C plotted as a function of time. Once the Zr peak area, at a unique pressure and temperature condition, became time-invariant it was interpreted to reflect the attainment of steady-state conditions and proximity to chemical equilibrium. c) The 2D SXRF map of the sample chamber containing the Zr-rutile and fluid.

Figure 3. The normalized integrated peak area of the Zr standard solutions demonstrate a linear relationship (line) between concentration and peak area.

Figure 4: The concentrations of Zr in experimental aqueous fluids plotted as a function of a) temperature, (b) pressure, and (c) fluid density. Uncertainties for Zr (ppm) are discussed in the text.

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Figure 5: The experimentally determined Zr concentrations in aqueous fluids plotted as a function of NaF concentration of the fluid. Each color represents a different temperature, and lines represent linear fits of the Zr vs. NaF data. The concentrations of NaF equivalent wt. % were calculated for the 30 wt% NaCl aqueous fluid (triangles) and a 10 wt% NaCl + 2 wt% NaF aqueous fluid (diamonds) based on the linear fits (Table 2).

Figure 6: The calculated Ti concentrations in the fluid plotted as a function of temperature. The symbols for the data from the current study are in color and are identical to those used in Figures 4 and 5. Also plotted are the data from Rapp et al. (2010) who investigated rutile solubility in pure water (circles) and in aqueous fluids containing 10 wt% NaCl (triangles) or 10 wt% NaF (squares), rutile solubility data in pure H₂O from Tropper and Manning, 2005 (T&M 2005), Audétat and Keppler, 2005 (A&K, 2005) and Antignano and Manning, 2008 (A&M 2008).

Figure 7. (a) The relation between the solubility of rutile and F concentration in the fluid. Rutile concentration is in ppm, and NaF concentration is in wt%. 1 wt% NaF is equivalent to a F⁻ concentration of 0.238 mol/kg. (b) The relationship between rutile solubility (in ppm) and Cl⁻ concentration in the fluid for NaCl-H₂O and KCl-H₂O fluids (in mol/kg). The equations shown in both figures are for the best-fit curves, with y being Ti (ppm) and x being either NaF wt% in (a) or Cl⁻ mol/kg in (b).

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674 Figure 1 (top, bottom)

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689 Figure 7 a and b

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