The mobility of Nb in rutile-saturated NaCl- and NaF-bearing aqueous fluids from 1-6.5 GPa and 300-800 °C

ELIZABETH A. TANIS1,2, ADAM SIMON1, OLIVER TSCHAUNER2,3, PAUL CHOW4, Yuming Xiao4, Pamela Burnley2,3, Christopher J. Cline II2,3, John M. Hanchar5, Thomas Pettke6, Guoyin Shen5, Yusheng Zhao5

1Earth & Environmental Sciences, University of Michigan
2High Pressure Science and Engineering Center, University of Nevada, Las Vegas
3Department of Geoscience, University of Nevada, Las Vegas
4HPCAT, Carnegie Institute of Washington, Argonne IL
5Earth Sciences, Memorial University of Newfoundland
6Institute of Geological Sciences, Bern, Switzerland

ABSTRACT

Rutile (TiO₂) is an important host phase for high field strength elements (HFSE) such as Nb in metamorphic and subduction zone environments. The observed depletion of Nb in arc rocks is often explained by the hypothesis that rutile sequesters HFSE in the subducted slab and overlying sediment, and is chemically inert with respect to aqueous fluids evolved during prograde metamorphism in the forearc to subarc environment. However, field observations of exhumed terranes, and experimental studies, indicate that HFSE may be soluble in complex aqueous fluids at high pressure (i.e., > 0.5 GPa) and moderate to high temperature (i.e., > 300 °C). In this study, we investigated experimentally the mobility of Nb in NaCl- and NaF-bearing aqueous fluids in equilibrium with Nb-bearing rutile at pressure-temperature conditions applicable to fluid evolution in arc environments. Niobium concentrations in aqueous fluid at rutile saturation were measured directly by using a hydrothermal diamond anvil cell (HDAC) and synchrotron x-ray fluorescence (SXRF) at 2.1 to 6.5 GPa and 300-500 °C, and indirectly by performing mass loss experiments in a piston-cylinder (PC) apparatus at ~1 GPa and 700-800 °C. The concentration of Nb in a 10 wt% NaCl aqueous fluid increases from 6 to 11 µg g⁻¹ as temperature increases from 300 to 500 °C, over a pressure range from 2.1 to 2.8 GPa, consistent with a positive temperature dependence. The concentration of Nb in a 20 wt% NaCl aqueous
fluid varies from 55 to 150 µg g\(^{-1}\) at 300 to 500 °C, over a pressure range from 1.8 to 6.4 GPa; however, there is no discernible temperature or pressure dependence. The Nb concentration in a 4 wt% NaF-bearing aqueous fluid increases from 180 to 910 µg g\(^{-1}\) as temperature increases from 300 to 500 °C over the pressure range 2.1 to 6.5 GPa. The data for the F-bearing fluid indicate that the Nb content of the fluid exhibits a dependence on temperature between 300 and 500 °C at ≥2 GPa, but there is no observed dependence on pressure. Together, the data demonstrate that the hydrothermal mobility of Nb is strongly controlled by the composition of the fluid, consistent with published data for Ti. At all experimental conditions, however, the concentration of Nb in the fluid is always lower than coexisting rutile, consistent with a role for rutile in moderating the Nb budget of arc rocks.

**INTRODUCTION**

Arc magmas bear a characteristic geochemical trace element signature consisting of a depletion of high field strength elements (HFSE) and enrichment in large ion lithophile elements (LILE) and light rare earth elements (LREE) relative to mid-ocean ridge basalts (Gill, 1981; Hawkesworth et al., 1991). Three working hypotheses have been developed to explain the geochemical signature of arc magmas. The first hypothesis is that ascending aqueous fluids from the slab are enriched in LILE and LREE, relative to HFSE, and thus transfer this signature to partial melts produced in the mantle. This hypothesis suggests that mineral phases (e.g., clinopyroxene) in the mantle control the HFSE budget of mantle-derived silicate melt (Hawkesworth, 1993a,b; Kelemen et al., 1990; Foley et al., 2000, Audétat and Keppler, 2005).

The second hypothesis is that melt extraction from the mantle at a back-arc spreading center depletes the mantle in HFSE prior to its interaction with slab-derived fluid at the base of the arc volcano plumbing system (McCulloch and Gamble, 1991; Woodhead et al., 1993). This
hypothesis requires the mantle wedge to be re-fertilized by fluids during melt extraction. The
downward motion of the subducted slab drags this depleted mantle material into the mantle
wedge above the slab, yielding a strong depletion of HFSE during subsequent partial melting of
the depleted mantle.

The third and most widely accepted hypothesis is that specific minerals in the subducted slab
retain the HFSE during slab dehydration; for example, rutile moderates Nb and Ta, and zircon
moderates Zr and Hf partitioning of the fluids that may ascend into the mantle (Saunders et al.,
The resulting trace element abundance patterns are preserved in arc magma owing to the very
low abundances of the HFSE in the mantle and slab-evolved fluid. Experimental studies of rutile
solubility in pure H₂O support this hypothesis (Audétat and Keppler, 2005; Tropper and
Manning, 2005). However, Manning (2004) emphasized that slab-derived fluids are not pure
H₂O, but rather contain significant amounts (i.e., up to and exceeding 10 wt% dissolved solutes)
of alkalis (Na, K), halogens (Cl, F) and aluminosilicate components (i.e., Si, Al). Experimental
data generated at 0.5-2 GPa and 700-1100 °C demonstrate that the addition of these solutes to
aqueous fluid increases the solubility of pure rutile in the fluid by several orders of magnitude
relative to pure water (Audétat and Keppler, 2005; Antignano and Manning, 2008; Manning et
al., 2008; Rapp et al., 2010; Hayden and Manning, 2011). For example, at 800 °C and 1 GPa, the
solubility of pure rutile in aqueous fluid increases from 18 ± 5 µg g⁻¹ Ti in pure water to 152 ± 5
µg g⁻¹ Ti in aqueous fluid that contains 3.162 – 2.423 wt% dissolved silicate (Antignano and
Manning, 2008). Rapp et al. (2010) reported that at 800 °C and 0.5 GPa, the solubility of pure
rutile in aqueous fluid increased from 212 ± 18 µg g⁻¹ Ti in pure water to 11,912 µg g⁻¹ Ti in fluid
that contains 10 wt% dissolved NaF. These experimental data evince that the solubility of pure
rutile in aqueous fluid varies with fluid chemistry. However, existing experimental data do not overlap with the pressure-temperature paths for subduction zones (Figure 1; Hacker, 2008) and require extrapolation when applied to the conditions of fluid evolution during prograde metamorphic devolatilization, which begins in the forearc at temperatures as low as 300 °C (cf. Bebout et al., 1999; Hacker, 2008). Notably, all of the aforementioned studies used the solubility of pure rutile in aqueous fluid as a proxy to predict the fluid mobility of all HFSE. It has been shown that this may be appropriate for Zr (Kelemen et al., 1990). However, Jenner et al. (1994) reported much higher rutile / tonalite melt partition coefficients for Nb \( (D_{\text{Nb}}) = 52.6 \) and Ta \( (D_{\text{Ta}} = 99.5) \) than for Zr \( (D_{\text{Zr}} = 4.76) \), indicating the potential error of inferring the mobility of Nb and Ta based on Ti.

The enhanced fluid compatibility of Ti in complex aqueous solutions suggests that Nb may be dissolved and transported in such fluids. There is an absence of data that constrain the mobility of HFSE such as Nb in aqueous fluid. Brenan et al. (1994) and Stalder et al. (1998) experimentally investigated the partitioning of Nb between rutile and aqueous fluid at 1-5 GPa and 900-1100 °C. These pressures overlap with those in the forearc to subarc region, but the temperatures are higher by several hundred degrees then those obtained during subduction (Figure 1). The experimental assemblage of Stalder et al. (1998) contained only pure H₂O, whereas Brenan et al. (1994) added 3 wt% SiO₂, in addition to HCl, NaCl and Al, to the fluid in three separate experiments. Brenan et al. (1994) reported that the addition of NaCl, HCl and Al to the fluid-rutile assemblage affected the value of \( D_{\text{Nb}} \). For example, at 900 °C and 1 GPa, the value of \( D_{\text{Nb}} \) (± 1σ) was 193 ± 44 for water with 3 wt% SiO₂, and increased to 217 ± 72 with the addition of 1m HCl-fluid; 325 ± 107 with the addition of 1m NaCl-fluid; and 484 ± 140 for fluid that contained 300 µg g⁻¹ Al. Similar results were reported for Ta (Brenan et al., 1994).
These results indicate that the compatibility of HFSE in pure H₂O and dilute aqueous fluid in equilibrium with rutile is generally quite low, and that the partitioning of HFSE from rutile to aqueous fluid actually decreases with increasing complexity of the aqueous fluid. However, this latter finding is not consistent with the solubility data for pure rutile in complex aqueous fluids as mentioned above (Audétat and Keppler, 2005; Antignano and Manning, 2008; Manning et al., 2008; Rapp et al., 2010; Hayden and Manning, 2011).

To quantitatively evaluate the fluid mobility of HFSE in light of the more recent experimental studies mentioned above that support a strong role of fluid chemistry in dissolving rutile (i.e., up to 1 wt% Ti in the fluid), and presumably other HFSE, there is the critical need to assess experimentally the effects of prograde metamorphic devolatilization and the relationship between fluid chemistry and trace element mobility at pressures and temperatures where fluids evolve during subduction (Figure 1). In this study, new experimental data are presented that quantify the mobility of Nb in rutile-saturated NaCl- and NaF-bearing aqueous fluids at 1 to 6.5 GPa and temperatures of 300 to 800 °C, pressure and temperature conditions appropriate for prograde devolatilization paths in cold to hot subduction zones (Figure 1).

EXPERIMENTAL METHODS

Rutile Synthesis and Characterization

The synthetic Nb-doped rutile (Nb-TiO₂) crystals used in this study were prepared following the method described in Hanchar et al. (2001). High-purity TiO₂ and Nb₂O₅ were weighed to achieve 6 mol% TiO₂ and 0.09 mol% Nb₂O₅, then mixed 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: 84 mol% MoO₃ and 10 mol% Li₂MoO₄; and the remaining TiO₂ - Nb₂O₅ mixture, mentioned above,
then allowed to dry. The mixture was then transferred to an HNO₃-cleaned 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. Using a type S control thermocouple, the temperature in the hot spot was measured to be stable within ±5 °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 done to ensure that the rutile structure was obtained and not the TiO₂ polymorphs brookite or anatase.

The concentrations of Nb, Ti and Mo in the starting rutile were quantified by using wavelength dispersive spectroscopy on a Cameca SX100 electron probe microanalyzer (EPMA) and laser ablation inductively coupled mass spectroscopy (LA-ICP-MS). For EMPA, a beam current of 50 nA (calibration and analysis) and an accelerating voltage of 15 kV were used. Counting times (30 s at the peak) yielded detection limits for Nb, Ti, and Mo of approximately 330, 590 and 300 µg g⁻¹, respectively. Standard ZAF techniques were used for the matrix corrections. The standards used included pure rutile (TiO₂), Nb₂O₅, and pure Mo metal. A different crystal and detector combination was used for each element: LIF for Ti; and LPET for Nb and Mo. Each crystal was imaged by using back-scattered electrons (BSE), and then a EMPA line traverse across the length of the sample was done to evaluate chemical homogeneity. The concentrations of Nb and Mo of starting crystals were 0.95 ± 0.1 wt%, and 0.02 ± 0.03 wt%, respectively; Mo is sourced from the flux used during mineral synthesis. Some crystals displayed zoning in BSE images, and for these crystals an analytical line traverse from the rim to the core of the crystal. The beam spot measured 5 µm and the step size for the rim to core line traverse...
was 2 µm (Figure 2 a, b). All totals summed to 100 ± 1%. Depth profiles of the Nb concentration through starting (Figure 2c, d, Figure 3a) and piston cylinder run-product (Figure 3b) crystals were also obtained by using LA-ICP-MS, by drilling perpendicular to crystal growth surfaces and integrating single pulses individually. The ablation rate of a single pulse amounted to about 0.10 µm depth. The LA-ICP-MS analyses were performed following the analytical method outlined in Pettke (2006) and Pettke et al. (2012). The data indicate that the starting crystals contain an average of 1.03 ± 0.2 wt% Nb, which is consistent with the EMPA results. The LA-ICP-MS data also indicate that some starting crystals have a rim (of several µm thickness) that is enriched in Nb and Mo (Figures 2c, d and 3a). For example, the LA-ICP-MS depth profile shown in Figure 2d indicates that the concentration of Nb at the rim of this starting rutile crystal was ~8 wt%, and decreased to ~1 wt% over a distance of 2 µm into the center of the crystal. This Nb-enriched rim likely reflects either a quench-effect during synthesis, or the kinetics of Nb incorporation into rutile during synthesis.

**SXRF experiments**

The HDAC (Bassett et al., 1993) used in the current study was equipped with two opposing 500 or 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 us to maintain temperature stability to ~5 °C. The HDAC was calibrated up to 800 °C by observing the melting point or phase transition temperature of NaNO₃, CsCl, and NaCl, and measured temperatures were systematically lower by ~0.85% relative to the actual melting point or phase transition (Kerrigan, 2011). A 1% H₂-Ar gas mixture flowed constantly through the HDAC.
during the measurements to prevent corrosion of the diamonds and the heaters.

A gold-lined rhenium gasket was pre-indentied to a thickness of ~120 µm and a hole of
200 µm or 400 µm diameter was drilled for 500 and 800 µm diamond culets, respectively. A Nb-
rutile crystal, measuring approximately 40x40x20 µm by using a optical microscope, was loaded
into the sample chamber. Fluids were prepared by adding known masses of NaCl and NaF to
deionized, lab grade water in calibrated volumetric flasks to make either 10 wt% NaCl, 20 wt%
NaCl or 4 wt% NaF aqueous solution. The fluid was then added by using a micro syringe and the
HDAC was immediately sealed and pressurized to ~0.5 GPa. There was no evaporation during
loading and no observed halite precipitation during any of the experiment runs; hence, the
salinity of the added fluid represents that added to the cell. Further, as described below, an on-
line microscope was used to make visual observations of the experimental sample chamber
during runs, and the presence of a salt crystal was never detected. The phase assemblage, based
on visual observation, consisted only of fluid and rutile crystal. Thus, we are confident that the
salinity of the fluid at all pressure-temperature conditions was equal to the salinity of the fluid
added to the sample chamber.

The SXRF experiments were done 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 35x50 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 projected 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 for pure Nb metal. There was no Nb contamination from any component of the HDAC, which was confirmed by SXRF analyses of an empty cell.

SXRF spectra of the empty HDAC (0 µg g$^{-1}$ Nb) and the same HDAC containing standard solutions of 300, and 1000 µg g$^{-1}$ Nb were collected before each experimental run and used to build a calibration curve to determine the Nb concentration of experimental fluids, similar to the process described in Tanis et al. (2012) and shown in Figure 5. The Nb-rutile crystal position was found visually by using an online optical microscope and confirmed by SXRF. The beam was then positioned ≥50 µm away from the crystal and the HDAC was rotated 5° to ensure no signal contamination from the crystal. The HDAC was heated from room temperature to 300 °C, and the pressure inside the sample chamber was determined by using XRD patterns from the Au gasket liner. The XRD data were collected by using a MAR 165 CCD detector placed in the forward scattering direction, and pressure was monitored throughout the run by collecting XRD patterns from the Au gasket liner. The variation of the Au lattice parameters change with pressure and, thus, act as an internal pressure standard. The XRD patterns showed no evidence of grain growth and displayed well-defined Debye rings at all temperatures. 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 diamonds used in the cell assembly did not contain any modifications, such as a recess for SXRF collection (e.g. Schmidt and Rickers, 2003) which allowed measurements to be
made at pressures higher than published studies in the HDAC and to collect SXRF data in a 170°
backscattering geometry.

Fluorescence spectra for Nb were collected iteratively in 300 s intervals. Steady state was
assessed by evaluating the time-dependence of the fluorescence signal. Once the Nb peak, at a
unique pressure and temperature condition, became time-invariant, it was interpreted to reflect
the attainment of steady-state conditions. This took approximately 30–40 minutes at each unique
pressure-temperature point. The time to reach steady state is consistent with observations
reported by Sanchez-Valle et al. (2003), Schmidt et al. (2007), Manning et al. (2008), and Louvel
et al. (2014). Once steady-state conditions were achieved, spectra were collected in 300 s
intervals for ~3 h. The temperature was then increased to 400 °C, and subsequently to 500 °C,
and the data collection procedure was repeated at each temperature (Figure 6). Steady state
conditions were further assessed after the experiment by looking at the integrated spectra for
each time step. Only experiments that contained an average standard deviation over the entire
time range of less than 15% were considered; afterwards, a fit of the data was made to ensure
that the R² value was <0.1, essentially time invariant. For example, in Figure 6, the integrated,
unnormalized, raw data as a function of time for Runs 20110804 (top) and 20110805 (bottom)
are shown. During Run 20110804, at 300 °C there were large variations (average standard
deviation >12%) in the signal, due to major beam fluctuations, therefore only 300°C data in the
later time frame (where R² of the fit <0.02) was used.

The experimental run conditions and results are reported in Table 1. Increasing the
temperature of the HDAC results in a change in the pressure of the sample chamber, owing to
relaxation of the Re-Au gasket. Pressure at each run temperature was quantified by using XRD
patterns of Au as previously described, which allowed us to monitor changes in pressure before
and after each sequence of fluorescence data were collected. The reported pressure is the average of starting and final pressure. The fluorescence spectra from the standard solutions (Figure 5) and high P-T experiments were separately summed, and normalized to the intensity of the incoming beam. Peak intensities were corrected for absorption in the fluid using the fluid composition and density, following the procedure described in Sanchez-Valle et al. (2003), Schmidt et al. (2007), Manning et al. (2008), and Louvel et al. (2014). A linear background was subtracted and the area of the Nb fluorescence peak was fit and integrated by using the program Fityk (Wojdyr, 2010). The integrated peak area was then normalized to time (Tanis et al., 2012). 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 EOS data for NaF-bearing aqueous fluid; hence, the EOS of a 4 wt% NaCl- H2O fluid was used as a proxy for the NaF-bearing aqueous fluid. Uncertainties for the Nb concentration of the fluids measured in the SXRF experiments at high pressures and temperatures were calculated based on the fitting errors of the summed spectra, and also include propagating the fitting errors from the standard calibration. The iterative nature of the SXRF experimental technique (i.e., loading one fluid-crystal assemblage and collecting fluorescence data at multiple P-T points during a single run) combined with the small size of the loaded crystal, prevented recovering and analyzing the rutile crystal from each unique P-T condition. Thus, partition coefficients for Nb between fluid and rutile were not determined. The experimentally determined diffusion coefficient of Nb in rutile ranges from D = 5.6 x10^{-19} to 3 x 10^{-21} m^2/s at 800°C (Sheppard et al., 2007; Marschall et al., 2013), and extrapolation indicates that Nb is effectively immobile in rutile at the experimental conditions of this study. Over the timescales of the experiments (t<10 hrs) the diffusion distance...
would be less than 0.14 µm. Therefore, it can be assumed that the Nb:Ti ratio of the rutile did not change during the experiments, and that the Nb concentration of the fluid is controlled by rutile solubility. However, the presence of Nb-enriched rims on rutile crystals disallowed the use of Nb/Ti ratios of the starting crystals in order to use the measured Nb content of the fluid to calculate apparent Ti values of the fluid. The data reported in the present study for the concentration of Nb in NaCl- and NaF-aqueous fluids demonstrate the strong effect of dissolved halogens on increasing the Nb concentration of aqueous fluid.

**SXRF Mapping**

For experimental run 20130205 (4 wt% NaF, 300-600 °C, 2.13-3.07 GPa), data were collected by using a SXRF mapping technique. The cell was positioned in direct line of the detector (versus angled to hide the crystal signal) to maximize Nb count rate. The position of the HDAC was moved in steps of 25 µm in the x (horizontal) and y (vertical) directions and SXRF spectra were taken at each x-y position, as well as, the values of the incoming and outgoing beam intensity. Figures 6a and b demonstrate how the sample chamber was mapped in 2-D (x and y position, where the color scale is beam intensity) and in 3-D (x and y position, where the z-axis and color scale are intensity), respectively. Figures 6c and d are similar 2-D and 3-D figures that show how the spatial position of the Nb-rutile crystal was constrained. The concentration of Nb in the fluid was determined by summing and integrating the normalized spectra, significantly away (50-75 µm) from the Nb-rutile crystal spectra. A SXRF map of the HDAC containing 300 and 600 µg g⁻¹ Nb standard were also collected for calibration.

**Piston Cylinder Mass Loss Experiments**

The mass loss experiments were done in a Griggs-type modified piston-cylinder apparatus. Piston cylinder run conditions and results are provided in Table 2. Temperature
gradients were modeled by using the “CellAssembly” thermal modeling program (Hernlund et al., 2006), and confirmed by using two thermocouples placed on each side of the capsule. The temperature gradient was a maximum of 5 °C across all dimensions (~7 mm long, 5 mm outer diameter) of the capsule. Confining pressure on the sample was derived from the oil pressure in the piston cylinder ram, which was measured with an Omegadyne pressure transducer. The nominal sample pressure was calculated by dividing the load exerted by the ram by the area of the confining pressure piston. The nominal sample pressure can deviate from the actual pressure by up to 10% owing to frictional effects (Bose and Ganguly, 1995; Burnley and Getting, 2012), which are more pronounced at low pressure. The experimental charges each contained a single crystal of Nb-rutile and 30 µg fluid in a platinum capsule. The capsule design was made by cutting a ~7 mm length piece of Pt tubing and welding a circular disk “lid” onto the bottom and top (after the crystal and fluid were loaded). The capsule was weighed before and after welding to ensure no fluid was lost. The starting crystal was weighed 4 times by using a Mettler XP26 DeltaRange balance, and the values averaged for accuracy, before being loaded into the capsule. The hot piston-in technique of Manning and Boettcher (1994) was used to cold compress to ~50 MPa and then heating and compressing in alternating increments to minimize compression and expansion of the capsule relative to other sample assembly parts. Conditions were maintained for ≥8 hours once the desired pressure and temperature were attained. The sample was quenched by shutting off power to the apparatus, which results in a temperature drop to <30 °C in <30 s. This minimizes, if not eliminates, back-reaction between the crystal and fluid during quench (Antignano and Manning, 2008). After quench, the capsule was cleaned and weighed, then punctured and dried at 120 °C for 1 hour. The capsule was weighed again, opened, and the crystal was removed. Comparison of the total capsule weight before and after the experiments
showed no fluid was lost during the experiment. The crystal was cleaned with isopropanol, weighed 4 times, and then averaged to determine the mass loss during the experiment.

Piston cylinder run products included the partially dissolved starting crystal and fine-grained quench “roe” crystals (ca. 20 µm diameter, run 20130522), consistent with crystals that formed during quench (cf. Antignano and Manning, 2008). In experiment 20130527, broken crystal fragments (ca. 0.5 mm) were recovered along with the primary crystal. Final concentrations of Nb and Mo of rutile crystals recovered from the mass-loss experiments were determined by using EMPA and LA-ICP-MS, as previously described (Table 2). The EMPA and LA-ICP-MS (Figure 3b) results demonstrate that run-product crystals were homogeneous with respect to Nb and Ti, and contained no detectable Mo. Uncertainties for Nb concentrations in the fluid from the mass loss experiments reflect propagation of weighing errors, the analytical error from the EMPA and LA-ICP-MS analysis, as well as consideration of the thin Nb-enriched rim on the starting rutile crystal. To account for the starting crystal containing a Nb-enriched rim, a minimum value of mass loss was calculated by using the final (bulk) Nb concentration of the recovered rutile crystal from each experiment, determined by using LA-ICP-MS, and a maximum value assuming 8 wt% Nb (Table 2). For example, in experiment 20130314 the mass loss is 24 µg. If a spherical crystal is assumed, this corresponds to a radius difference of ~5 µm, which is on the order of the rim distance for some of the starting crystals. Therefore, it can be assumed that if the crystal is homogeneous, the minimum amount of Nb dissolved into the fluid based on the final composition (0.9 wt%) is 11 µg g⁻¹. The maximum amount of Nb dissolved into the fluid if 8 wt% Nb is assumed, is 95 µg g⁻¹.

RESULTS
The concentration data for Nb in a 10 wt% NaCl - H$_2$O fluid, 20 wt% NaCl - H$_2$O fluid, and 4 wt% NaF - H$_2$O fluid are provided in Tables 1 (HDAC) and 2 (piston cylinder), respectively. Niobium concentrations in the fluid as a function of: a) temperature; b) pressure; and c) density are presented in Figure 7. Lines in Figure 7 are to provide qualitative insight to the general trends of the data and are not statistical best fits.

Niobium concentrations in 10 wt% NaCl-bearing aqueous fluid at 2.1-2.8 GPa range from 6 µg g$^{-1}$ at 300 °C to 11 µg g$^{-1}$ at 500 °C (Table 1; Figure 7), and at 1 GPa from 11-95 µg g$^{-1}$ (minimum to maximum calculated owing to Nb-enriched rims) at 700 °C, to 80-600 µg g$^{-1}$ (minimum to maximum) at 800 °C (Table 2; Figure 7a). The data indicate a positive temperature dependence for the concentration of Nb in the 10 wt% NaCl-bearing aqueous fluid, and a negative pressure and density dependence (Figure 7). The concentration of Nb in a 20 wt% NaCl-bearing aqueous fluid over the temperature range of 300 to 600 °C varies from 55 to 150 µg g$^{-1}$, which is an increase of 2 to 3 times that of the 10 wt% NaCl-bearing fluid. There is no apparent temperature, pressure, or density dependence observed for the 20 wt% NaCl-bearing aqueous fluid. Visual observation of the sample chamber for the experiments with 20 wt% NaCl-bearing fluid indicated that only fluid and Nb-rutile were present; i.e., no salt crystal was observed that could have modified the salinity of the fluid phase. The Nb concentration of the 4 wt% NaF-bearing fluid ranges from 180 µg g$^{-1}$ to 980 µg g$^{-1}$ from 300 °C and 2.13 GPa to 500 °C and 3.07 GPa, and is 220-1715 µgg$^{-1}$ (minimum to maximum) at 700 °C and 1 GPa. Thus, the addition of NaF to the aqueous fluid increases the concentration of Nb in the fluid by 1 to 2 orders of magnitude relative to the addition of NaCl. The concentration of Nb in the 4 wt% NaF-bearing fluid exhibits a positive temperature dependence between 300 and 500 °C at >2 GPa, and no pressure or density dependence. Overall, the new data presented here indicate that the
concentration of Nb and rutile solubility in saline fluids is strongly dependent on the nature and concentration of the predominant anion (i.e., Cl vs. F) of the fluid.

**DISCUSSION**

In Figure 7, the experimentally determined Nb concentrations of rutile-saturated aqueous fluids from two published studies are plotted with data from the current study for comparison. Stalder et al. (1998) equilibrated a solid assemblage of clinopyroxene and rutile with pure H$_2$O at 5 GPa and 1000 °C; the clinopyroxene:rutile ratio was 9:1 and 1:1 in the two experiments. They reported that the fluid contained 10.9 µg g$^{-1}$ and 37.6 µg g$^{-1}$ in the two assemblages, respectively, and that the value of $D_{Nb}^{rutil/melt}$ decreased from 0.12 to 0.05, respectively. Brenan et al. (1994) equilibrated rutile and aqueous fluid at 1 and 2 GPa and 900 and 1100 °C. The experimental fluids in that study all contained ~3 wt% dissolved SiO$_2$, and varied from pure SiO$_2$-bearing H$_2$O, to 3.6 wt% HCl-bearing H$_2$O, to 5.8 wt% NaCl-bearing H$_2$O, and one experiment with ~300 µg g$^{-1}$ dissolved Al. Their data indicate that the concentration of Nb in the fluid phase varies by one order of magnitude, from ~20 to 300 µg g$^{-1}$, for pure H$_2$O, and was ~30 µg g$^{-1}$ for a 5.8 wt% NaCl-bearing fluid.

The data for pure H$_2$O from Brenan et al. (1994) and Stalder et al. (1998) indicate that the concentration of Nb in rutile-saturated H$_2$O exhibits a positive temperature dependence over the range 900 to 1100 °C (Figure 7a). This is consistent with the new data presented here for the concentration of Nb in a 10 wt% NaCl- and 4 wt% NaF-bearing aqueous fluid (Figure 7a). These observations suggest that temperature has a strong effect on (Ti, Nb)-Cl and (Ti, Nb)-F complexes at moderate to high temperature. However, at higher dissolved salt concentrations, the anion abundance dominates over temperature. This is demonstrated by comparing the data for pure H$_2$O to the data for 10 and 20 wt% NaCl-bearing aqueous fluids. The apparent temperature
dependence decreases as the salinity of the fluid increases, until there is an absence of, or at best a very weak, temperature dependence for the 20 wt% NaCl-bearing aqueous fluid. The reduced effect of temperature on the concentration of Nb in fluid as the salinity increases from 10 to 20 wt% NaCl most likely reflects the effect of salting out, wherein the concentration of a sparingly soluble metal in aqueous fluid is effected by the strong hydration complexes that form between H₂O and dissociated Na⁺, Cl⁻ and associated NaCl, as the ionic strength of the fluid increases. These hydration complexes effectively reduce the amount of free H₂O molecules available to solvate neutral Nb-Cl complexes. The temperature dependence of Nb in 4 wt% NaF-bearing fluid is also not as pronounced as in pure water or 10 wt% NaCl. It is possible that at lower concentrations of dissolved NaF in aqueous fluid, the relative effect of temperature may be stronger than observed in the present study. These observations are consistent with data in published studies of metal dissolution in NaCl-bearing aqueous fluid (e.g., Hanley et al., 2005), as well as studies of SiO₂ and TiO₂ solubility (Ayers and Watson, 1993; Manning and Boettcher, 1994), which have determined experimentally that the influence of temperature on mineral solubility was negligible compared to the effects of fluid composition (Knauss et al., 2001; Rapp et al., 2010; and Wu and Konga, 2013).

The data from Brenan et al. (1994) for the concentration of Nb in pure H₂O also indicate that the concentration of Nb in the fluid decreases with pressure (Figure 7b) and density (Figure 7c). This is consistent with the results presented here for the concentration of Nb in 10 wt% NaCl-bearing aqueous fluid. This suggests that the stability of the (Ti, Nb)-Cl complex(es) in the fluid decreases with pressure – either in total or by replacement of the dominant complex at low pressure by a different complex at high pressure, which does not complex with Ti or Nb as strongly. The data for 4 wt% NaF- and 20wt% NaCl-bearing fluids do not exhibit any pressure
dependence. This can be rationalized as a pressure-invariant stability of (Ti, Nb)-halogen complexes. However, it does also imply that these complexes may be different than those dominant in the 10 wt% NaCl-bearing fluid, or that the strong hydration complexes between H$_2$O and halogens effectively reduce the ability of the fluid to solvate neutral Nb-halogen complexes at higher halogen concentrations. The absence of a temperature dependence of Nb-solubility for the 20 wt% NaCl-bearing fluid and the weak dependence of the solubility on the 4 wt% NaF-bearing fluid are consistent with this. The new experimental data presented here demonstrate that at temperatures of 300 to 800 °C and pressures $\geq$ 1 GPa, the addition of NaCl and NaF to rutile-saturated aqueous fluid increases the concentration of Nb in the fluid to values higher than predicted from down-temperature extrapolations of experimental data for pure H$_2$O (Figure 7a). These new results for Nb are consistent with Rapp et al. (2010), who reported that the solubility of pure rutile in aqueous fluid, at 800-1000 °C and 0.5 GPa, increased by approximately two orders of magnitude in aqueous fluid that contained 10 wt% NaCl and 10 wt% NaF, relative to pure H$_2$O. The new data suggest that Ti and Nb are complexed as (Ti, Nb)-chloride and (Ti, Nb)-fluoride in the NaCl-bearing and NaF-bearing experimental fluids, respectively. The determination that NaF enhances the solubility of rutile in aqueous fluid is consistent with predictions based on hard acid – soft base (HASB) considerations (Pearson, 1963), and observations from natural systems that Ti and Nb are hydrothermally transported during the evolution of ore deposits associated with alkaline magmatic systems (e.g., carbonatites; Singer, 1986; Verplanck and Van Gosen, 2011).

Timofeev et al. (2014) measured experimentally the solubility of Nb-oxide in F-bearing aqueous fluids at temperatures of 150 to 250°C and saturated water vapor pressure (SWVP). The activity of fluoride ($a(F)$) and pH were varied from $\sim10^5$ to $10^{-2}$ mF and 2.1 to 2.4, respectively.
They reported that at low $a(F)$, the concentration of Nb in the fluid was pH dependent, interpreted to indicate that Nb-fluoride complexes are present in the fluid. The concentration of Nb in the fluid increased with increasing $a(F)$, independent of pH, which was interpreted to indicate that Nb in the fluid was present as a hydroxyfluoride complex. The relative strength of Nb-halide complexes was assessed computationally by Siegbahn (1993) who performed ab initio calculations to constrain the binding energies of Nb-halide complexes. Siegbahn (1993) reported that the binding energy of Nb-F (135 kcal/mol; bond distance of 1.97 Å) is greater than Nb-Cl (101 kcal/mol; bond distance of 2.46 Å), which is consistent with the measured increase of Nb in the F-bearing aqueous fluid relative to the Cl-bearing aqueous fluid in the present study. In general, binding energies for metal-halide complexes increase in the order Y > Zr > Nb > Mo > Tc > Ru > Rh > Pd, which is also consistent with findings for the strongly enhanced concentration of Y in Cl-bearing aqueous fluids at pressure-temperature conditions similar to those in the present study (Tanis et al., 2012). Siegbahn (1993) found that the increased strength of Nb-F relative to Nb-Cl is related to the interaction between the $4d_\pi$ orbital and the lone pairs of halides, which yields a symmetry that is conducive to attraction by electron donation. The consistency among experimental data sets reported by Timofeev et al. (2014) and Rapp et al. (2010), as well as the ab initio results reported by Siegbahn (1993), with the new data presented in this study, seems to convincingly demonstrate that Nb is fluid-mobile as a Nb-halide complex in saline aqueous fluids.

**IMPLICATIONS**

The new data presented in this study have implications for the mobility of HFSE in aqueous fluids evolved during prograde metamorphic dehydration reactions that occur during subduction. Brouwer et al. (2012) reported an order of magnitude variation in the concentration
of Nb in eclogites from the Franciscan Complex (California) and the Monviso Complex (Western Alps Lago Superiore region). These exhumed terranes equilibrated at a pressure of 1.05 GPa and 600 and 500 °C, respectively. Brouwer et al. (2012) invoked the composition of the fluid and degree of fluid-rock interaction as the cause of the order-of-magnitude variation in measured Nb concentrations of the residual rock. The new data presented here indicate that moderately saline aqueous fluid could affect the variability observed in the Franciscan and Monviso Complexes.

Spandler et al. (2011) reported that high-pressure veins that cut through eclogite facies (~2 GPa, ~600 ºC) Fe-Ti metagabbros in the Monviso Lago Superiore region record subsolidus influx of multiple generations of internally- and externally-derived fluid. The veins contain rutile, garnet, talc and accessory ziron, and the authors reported that rutile grains exhibit zonation of Nb similar to that displayed by other trace elements (e.g., Cr). They also reported extreme Nb enrichment of other minerals such as high-Cr omphacite and garnet, which were assumed to co-precipitate from aqueous fluid. They concluded that the composition of the externally derived fluid responsible for the precipitation of these Cr-rich and Nb-bearing vein minerals (e.g., omphacite, garnet and rutile) was not only rich in Cr, but also rich in Ni, B, As, Sb and LREE/MREE. The authors noted that Nb might also have been enriched in the fluid phase, although they did not rule out that crystal-chemical effects might dominate Nb incorporation into rutile. Dehydration of serpentinite was invoked as the most plausible source of fluid that would provide multiple episodes of fluid influx and produce the chemistry of the veins (Spandler et al., 2011). Serpentinite dehydration can liberate up to 90% of Cl, more than 80% of B and about 50% of Sr from the serpentinite into the fluid, and such fluids can be enriched in Nb, Zr, and LREE (Spandler et al., 2009; Kodolányi and Pettke, 2011). While Nb and other elements such as...
Ti, Zr, Hf, Cr and Ni, are generally regarded as fluid-immobile in subduction zone environments, Spandler et al. (2011) pointed out that the chemical signatures of the veins at Monviso require fluid mobility of Nb and these other elements. Elevated Cl abundances in aqueous fluid would favor scavenging and transport of Nb, as indicated by the data presented in the current study. In fact, high salinity fluid inclusions have been reported for the Monviso gabbros, consistent with the presence of a saline fluid during prograde metamorphism (Barnicoat and Cartwright, 1997; Philippot et al., 1998).

Gao et al. (2007) reported the presence of rutile crystals in hydrothermal veins located at the contact between blueschist and eclogite in exhumed rocks in the Tian Shan complex, northwest China. These hydrothermal veins were interpreted by Gao et al. (2007) as evidence for local (i.e., cm to m) transport of HFSE in aqueous fluid evolved during prograde metamorphic dehydration. The eclogite records conditions of ~1.9 GPa and 500 to 600 °C, and the vein records conditions of 1.9 GPa and 490 to 580 °C. These authors reported the presence of aqueous fluid inclusions with salinities of 1.57 to 4.49 wt% NaCl equivalent, and concluded that Nb, Ti and Ta were scavenged by an aqueous fluid during the dehydration of blueschist to eclogite. The new experimental data presented here indicate that Nb would be mobile in a fluid of this composition. Gao et al. (2007) reported that fluid evolution and migration fractionated Nb, Ti and Ta from Zr and Hf, which were sequestered by titanite. Gao et al. (2007) reported that rutile and apatite co-precipitated in the hydrothermal veins. Precipitation of Cl- and F-bearing apatite would result in rapid depletion of these halogens in the fluid, resulting in destabilization of HFSE-fluorine and/or HFSE-chlorine complexes in the fluid. In turn, this would result in precipitation of rutile, which would sequester Nb and other HFSE from the fluid.

The sum of observations from natural and experimental systems demonstrate that HFSE
are mobile in aqueous fluid, and that hydrothermal transport is a function of fluid composition, temperature, and for fluids with ≤10 wt% NaCl equivalent, also dependent on pressure and fluid density. Even in assemblages where rutile is a stable residual phase during prograde fluid evolution, effective mass transfer of Nb to the fluid phase can occur. This was demonstrated by Kessel et al. (2005) who equilibrated aqueous fluid and basaltic eclogite at 4 and 6 GPa and 700 to 1200 °C, and reported that $D_{\text{Nb}}^{\text{fluid/solid}}$ varies by less than a factor of about 5 between rutile-absent and rutile-present assemblages. Kessel et al. (2005) reported that the key parameter, at a given pressure, influencing the fluid mobility of the HFSE in aqueous subcritical fluids, melts and supercritical liquids is temperature. The new data reported here suggest that the findings of Kessel et al. (2005) could represent conservative behavior, and that by adding F and Cl to the aqueous fluid, the mobility of Nb (and thus most of, if not all HFSE) is increased (Figure 7), consistent with observations from exhumed terranes.
ACKNOWLEDGEMENTS

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fluid inclusions by laser ablation single and multiple collector ICP-MS. Ore Geology Reviews, 44, 10-38.


Figure 1. The experimental P-T conditions for the current study are plotted with respect to subduction paths for cold and hot subduction (cf. Hacker et al., 2008). The P-T conditions for published experimental data for the solubility of pure rutile in pure H₂O (circles, Tropper and Manning, 2005; Audétat and Kepller, 2005; Antignano and Manning 2008; Rapp et al., 2010), NaCl-aqueous fluids (triangles, Rapp et al., 2010) and NaF-aqueous fluids (diamonds, Rapp et al., 2010). The P-T conditions for studies of Nb partitioning between rutile and aqueous fluid and silicate melt are also plotted (pentagons; Brenan et al., 1994, Stalder et al., 1998, Foley et al., 2000).

Figure 2. EPMA-determined Nb (squares) and Mo (triangles) concentrations (wt%) of polished, randomly selected starting crystals as a function of distance from the rim towards the center of the crystal (a, b), and LA-ICP-MS depth profiles into the crystals perpendicular to the growth surface (c, d). The error is within the size of the symbol.

Figure 3. The LA-ICP-MS depth profiles of ⁴⁹Ti (blue circles) and ⁹³Nb (red squares) concentrations in the (a) starting crystal and (b) run-product crystal from the piston cylinder-mass loss experiment 20130314. Gas background is measured for the first 30-40 seconds at which time the laser is turned on and used to ablate the crystal. The elevated Nb signal duration in (a) corresponds to several µm thickness ablated at the LA-ICP-MS conditions employed.

Figure 4. The normalized experimental spectra of the 1000 µg g⁻¹ Nb standard.
Figure 5. The Nb standard calibration. The normalized integrated peak area of SXRF spectra from the 300 and 1000 µg g⁻¹ Nb standard plotted against concentration to demonstrate linearity of the calibration.

Figure 6. The integrated, unnormalized, raw data as a function of time for Runs 20110804 (top) and 20110805 (bottom) are shown. Experimental data that contained an average standard deviation over the entire time range of less then 15% were used in further analysis. A fit of the data was made to ensure that the R² value was <0.1, essentially time invariant. During Run 20110804, at 300 °C there were large variations (average standard deviation >12%) in the signal, due to major beam fluctuations, therefore only 300°C data in the later time frame (where R² of the fit <0.02) was used.

SXRF maps of the sample chamber. a) (top left) and b) (top right) 2-D and 3-D, respectively, false-color maps of x-ray beam intensity that passed through sample chamber. c) (bottom left) and d) (bottom right) 2-D and 3-D false-color maps, respectively, of the Nb signal intensity from the sample chamber. The color bar is based on beam (for a and b) or Nb intensity (for c and d). Red colors are high intensity and purple colors are low intensity. The scale is divided into 4000 count increments for beam intensity and 10 count increments for Nb intensity.

Figure 7. Nb concentrations in experimental aqueous fluids plotted as a function of (a) temperature, (b) pressure, and (c) fluid density. Also plotted are published data from Brenan et al., (1994) and Stalder et al., (1998). Uncertainties for Nb (µg g⁻¹) are discussed in the text. The
bars without symbols represent the piston cylinder data (1 GPa, 700 and 800 °C) minimum and
maximum Nb concentrations as described in the text.
Table 1: HDAC-SXRF experimental conditions and results

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Fluid Type (wt%)</th>
<th>Temperature (°C)</th>
<th>Pressure (GPa) (±1σ)</th>
<th>Fluid Density (g/cm³)</th>
<th>µg g⁻¹ Nb in the fluid (±1σ)ᵇᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>20110801</td>
<td>10% NaCl</td>
<td>300</td>
<td>2.10(0.1)</td>
<td>1.25</td>
<td>6(1)</td>
</tr>
<tr>
<td>20110801</td>
<td>10% NaCl</td>
<td>400</td>
<td>2.80(0.1)</td>
<td>1.28</td>
<td>8(1)</td>
</tr>
<tr>
<td>20110801</td>
<td>10% NaCl</td>
<td>500</td>
<td>2.80(0.1)</td>
<td>1.25</td>
<td>11(2)</td>
</tr>
<tr>
<td>20110804</td>
<td>20% NaCl</td>
<td>300</td>
<td>2.05(0.1)</td>
<td>1.38</td>
<td>140(20)</td>
</tr>
<tr>
<td>20110804</td>
<td>20% NaCl</td>
<td>400</td>
<td>2.62(0.1)</td>
<td>1.41</td>
<td>150(20)</td>
</tr>
<tr>
<td>20110804</td>
<td>20% NaCl</td>
<td>500</td>
<td>4.56(0.2)</td>
<td>1.54</td>
<td>150(20)</td>
</tr>
<tr>
<td>20110804</td>
<td>20% NaCl</td>
<td>600</td>
<td>6.36(0.2)</td>
<td>1.63</td>
<td>140(20)</td>
</tr>
<tr>
<td>20110805</td>
<td>20% NaCl</td>
<td>300</td>
<td>1.80(0.1)</td>
<td>1.21</td>
<td>75(7)</td>
</tr>
<tr>
<td>20110805</td>
<td>20% NaCl</td>
<td>400</td>
<td>2.60(0.1)</td>
<td>1.27</td>
<td>65(7)</td>
</tr>
<tr>
<td>20110805</td>
<td>20% NaCl</td>
<td>500</td>
<td>4.50(0.2)</td>
<td>1.38</td>
<td>55(7)</td>
</tr>
<tr>
<td>20120802</td>
<td>4% NaF</td>
<td>308</td>
<td>5.14(1.1)</td>
<td>1.50</td>
<td>190(25)</td>
</tr>
<tr>
<td>20120802</td>
<td>4% NaF</td>
<td>401</td>
<td>5.19(1.1)</td>
<td>1.49</td>
<td>560(65)</td>
</tr>
<tr>
<td>20120802</td>
<td>4% NaF</td>
<td>503</td>
<td>6.53(1.4)</td>
<td>1.54</td>
<td>700(70)</td>
</tr>
<tr>
<td>20130202</td>
<td>4% NaF</td>
<td>300</td>
<td>3.21(0.4)</td>
<td>1.39</td>
<td>200(40)</td>
</tr>
<tr>
<td>20130202</td>
<td>4% NaF</td>
<td>400</td>
<td>3.48(1.0)</td>
<td>1.37</td>
<td>420(80)</td>
</tr>
<tr>
<td>20130205</td>
<td>4% NaF</td>
<td>300</td>
<td>2.13(0.6)</td>
<td>1.29</td>
<td>180(20)</td>
</tr>
<tr>
<td>20130205</td>
<td>4% NaF</td>
<td>400</td>
<td>2.48(0.3)</td>
<td>1.30</td>
<td>910(90)</td>
</tr>
<tr>
<td>20130205</td>
<td>4% NaF</td>
<td>500</td>
<td>3.07(0.4)</td>
<td>1.32</td>
<td>980(50)</td>
</tr>
</tbody>
</table>

ᵃEach experimental SXRF run allows us to measure the concentration of Nb in aqueous fluid at multiple P-T conditions. Rutile crystals are not recovered at each unique PT point; thus, partition coefficients are not reported.
ᵇThe reported uncertainty for the SXRF data reflects propagation of error from the standard calibration and peak fitting.
ᶜCorrected for absorption and density as described in the text.
Table 2: Piston cylinder experimental conditions and results

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>20130314</th>
<th>20130522</th>
<th>20130527$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid Composition (wt%)</td>
<td>10% NaCl</td>
<td>10% NaCl</td>
<td>4% NaF</td>
</tr>
<tr>
<td>Time (h)</td>
<td>8:31</td>
<td>27:15</td>
<td>12:00</td>
</tr>
<tr>
<td>Temperature (°C) (±1σ)</td>
<td>687(2)</td>
<td>793(11)</td>
<td>692(7)</td>
</tr>
<tr>
<td>Pressure (GPa) (±1σ)</td>
<td>1.09(0.06)</td>
<td>1.04(0.02)</td>
<td>0.97(0.02)</td>
</tr>
<tr>
<td>Fluid (mg)</td>
<td>23.4</td>
<td>31.2</td>
<td>29.5</td>
</tr>
<tr>
<td>Fluid Density (g/cm³)</td>
<td>1.06</td>
<td>1.01</td>
<td>0.91</td>
</tr>
<tr>
<td>*Crystal weight in (μg) (±1σ)</td>
<td>547(12)</td>
<td>887(5)</td>
<td>1088(1)</td>
</tr>
<tr>
<td>*Crystal weight out (μg) (±1σ)</td>
<td>523(6)</td>
<td>734(5)</td>
<td>651(162)</td>
</tr>
<tr>
<td>Mass loss (μg)</td>
<td>24</td>
<td>153</td>
<td>437</td>
</tr>
<tr>
<td>*Wt% Nb in product crystal</td>
<td>0.9307(.04)</td>
<td>1.0456(0.06)</td>
<td>1.0275(0.22)</td>
</tr>
<tr>
<td>$^{a}$μg g⁻¹ Nb in Fluid min (±1σ)</td>
<td>11(1)</td>
<td>80(5)</td>
<td>220(50)</td>
</tr>
<tr>
<td>$^{e}$μg g⁻¹ Nb in Fluid max (±1σ)</td>
<td>95(5)</td>
<td>600(35)</td>
<td>1715(370)</td>
</tr>
</tbody>
</table>

$^a$The crystal was weighed four times and the average mass is reported. The one sigma standard deviation of the average mass is provided in parentheses.

$^b$Run products contained broken crystal fragments as well as the primary crystals.

$^c$Wt% Nb for final run products are from LA-ICP-MS analysis.

$^d$Minimum Nb concentration in the fluid calculated by using the final wt% Nb from LA-ICP-MS.

$^e$Maximum Nb concentration in the fluid is calculated by using 8 wt% Nb (see text for discussion).
FIGURES

Figure 1.
Figure 2

![Graphs showing Wt% of Nb and Mo for EMPA Crystal A, EMPA Crystal B, LA-ICP-MS Crystal C, and LA-ICP-MS Crystal D.](image)

Distance (rim to center) or Depth (below surface) (µm)
Figure 3

![Graph](image-url)

(a) Starting Crystal

(b) Run Crystal

Time (s)

Intensity (cps)

Laser ON

49 Ti

93 Nb

30 40 50 60 70

10^6

10^7

10^8

10^9

10^10

10^11

10^12

10^13

10^14

10^15
Figure 4

Normalized Intensity (A.U.) vs. Energy (keV) for Nb.
Figure 5:

![Graph showing the relationship between Nb (g g⁻¹) in the fluid and the normalized integrated area (a.u.).](image-url)
Figure 6

R$^2=0.0015$
Avg Sd.Dev. = 11%

R$^2=0.0228$
Avg Sd.Dev. = 7%

R$^2=0.0003$
Avg Sd.Dev. = 9%

Integrated Raw Counts

$300^\circ$C
R$^2=0.0238$
Avg Sd.Dev. = 12%

$400^\circ$C
R$^2=0.0003$
Avg Sd.Dev. = 9%

$500^\circ$C
R$^2=0.0228$
Avg Sd.Dev. = 7%

$600^\circ$C
R$^2=0.0015$
Avg Sd.Dev. = 11%

Run 20110804

Run 20110805

Time (min)
Figure 7

![Graph A](image1.png)

![Graph B](image2.png)

![Graph C](image3.png)

![Graph D](image4.png)
Figure 8

(a) Nb (µg g⁻¹) in the fluid vs. Temperature (°C)

(b) Nb (µg g⁻¹) in the fluid vs. Pressure (GPa)

(c) Nb (µg g⁻¹) in the fluid vs. Density (g/cm³)

Legend:
- This Study
- Brenan et al., 1994
- H₂O
- H₂O+3 wt% SiO₂
- H₂O+3 wt% SiO₂+5.8 wt% NaCl
- 10 wt% NaCl
- 20 wt% NaCl
- 20130804
- 20130805
- Stalder et al. 1998
- 4 wt% NaF
- H₂O
- 20130806