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9 **Nb and Ta Diffusion in Titanite**

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Abstract

Chemical diffusion of Nb and Ta under anhydrous, pO_2 -buffered conditions has been measured in natural titanite. The source of diffusants were mixtures of $CaSiO_3$, TiO_2 , and Al_2O_3 powders, with either Nb or Ta oxides added. Experiments were run in evacuated sealed silica glass ampoules with solid buffers (buffered at NNO). Rutherford Backscattering Spectrometry (RBS) was used to measure Nb and Ta concentration profiles. The following Arrhenius parameters were obtained for Nb and Ta diffusion parallel to c over the temperature range 850-1252°C under NNO-buffered conditions:

$$D_{Nb} = 3.23 \times 10^{-9} \exp(-299 \pm 12 \text{ kJ mol}^{-1} / RT) \text{ m}^2\text{sec}^{-1}$$

$$D_{Ta} = 4.34 \times 10^{-10} \exp(-281 \pm 10 \text{ kJ mol}^{-1} / RT) \text{ m}^2\text{sec}^{-1}$$

In contrast to the findings of Marschall et al. (2013) for rutile, there do not appear to be large differences between Ta and Nb diffusivities in titanite, so the likelihood of diffusive fractionation of these elements will not be great. Values for diffusion coefficients measured parallel to the a-axis for both elements are similar to those parallel to c, indicating that Nb and Ta diffusivities in titanite do not exhibit significant anisotropy. Nb and Ta diffusion in rutile is faster than diffusion of these elements in titanite at higher temperatures (by about 2 and 1.5 orders of magnitude at 700°C for Nb and Ta, respectively), but because of the higher activation energies for diffusion of Nb and Ta in rutile, they will approach values for titanite with decreasing T. Our diffusion data indicate that titanite should be moderately retentive of Nb and Ta chemical signatures, with diffusivities slower than those for Zr, O and Pb in titanite, but faster than those for the REE under most geologic conditions. These differences among diffusivities suggest that information derived from Zr thermometry, U-Pb geochronology, and geochemical tracers such as Ta, Nb and the REE may be decoupled in titanite under some conditions.

Introduction

Titanite is an accessory mineral widely found in igneous and metamorphic rocks. Because it can include U, Th, REE, as well high field strength elements as substituents in its lattice, it plays an important role as carrier of trace elements useful as petrogenetic indicators and in geochronology, and may have significant influence on the distribution of these trace elements during many geological processes, including late-stage fractional crystallization and partial melting. The behaviors of Nb and Ta are critical in understanding crustal formation processes (e.g., Green, 1995; Foley, 2008). Both depleted mantle and continental crust have subchondritic Nb/Ta ratios, suggesting an apparent deficit of Nb in the accessible silicate earth, the so-called "missing Nb paradox" (e.g., Rudnick et al., 2000). It is argued that equilibrium-melting models cannot fully account for observed crustal Nb/Ta patterns, and Marschall et al. (2013) have recently measured differences between diffusivities of Nb and Ta in rutile, which they propose as a contributing factor to the low Nb/Ta ratios observed in continental crust.

Although rutile is the dominant mineral phase to incorporate Nb and Ta into its lattice, titanite may accommodate significant amounts of these elements as well (e.g., Sahama, 1946, Černý and Riva di Sanseverino, 1972; Clark, 1974; Paul et al., 1981, Woolley et al., 1992; Russell et al., 1994; Černý et al., 1995; Tiepolo et al. 2002, Chakhmouradian and Zaitsev 2002, Chakhmouradian, 2004; Brigatti et al., 2004). The relative modal abundances of titanite and rutile may affect Nb/Ta ratios of melts (e.g., John, 2011), so it is important to characterize the behavior of these elements in both phases. To better constrain Nb-Ta systematics, it is critical to measure Nb and Ta diffusion in titanite in order to assess the relative resistance of Ta and Nb concentrations in titanite to thermal alteration, and to evaluate whether diffusive fractionation of Nb and Ta occurs in titanite as in rutile.

In addition, materials with the titanite structure are potential candidates as phases for nuclear waste disposal (e.g., Hayward et al. 1983; Gascoyne, 1986). Niobium is a common component of nuclear waste, produced from activation of zirconium used in nuclear fuel pellets, so determination of Nb diffusion coefficients in titanite may provide insight in the ability of this phase to retain radioactive waste constituents.

Experimental procedure

The mineral specimens used in this study were from a natural titanite from Minas Gerais, Brazil. Specimens from this locality have been used previously in our investigations of Pb (Cherniak, 1993), Zr (Cherniak, 2006) and oxygen diffusion (Zhang et al, 2006). Compositional analyses of this titanite were reported in Cherniak (1993).

Titanite specimens were cut normal to the a- or c-axes and polished with SiC papers and 1.0 and 0.3 μm alumina, followed by a chemical polish with colloidal silica. The polished titanite was then cut into pieces a few mm on a side. Since a coupled substitution with Al has been proposed as a dominant mechanism for Nb and Ta exchange (i.e., $(\text{Ta,Nb})^{+5} + \text{Al}^{+3} \leftrightarrow 2\text{Ti}^{+4}$; Liferovich and Mitchell, 2006a;b; Seifert and Kramer, 2003), sources consisting of CaSiO_3 and TiO_2 powders were used for experiments, with Al_2O_3 and Nb_2O_5 or Ta_2O_5 added in substitution for a portion of the TiO_2 . The sources for the Nb diffusion experiments were made by combining CaSiO_3 , TiO_2 , Al_2O_3 and Nb_2O_5 powders in a molar ratio of 40:36:1:1, grinding under ethanol, and annealing in a Pt crucible at 1200°C for 1 day. The sources for the Ta diffusion experiments were prepared in a similar manner, substituting Ta_2O_5 for the Nb oxide. For one set of experiments, the sources prepared as above (referred to as "source a" in Tables 1 and 2) were

used. For a second set of experiments, sources were prepared with lower concentrations of Nb and Ta by combining the sources described above with titanite powder in a 1:10 (by weight) ratio; these mixtures were ground under ethanol, dried, and heated in Pt crucibles at 1250°C for 1 day. These sources are designated as "source b" in Tables 1 and 2. To assemble experiments, the source material was loaded into Pt capsules with the prepared titanite. The capsules were crimped shut and placed in silica glass capsules along with solid buffer mixture of nickel metal powder and nickel oxide powder (to buffer at NNO), which was also contained in a crimped Pt capsule. Inside the silica glass capsules, silica glass chips were placed between the solid buffer and the capsule containing the source and sample to physically separate the sample and buffer. The assemblies in the silica glass tubes were sealed under vacuum, and annealed in vertical tube furnaces for temperatures ranging from 850 to 1252°C, and times from 35 minutes to nine weeks. All of the experiments below 1100°C were run in Kanthal-wound vertical tube furnaces, with temperatures monitored with type K (chromel-alumel) thermocouples during the course of the anneals; temperature uncertainties are $\sim \pm 2^\circ\text{C}$. Experiments at 1100°C and above were run in furnaces with MoSi₂ heating elements; type S (Pt-Pt10%Rh) thermocouples were used to monitor these experiments, with similar temperature uncertainty. On completion of the anneals, samples were quenched by removing them from furnaces and permitting them to cool in air. Samples were then removed from capsules, freed of residual source material and cleaned ultrasonically in successive baths of distilled water and ethanol.

RBS Analysis

RBS has been used in many of our diffusion studies, including those investigating Zr (Cherniak, 2006), Pb (Cherniak, 1993) and Sr and Nd (Cherniak, 1995) diffusion in titanite. The analytical approaches used here are similar to those used in these studies, with 2 MeV $^4\text{He}^+$ beams used for analysis. Spectra were converted to Nb and Ta concentration profiles employing procedures similar to those outlined in these earlier publications. The resultant concentration profiles were fit with a model to determine the diffusion coefficients (D). Diffusion is modeled as simple one-dimensional, concentration independent diffusion in a semi-infinite medium with a source reservoir maintained at constant concentration (i.e., a complementary error function solution). The rationale for the use of this model has been discussed in previous publications (e.g., Cherniak and Watson, 1992; 1994). Diffusivities are evaluated by plotting the inverse of the error function (i.e., $\text{erf}^{-1}((C_o - C(x,t))/C_o)$) vs. depth (x) in the sample. A straight line of slope $(4Dt)^{-1/2}$ results if the data satisfy the conditions of the model. C_o , the surface concentration of diffusant, is determined by iteratively varying its value until the intercept of the line converges on zero. In **Figure 1**, typical diffusion profiles for Nb and Ta and their inversions through the error function are shown. The uncertainties in concentration and depth from each data point (mainly derived from counting statistics in the former and detector resolution in the latter) were used to evaluate the uncertainties in the diffusivities determined from the fits to the model. Nb and Ta profiles measured from all experiments conformed to complementary error function curves, with no evidence of profile shapes that would suggest concentration dependence of diffusion.

NRA analyses of Al

In addition to the RBS analyses, Al was profiled in some of the titanite samples using the nuclear reaction $^{27}\text{Al}(p,\gamma)^{28}\text{Si}$ to assess the importance of Al in substitutional processes for Ta and Nb exchange. These analyses were also performed at the Ion Beam Laboratory at the University at Albany, using a proton beam produced by the Dynamitron accelerator. The 992 keV resonance of the reaction was employed, with a bismuth germanate (BGO) detector used to detect gamma rays produced in the reaction (Cherniak, 1995; Cherniak and Watson, 1992). Energy steps of 1 - 0.5 keV for the incident proton beam were taken near the resonance energy to profile near-surface Al, with larger energy steps (2-5 keV) at greater depths (above ~120 nm). Reference spectra from an untreated specimen of titanite were also recorded at each energy step to evaluate background levels and contributions from natural Al abundances in the titanite in the gamma energy region of interest. Depth scales for the Al profiles were calculated from the energy difference between the incident proton beam and the resonance energy, and by the stopping power (energy loss of the protons as a function of depth in the material) (e.g., Cherniak and Lanford, 2001); stopping powers for protons in the titanite matrix over the energy range employed in depth profiling were obtained from the software SRIM (Ziegler and Biersack, 2006).

Results

The results from Nb and Ta diffusion experiments on titanite presented in Table 1 and plotted in **Figure 2**. For Nb diffusion parallel to c, an activation energy of $299 \pm 12 \text{ kJ mol}^{-1}$ and pre-exponential factor of $3.23 \times 10^{-9} \text{ m}^2 \text{ sec}^{-1}$ ($\log D_0 = -8.49 \pm 0.47$) are obtained. For Ta, again for diffusion parallel to c, an activation energy of $281 \pm 10 \text{ kJ mol}^{-1}$ and pre-exponential factor of

186 $4.34 \times 10^{-10} \text{ m}^2 \text{ sec}^{-1}$ ($\log D_0 = -9.36 \pm 0.40$) are determined. Arrhenius parameters for Nb and Ta
187 differ slightly, but are in agreement within uncertainties. Diffusion coefficients for transport
188 parallel to the a-axis are similar to those for diffusion parallel to c for both elements, indicating
189 little anisotropy for Nb and Ta diffusion. Experiments conducted with the sources containing
190 different concentrations of the diffusants (the "a" and "b" sources) yield similar diffusivities,
191 with surface concentrations ranging from 3 atomic percent, down to 900 and 200 $\mu\text{mol/mol}$ for
192 Nb and Ta, respectively.

193 We performed a time-series study for Nb diffusion at 1000°C in order to verify that the
194 measured concentration profiles represent volume diffusion and are not a consequence of other
195 phenomena such as surface reaction that may otherwise result in enhanced Nb concentrations in
196 the near-surface region. In [Figure 3](#), the results of the time series at 1000°C for Nb diffusion
197 parallel to c in titanite are plotted. Diffusivities are quite similar for times ranging over more
198 than a factor of 7, suggesting that volume diffusion is the dominant contributor to the observed
199 diffusion profiles.

200 The results from Al profiling show increases in Al above natural abundances in these titanite
201 specimens (~0.55 atomic %; Cherniak, 1993) to depths similar in length to the Ta and Nb
202 profiles (Figure 4). In the samples analyzed for Al, maximum Al concentrations above natural
203 abundances are in the range of 20 to 60 percent of the surface concentrations of Nb and Ta.
204 Coupled substitutions of Nb and Al can be a dominant means of charge compensation in titanite;
205 titanites have been synthesized with up to 0.25 Nb per titanite formula unit (3.1 at%) in
206 substitution on the Ti site with charge compensation by Al or Fe^{+3} (Liferovich and Mitchell,
207 2006a). Charge balance can also be achieved by the substitution of Na^+ for Ca^{+2} , or by anionic
208 substitutions of F or hydroxyl on the O(1) site. Ta can be incorporated in a similar manner, with

up to 0.30 Ta per formula unit in substitution on the Ti site with charge compensation by Al^{+3} (Liferovich and Mitchell, 2006b). In our experiments, Nb and Ta concentrations range from 0.007- 0.243 and 0.002 - 0.266 per titanite formula unit, respectively. For each diffusant source, there is no clear correlation of Nb or Ta surface concentrations with temperature or other parameters. These findings from Al profiling suggest that coupled substitutions of (Nb,Ta)-Al are an important means of charge compensation, but that other species (e.g., Fe^{+3}) may also play a role in some cases. Results for REE diffusion in titanite (Cherniak, 1995) indicate that multiple substitutional mechanisms may operate to achieve charge balance, with Al as a charge compensating species dominant under lower $f\text{O}_2$ conditions, with Fe, and possibly anionic substitutions, more prevalent under more oxidizing conditions. Partitioning studies of trace elements in titanite (Prowatke and Klemme, 2005) also indicate that incorporation of Nb, Ta and REE is not controlled via simple substitution mechanisms.

Discussion

Diffusion of Ta and Nb in titanite and rutile

In [Figure 5](#), Ta and Nb diffusivities in rutile from the work of Marschall et al. (2013) are plotted with Nb and Ta diffusion data for titanite. Nb and Ta diffusivities in titanite are slower than diffusion of these species in rutile (Marschall et al., 2013) over the investigated temperature range. In this temperature range, Nb diffusion is two orders of magnitude smaller in titanite than in rutile, but because Nb diffusion in rutile has a higher activation energy (378 kJmol^{-1} , compared with 299 kJmol^{-1} for titanite), this variance will decrease with decreasing

temperatures. However, Nb diffusivities in rutile would only approach values for Nb diffusion in titanite at $T \sim 400^{\circ}\text{C}$, when diffusivities will be extremely small ($\sim 10^{-32} \text{ m}^2/\text{sec}$, which would correspond to diffusion distances of a few tens of nm over times on the order of the age of the earth). Ta diffusivities in rutile would approach those in titanite at $\sim 500^{\circ}\text{C}$, where diffusivities would be on order of $10^{-28} \text{ m}^2/\text{sec}$.

Marschall et al. (2013) measured faster diffusivities for Nb than Ta in rutile, with diffusion coefficients differing by about one-half to three quarters of a log unit over temperatures of geologic interest. In titanite, diffusivities for Nb and Ta would differ by less than a quarter of a log unit over this temperature range. It is not clear why these differences between rutile and titanite exist. It may be a consequence of differences in the types of substitutional mechanisms and means of charge compensation for incorporation of pentavalent species in rutile compared with those for titanite. In rutile, charge balance is likely achieved through oxygen vacancies and/or free electrons, depending on $f\text{O}_2$ in synthetic rutile (e.g., Bak et al. 2003), while in natural rutile, Fe^{3+} and other trivalent cations could also contribute to or dominate the charge balance. In titanite, charge balance appears to be predominately through Al-(Nb,Ta) coupled substitutions, with possible contributions from Fe and anionic substitutions. Marschall et al. (2013) suggest that differences between Ta and Nb diffusivities in rutile may be attributable to the differences in electronegativities and first ionization potentials of these elements, which will result in differences in bond strengths in the mineral structure. It may be that effects such as these are more pronounced in rutile than in titanite. Zr, with lower activation energy for diffusion but significantly slower diffusivities (Cherniak et al., 2007), appears to behave very differently from Ta and Nb in rutile, in contrast to the apparently more systematic behavior of Zr with respect to

Ta and Nb diffusion in titanite (see discussion below), suggesting that the interplay of elemental characteristics, substitutional processes, and diffusion mechanisms in rutile may be complex.

Geological Implications

Preservation of Nb and Ta concentrations in titanite and rutile

We can use these diffusion data to briefly explore the ways in which Nb and Ta in titanite might be affected by volume diffusion, and also consider the relative retentivity of Nb and Ta chemical signatures when compared with those of rutile in order to better refine thermal histories and understand petrogenetic processes. Through simple calculations, we can evaluate the resistance of Ta and Nb to diffusional alteration by determining the extent to which grains will chemically equilibrate with their external environments during thermal events if the surroundings of the grains provide a sink or source for these elements. In addition, the conditions for preservation of Nb and Ta compositions in titanite can be considered with respect to those for other minor and trace elements important as petrogenetic indicators and in thermometry and geochronology, including Zr, the REE, and Pb.

We use a simple model in which the titanite grains are spheres with radii a and initial uniform concentration of C_i , and are exposed to a medium with concentration C_0 . The solution to the diffusion equation at the center of the spheres can then be derived (e.g., Crank, 1975) given these conditions. When the dimensionless parameter Dt/a^2 (where D is the diffusion coefficient and t is the time) is less than or equal to 0.03, the concentration at the center of the sphere remains unchanged from its initial value. Above 0.03, the concentration at the center of the sphere is

affected by the externally imposed concentration C_0 . A spherical model is also used in calculations for rutile, although rutile typically has elongate grain habits. Diffusion in rutile is anisotropic, with diffusion parallel to c a factor of ~ 8 faster than diffusion parallel to a , so the effect of the non-isometric shape of rutile grains is offset by diffusional anisotropy. Hence, for grain aspect ratios less than ~ 2.8 (the square root of 8), the spherical diffusion model may be more suitable than cylindrical models.. In [Figure 6](#) curves representing these conditions are plotted, using an effective diffusion radius of $250\mu\text{m}$. The calculated curves for Nb and Ta in titanite are plotted for comparison against those for rutile, using the diffusion parameters from Marschall et al. (2013) for diffusion parallel to the c -axis. The curves define the time-temperature limits under which initial Nb and Ta compositional information will be retained in grain centers for each of these phases. For times and temperatures below the curves, Ta or Nb concentrations at crystal cores will remain unaffected, but will be influenced by the concentration of these elements in the surrounding medium when conditions above the curves prevail.

Both Ta and Nb will equilibrate more rapidly in rutile than in titanite, except at low temperatures when equilibration times for grains in all cases would be in excess of the age of the earth. For example, at 700°C , the centers of 0.5mm diameter titanite grains will retain initial concentrations of Nb over times up to about 200 million years; for rutile, Nb concentrations would be retained over times up to 2 Myr. For Ta, times at this temperature would be 200 Myr and 10 Myr for titanite and rutile, respectively.

Diffusion of other elements in titanite

In **Figure 7**, diffusivities of Ta and Nb measured in this study are plotted along with Arrhenius relations for diffusion of other cations in titanite. Diffusion of Ta and Nb are about an order of magnitude slower than diffusion of Zr, but with comparable activation energies for diffusion (325 ± 30 , 302 ± 14 , and 285 ± 13 kJmol⁻¹ for Zr, Nb, and Ta, respectively). Zr, which also substitutes for Ti in titanite, is slightly larger than Ta or Nb (72 pm for Zr⁺⁴ vs. 64 pm for Ta⁺⁵ and Nb⁺⁵ in 6-fold coordination; Shannon, 1976), but its smaller charge may contribute to its faster transport. Both Sr and Nd, which substitute for Ca in the titanite lattice (e.g. Hughes et al., 1997; Ribbe, 1980; Higgins and Ribbe, 1976), have significantly higher activation energies for diffusion (415 and 498 kJmol⁻¹ for Sr and Nd, respectively) than Nb or Ta.

Retentivity of zoning of Nb, Ta and other elements in titanite

Diffusivities of important geochemical tracers in titanite, as summarized in **Figure 7**, can be used in calculations to evaluate to the possible retention or diffusional loss of intracrystalline zoning and chemical signatures. Nb and Ta can be compositionally zoned in titanite, as well as other trace and minor elements of geochemical interest (e.g., Chakhmouradian, 2004; Černý et al., 1995; Paterson and Stephens, 1992). It is useful to consider the conditions under which zoning may be lost. Ideally, it may be possible to qualitatively evaluate the degree of diffusive exchange by assessing the dimensions of zones and variations in concentrations of various trace elements (analyzed via electron or ion microprobe, for example) across a titanite grain. If diffusivities of several elements are known, and differences among them are significant, this may provide additional means to better constrain thermal histories.

For these calculations we use a simple model, with zones in a titanite crystal modeled as a series of plane sheets of thickness l , with adjacent planes having different concentrations of the diffusant. Only diffusion normal to the planar interface is considered. A (somewhat arbitrary) criterion for alteration of zones is employed. Zones are considered to be "lost" if a compositional change of 10% is attained in the zone's center; the dimensionless parameter Dt/l^2 will be equal to 3.3×10^{-2} when this condition occurs.

Figure 8 shows curves constraining the time-temperature conditions under which Nb and Ta zoning on scales of 5 and 50 μm will be retained in titanite given the above criteria. Zoning will be "lost" if titanite experiences time-temperature conditions that fall above the curves, but retained for conditions below the curves. These are compared with curves calculated to evaluate retention of zoning of Pb, REE and Zr, using diffusivities obtained from the data of Cherniak (1993; 1995; and 2006, respectively) and the model described above. Titanite will be considerably more retentive of Nb zoning than that of Pb, but Nb compositional differences will be much less likely to be retained than REE zoning. Nb zoning will be better preserved than Zr zoning at high temperatures, but would be retained to a similar extent at lower temperatures (requiring long timescales). As an example, at 700°C, times for diffusional alteration of compositional variations on the 50 μm scale would be about 10 Myr for Nb, 10,000 years for Pb, and 1.5 Myr for Zr, but 5 Gyr for the REE. This difference in preservation of compositional variations for these elements in titanite following thermal events indicates that there may not necessarily be correspondence between U-Pb ages, past temperatures extracted from Zr concentrations, and information provided by geochemical tracers such as Nb, Ta and the REE from analyses of titanite grains. A good example for potential application would be on slow-cooled, high T granitoids.

Along with the blurring and loss of zones described above, one can also consider the example of a compositional interface, where the concentrations of the trace or minor element are initially a step function, which relaxes over time due to diffusional exchange during a thermal event. The concentration profiles can be described by a simple complementary error function solution to the diffusion equation. Example profiles for a set of elements experiencing a cooling event (linear cooling from 800°C at 10°C/Myr) are shown in figure 9. The slope at the midpoint of the profile is proportional to $(Dt)^{-1/2}$, where Dt , in the case of non-isothermal heating, is the integrated Dt over the thermal history.

A simple equation can be derived from numerical simulations and analytical solutions for the case of linear cooling, in which the slope is a function of the peak temperature T_i and the cooling rate ($\dot{T}$) (Watson and Cherniak, 2015):

$$\log S_0 = 2.504 - \frac{1}{2} \log D_0 - \log T_i + \frac{1}{2} \log E_a + \frac{1}{2} \log \dot{T} + \left(26.11 \frac{E_a}{T_i} \right) \quad (1)$$

where the initial temperature T_i is expressed in kelvins, $\dot{T}$ is in Kelvin/s, D_0 is in m^2/s , E_a is in kJ/mol, and the slope is %/m (where concentrations of the diffusing species are normalized to 100%). With this expression, if the slopes (S_0) of relaxed diffusion profiles (as illustrated in figure 9) can be measured for two elements for which diffusion laws are known, then both T_i and cooling rate can be determined, providing a few conditions are met. These include the condition that the alterations in concentrations are due to volume diffusion, the initial compositional distributions approximate step functions, and that values for Dt are sufficiently small such that the constraints for diffusion in a semi-infinite medium can be applied.

In the case of a parabolic path, which might be more appropriate for tectonic scenarios than a linear path, cooling can be described by:

$$T = T_i - \left[\frac{T_i - 293}{\tau^2} \right] \cdot t^2 \quad (2)$$

where τ is the timespan of the path from T_i to 293K. Expressions similar to eq. 1 are determined from numerical simulations using this cooling trajectory, with the only differences being in the leading constant term, where the value would be 2.165 instead of 2.504, and the single-valued cooling rate $\dot{T}$ would be replaced by the average value for cooling along the parabolic path, $(T_i - 293)/\tau$. The difference in the expressions is a consequence of the longer duration at higher temperatures (where most of the diffusion takes place) for parabolic cooling paths compared with linear cooling, which will lead to shallower slopes (i.e., a greater extent of diffusion) for a given peak temperature and duration of cooling. A more detailed presentation of these findings is in Watson and Cherniak (2015). Titanite provides a good case for potential application of this method, since diffusion parameters for several minor and trace elements have been measured, and diffusivities along some of these elements differ sufficiently widely for there to be significant differences in slopes for a given thermal history.

Acknowledgements – Thanks to Bruce Watson for helpful discussion during the course of this work, to Mike Ackerson for his comments on an earlier version of this manuscript, and to Ralf Dohmen and Horst Marschall for their insightful reviews. This work was supported by grant EAR-0948204 from the National Science Foundation (to E.B. Watson).

385 Table 1. Nb diffusion in titanite

	$T(^{\circ}C)$	$time(s)$	$D(m^2sec^{-1})$	$\log D$	+/-
386	<i>Parallel to c:</i>				
	NbSph-9*	850	4.82x10 ⁶	3.84x10 ⁻²³	-22.42 0.20
	NbSph-8*	900	2.75x10 ⁶	8.19x10 ⁻²³	-22.09 0.18
	NbSph-2*	952	7.63x10 ⁵	3.98x10 ⁻²²	-21.40 0.12
	NbSph-1*	1000	2.70x10 ⁵	1.85x10 ⁻²¹	-20.73 0.20
	NbSph-10*	1000	6.84x10 ⁵	3.13x10 ⁻²¹	-20.50 0.12
	NbSph-11*	1000	9.00x10 ⁴	4.25x10 ⁻²¹	-20.37 0.15
	NbSph-17 [§]	1000	3.42x10 ⁵	1.46x10 ⁻²¹	-20.84 0.13
	NbSph-7*	1050	2.45x10 ⁵	5.59x10 ⁻²¹	-20.25 0.09
	NbSph-3*	1102	8.64x10 ⁴	4.71x10 ⁻²¹	-20.33 0.12
	NbSph-15 [§]	1099	8.28x10 ⁴	8.99x10 ⁻²¹	-20.05 0.15
	NbSph-4*	1150	1.62x10 ⁴	2.63x10 ⁻²⁰	-19.58 0.17
	NbSph-16 [§]	1152	2.16x10 ⁴	4.03x10 ⁻²⁰	-19.39 0.12
	NbSph-5*	1202	7.20x10 ³	8.00x10 ⁻²⁰	-19.09 0.11
	NbSph-6*	1252	2.40x10 ³	3.15x10 ⁻¹⁹	-18.50 0.15
387	<i>Parallel to a:</i>				
	NbSph-12	1000	6.95x10 ⁵	1.11x10 ⁻²¹	-20.95 0.10
	NbSph-13	1100	8.64x10 ⁴	5.77x10 ⁻²¹	-20.24 0.09

388 * = source "a"; § = source "b"

389

390 Table 2. Ta diffusion in titanite

	$T(^{\circ}C)$	$time(s)$	$D(m^2sec^{-1})$	$\log D$	+/-
391	<i>Parallel to c:</i>				
	TaSph-9*	850	5.53x10 ⁶	4.31x10 ⁻²³	-22.37 0.17
	TaSph-3*	900	2.43x10 ⁶	2.16x10 ⁻²²	-21.67 0.10
	TaSph-2*	950	6.08x10 ⁵	6.91x10 ⁻²²	-21.16 0.12
	TaSph-1*	1000	4.16x10 ⁵	7.37x10 ⁻²²	-21.13 0.17
	TaSph-11 [§]	1000	2.83x10 ⁵	2.16x10 ⁻²¹	-20.67 0.18
	TaSph-14 [§]	1000	3.42x10 ⁵	9.21x10 ⁻²¹	-21.04 0.14
	TaSph-8*	1049	4.07x10 ⁵	1.46x10 ⁻²¹	-20.83 0.12
	TaSph-7*	1100	9.18x10 ⁴	4.52x10 ⁻²¹	-20.34 0.10
	TaSph-12 [§]	1099	8.28x10 ⁴	7.04x10 ⁻²¹	-20.15 0.11
	TaSph-6*	1151	1.44x10 ⁴	2.70x10 ⁻²⁰	-19.57 0.09
	TaSph-13 [§]	1152	2.16x10 ⁴	1.37x10 ⁻²⁰	-19.86 0.14
	TaSph-4*	1201	7.20x10 ³	6.28x10 ⁻²⁰	-19.20 0.11
	TaSph-5*	1251	2.10x10 ³	3.85x10 ⁻¹⁹	-18.41 0.14
392	<i>Parallel to a:</i>				
	TaSph-10*	1100	8.64x10 ⁴	6.83x10 ⁻²¹	-20.17 0.11

393 * = source "a"; § = source "b"

394

Captions for figures

Figure 1. Typical profiles from Ta and Nb diffusion experiments. In (a) and (c), the measured diffusion profiles for Nb and Ta, respectively, are plotted with complementary error function curves. In (b) and (d), the data are linearized by inversion through the error function. Slope of the lines are equal to $(4Dt)^{-1/2}$.

Figure 2. Arrhenius plot of Nb (black symbols) and Ta (white symbols) diffusion data for titanite. For Nb diffusion parallel to the c-axis (circles), we obtain an activation energy of 299 ± 12 kJ mol⁻¹ and pre-exponential factor of 3.23×10^{-9} m²sec⁻¹. For Ta, an activation energy of 281 ± 10 kJ mol⁻¹ and pre-exponential factor of 4.34×10^{-10} m²sec⁻¹, also for diffusion parallel to c. Diffusivities parallel to the a-axis (square symbols) are similar to those measured for diffusion parallel to c for both Ta and Nb, indicating little anisotropy of diffusion for these elements in titanite.

Figure 3. Time series for Nb diffusion parallel to c in titanite for anneals at 1000°C. Diffusivities are similar, despite differences in experiment durations ranging over more than a factor of 7, suggesting that the dominant process being measured is volume diffusion.

Figure 4. Concentration profile for Ta plotted with Al concentration (above natural abundance in the sample). Ta is measured with RBS, Al is measured with NRA. These observations suggest that coupled substitutions of (Nb,Ta)-Al are an important means of charge compensation, but that other species (e.g., Fe⁺³) may also play a role.

418

419 **Figure 5.** Diffusion of Ta and Nb in titanite and rutile. Sources for data: Nb and Ta- rutile:

420 Marschall et al., 2013; Nb and Ta- titanite: this study.

421

422 **Figure 6.** Conditions for diffusional loss of Nb and Ta in titanite and rutile for grains of effective

423 radii of 250 μ m. Curves represent time-temperature conditions under which each mineral will

424 lose compositional information on Ta or Nb at the center of grains.

425

426 **Figure 7.** Arrhenius plot of data for cation diffusion in titanite. Sources for data: Nd (QFM

427 buffer), Sr – Cherniak, 1995, Pb – Cherniak, 1993; Zr - Cherniak 2006; Ta, Nb - this study.

428

429 **Figure 8.** Preservation of Nb zoning in titanite. The curves plotted represent maximum time-

430 temperature conditions under which zoning of Nb and Ta on 5 and 50 μ m scales will be

431 preserved in titanite. For conditions above the curves, well-defined zoning on these scales will

432 be lost. Also plotted for comparison are curves for Nd, Pb and Zr, calculated using the Arrhenius

433 relations presented in Figure 6.

434

435 **Figure 9.** Example diffusion profiles for Nd, Sr, Nb, Ta, Zr and Pb in titanite produced during

436 cooling from 800°C at 10°/Myr, calculated using the Arrhenius parameters plotted in Figure 6,

437 and assuming an initial step function distribution of all elements, with concentrations normalized

438 on a 0-100% scale. Since diffusion of these elements is governed by widely varying diffusion

439 parameters, there are correspondingly large differences in slope (S_0) of the profiles. Given

440 profiles of two or more elements in a titanite grain with differing and known diffusion

441 parameters, the slopes of the profiles can be used in equation (1) to solve for cooling rate and
442 initial temperature, provided certain conditions are met.

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Figure

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