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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:

$$D_{Nb} = 3.23 \times 10^{-9} \exp\left(-299 \pm 12\ \text{kJ mol}^{-1}/RT\right)\ \text{m}^2\ \text{s}^{-1}$$
$$D_{Ta} = 4.34 \times 10^{-10} \exp\left(-281 \pm 10\ \text{kJ mol}^{-1}/RT\right)\ \text{m}^2\ \text{s}^{-1}.$$

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. These 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.

1. Introduction

Titanite is an accessory mineral widely found in igneous and metamorphic rocks. Because it can include U, Th, REE, as well as 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; Cerny and Riva di Sanseverino, 1972; Clark, 1974; Paul et al., 1981; Woolley et al., 1992; Russell et al., 1994; Cerny et al., 1995; Chakhmouradian and Zaitsev, 2002; Tiepolo et al., 2002; Brigatti et al., 2004; Chakhmouradian, 2004). The relative modal abundances of titanite and rutile may affect Nb/Ta ratios of melts (e.g., John et al., 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;

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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.

2. 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-axis 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., $(\mathrm{Ta,Nb})^{+5} + \mathrm{Al}^{+3} \leftrightarrow 2\mathrm{Ti}^{+4}$; 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 power 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 min 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 ~±2 °C. Experiments at 1100 °C and above were run in furnaces with $MoSi_2$ 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.

Table 1
Nb diffusion in titanite.

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

[a] Source “a”.
[b] Source “b”.

Table 2
Ta diffusion in titanite.

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

[a] Source “a”.
[b] Source “b”.

3. 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 $^4He^+$ 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., $\mathrm{erf}^{-1}((C_o - C(x,t)) / C_o)$) 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 Fig. 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.

4. NRA analyses of Al

In addition to the RBS analyses, Al was profiled in some of the titanite samples using the nuclear reaction $^{27}\mathrm{Al}(p,\gamma)^{28}\mathrm{Si}$ to assess the importance of Al in substitutional processes for Ta and Nb exchange. These