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Letters

Diffusion-induced fractionation of niobium and tantalum during continental crust formation

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ABSTRACT

Differentiation of the Earth into its major spheres – crust, mantle and core – has proceeded dominantly through magmatic processes involving melting and melt separation. Models that describe these differentiation processes are guided by elemental abundances in the different reservoirs. Elements are fractionated between coexisting phases during partial melting, and geochemical models are generally based on the fundamental assumption that trace-element equilibrium is established between the partial melts and the restitic minerals. The element pair niobium and tantalum is key to the distinction of different melting regimes involved in crustal differentiation, but equilibrium partition models have largely failed to reproduce the Nb/Ta patterns observed in nature, posing a long-standing geochemical conundrum. Here we demonstrate that kinetic fractionation of Nb and Ta by diffusion may have produced the low Nb/Ta observed in the continental crust. On the basis of the diffusivities of Nb and Ta in rutile (TiO₂) determined experimentally in this study, we conclude that equilibrium cannot be expected for the natural range of grain sizes, temperatures and time scales involved in partial melting of crustal rocks. Instead, the observed fractionation of the geochemical twins, Nb and Ta, in the silicate Earth most likely proceeds by partial – as opposed to complete – equilibration of rutile and melt. Hence, the assumption of bulk equilibrium during partial melting for the processes of crustal differentiation may not be justified, as is demonstrated here for Nb/Ta. The concept presented here is based on kinetic fractionation melting and explains the observed low Nb/Ta ratio of the continental crust.

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1. Introduction

1.1. The Nb–Ta geochemical conundrum

Fundamental questions about the differentiation of the silicate Earth include the timing and mechanism of the formation and differentiation of the continental crust (Rudnick et al., 2000). Among the most characteristic geochemical anomalies of continental rocks are a depletion of the elements Nb, Ta and Ti relative to elements with similar melt–rock partitioning behaviour and relative to their abundances in the mantle and in primitive basalts (Hofmann, 1988). In addition, the Nb/Ta ratios of the accessible crust and mantle are lower than that of primitive chondrites, and it has been suggested that Nb is preferentially enriched in the core, leaving the silicate Earth with a sub-chondritic Nb/Ta ratio

(Münker et al., 2003). Furthermore, differentiation of the crust–mantle system has produced a significant variation in Nb/Ta ratios, and this ratio has been identified as a key geochemical tool to identify crust formation processes (Green, 1995; Foley et al., 2002; Rapp et al., 2003). Most importantly, the continental crust has a lower Nb/Ta ratio (=12 to 13) than the bulk silicate Earth (BSE; Nb/Ta = 14 ± 0.3 ; Münker et al., 2003). The geochemical behaviour of the trace elements Nb and Ta is intimately linked to that of the more abundant element titanium. The dominant mineral hosts of Ti, Nb and Ta in crustal rocks are sphene (=titanite) and the Ti ± Fe oxides rutile, ilmenite and Ti-magnetite.

Rocks of basaltic composition are metamorphosed to eclogite at conditions prevailing in the upper mantle and in deep sections of thickened crust, where partial melting processes can take place. The Nb and Ta budget in eclogites is almost exclusively stored in the ubiquitous mineral rutile (Zack et al., 2002; Aulbach et al., 2008), and eclogites retain rutile in the restite during partial melting processes (Ryerson and Watson, 1987; Klemme et al., 2002; Gaetani et al., 2008; Xiong et al., 2011). Consequently, Nb–Ta fractionation processes have to be approached with a close focus

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on Ti minerals and their ability to fractionate Nb from Ta during partial melting processes (Green and Pearson, 1987; Rapp et al., 2003; Schmidt et al., 2004; Klemme et al., 2005; Xiong et al., 2011; John et al., 2011).

Experimental work on Nb and Ta partitioning between rutile and silicate liquid has revealed that both elements are strongly compatible in rutile and that Ta is either equally or more compatible than Nb (Green and Pearson, 1987; Schmidt et al., 2004; Klemme et al., 2005; Xiong et al., 2011). This invariably leads to the prediction that melts in equilibrium with any rock containing restitic rutile will have Nb/Ta ratios similar to or higher than its protolith. This is in stark contrast to the low Nb/Ta ratios observed in the continental crust, which represents the extracted magmas produced by partial melting.

Equilibrium-melting models largely fail to explain the Ti–Nb–Ta depletion of the continental crust in combination with its low Nb/Ta ratio (see detailed discussion in Supplementary material). Consequently, the assumption of equilibrium between minerals and liquid during melting and melt extraction has to be revisited, and effects of kinetic fractionation of trace elements need to be considered. We, therefore, determined kinetic fractionation of Nb and Ta during diffusion in rutile and investigate the consequences for Nb–Ta fractionation during partial melting. Diffusive equilibration of melt and restitic minerals is controlled by (i) melting temperature, (ii) the duration of melt–rock interaction prior to melt extraction, (iii) the grain size distribution in the restite and (iv) the diffusivities of the trace elements in the trace-element hosting minerals. Whereas the first three parameters can be derived from published models and experimental data and from observations in natural rocks, the diffusivities of Nb and Ta in rutile have to be determined experimentally.

1.2. Previously published diffusion data on Nb and Ta in rutile

Self-diffusion of O and Ti and tracer diffusion of mono-, di-, tri- and tetravalent ions in rutile has been investigated in a number of studies (review by van Orman and Crispin, 2010). The pentavalent cations, however, have not been studied in great detail, despite their high abundance in natural rutile (Zack et al., 2004; Meinhold, 2010) and their importance for technical applications (Sheppard et al., 2007b). Sheppard et al. (2007a, 2009) have investigated Nb diffusion in pure and Nb-doped rutile at oxidising conditions ($fO_2 = \text{air}$). In both cases they found diffusivities slightly slower than those reported for Ti self-diffusion in rutile under the same conditions. However, their experiments were affected by recrystallisation of the diffusion couple and they could only use certain sections of the analysed profiles that they interpreted as diffusion controlled. The results of these studies have been rejected by other workers (van Orman and Crispin, 2010). No data on Ta diffusion (or any other pentavalent ion) in rutile have been published to date.

In this paper, we present the results of a series of experiments on Nb and Ta diffusion in rutile over a wide temperature range at oxidation conditions relevant for geologic processes.

1.3. Substitution of Nb and Ta in rutile

The incorporation of Nb and Ta into the mineral structure of rutile has been the centre of attention in a number of studies in the mineralogical and geochemical sciences, as well as in material science. Most geochemical studies treat rutile as stoichiometric TiO_2 and search for substitution mechanisms that charge balance the incorporation of pentavalent Nb and Ta into octahedral Ti sites, where they replace tetravalent Ti. The dominant substitution mechanism for Nb and Ta in rutile in equilibrium with natural silicate melts is probably a coupled substitution involving trivalent

cations, such as $Al^{3+} + Nb^{5+} = 2Ti^{4+}$ (Hornig and Hess, 2000; Klemme et al., 2005; Xiong et al., 2011). It has also been suggested that Nb and Ta may be substituting for octahedral Ti charge balanced by the creation of octahedral Ti vacancies, i.e., $4Nb^{5+} + \square = 5Ti^{4+}$ (Klemme et al., 2005; Xiong et al., 2011). However, cation vacancies are rare in the rutile structure at geologically relevant conditions, and become only relevant at fO_2 much higher than 10^5 Pa (Sasaki et al., 1985; Nowotny et al., 2008). The cation vacancy mechanism is therefore not likely to be relevant for rutile in geologic settings.

Rutile is close to stoichiometric TiO_2 at oxygen partial pressure of air at atmospheric pressure ($fO_2 = 20$ kPa). However, at reducing conditions, relevant to geologic settings, a number of defects become more frequent and rutile is better represented by the formula TiO_{2-x} (Sasaki et al., 1985; Nowotny et al., 2008). The dominant defects are interstitial Ti^{3+} , interstitial Ti^{4+} and O vacancies (Nowotny et al., 2006, 2008). The density of O vacancies is high and whereas it is largely independent of fO_2 at oxidising conditions, it increases with decreasing fO_2 at low oxygen fugacity (Nowotny et al., 2008). At constant temperature, the density of tri- and quadrivalent Ti interstitials increases by ~ 2.5 orders of magnitude between oxidising (air) and reducing conditions (i.e., at the fayalite=magnetite + quartz buffer, FMQ) (Nowotny et al., 2008). At oxygen fugacities relevant for geological conditions (fO_2 between the iron-wustite and haematite–magnetite buffers), natural rutile is hardly translucent and has a metallic lustre. This is due to the delocalisation of electrons and the narrowing of the band gap between the valence band and the conduction band, turning rutile (TiO_{2-x}) into a semiconductor (Nowotny et al., 2008). Pure rutile is translucent and almost colourless at $fO_2 = \text{air}$ and is an electric insulator with a large band gap (Nowotny et al., 2008; Colasanti et al., 2011). At fO_2 of the haematite–magnetite buffer (and below) pure rutile acquires a deep blue colour due to the presence of significant trivalent Ti and the Ti^{3+} – Ti^{4+} charge transfer absorption (Colasanti et al., 2011). The high density of vacancies and the delocalisation of electrons facilitates the incorporation of pentavalent cations without the need for charge-compensating trivalent cations and it enables the diffusion of the aliovalent Nb and Ta into pure rutile. Charge balance of Nb^{5+} and Ta^{5+} on octahedral Ti sites and interstitial sites is provided by O vacancies over a wide range of fO_2 , and may be expressed by the substitution $2Nb^{5+} + O^{2-} = 2Ti^{4+} + \square^0$ (where \square^0 is an O vacancy) or $Nb_M^{5+} + Ti_i^{3+} = Ti_M^{4+} + Ti_i^{4+}$ (where M and i are metal and interstitial sites, respectively). Diffusion coefficients for self-diffusion of O and Ti in rutile (van Orman and Crispin, 2010) are significantly higher than the coefficients for Nb and Ta (this study; Fig. 3) and are therefore not limiting the diffusivities of the pentavalent ions.

It has also been suggested that Nb incorporation into rutile and the fractionation of Nb/Ta in nature could be caused by a partial reduction of Nb to trivalent Nb (Hornig and Hess, 2000). However, the existence of significant Nb^{3+} in rutile or silicate melt has been disproved by experimental work over a wide range of fO_2 (Klemme et al., 2005; Burnham et al., 2012). The relative partitioning of Nb and Ta between rutile and melt is independent of fO_2 (Klemme et al., 2005), and XANES spectroscopy on glasses over a large range in T , P and fO_2 demonstrated that Nb and Ta were exclusively present in the pentavalent state (Burnham et al., 2012).

2. Experimental methods

In this study, two different experimental setups were employed to determine diffusivities of Nb and Ta in crystallographically oriented rutile: (1) Thin film diffusion couples were prepared by pulsed laser deposition (Dohmen et al., 2002a) and annealed in

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