Nb-Ta fractionation in peraluminous granites: A marker of the magmatic-hydrothermal transition

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ABSTRACT

In their late stages of evolution, peraluminous granitic melts exsolve large amounts of fluids which can modify the chemical composition of granitic whole-rock samples. The niobium/tantalum (Nb/Ta) ratio is expected to decrease during the magmatic differentiation of granitic melts, but the behavior of both elements at the magmatic-hydrothermal transition remains unclear. Using a compilation of whole-rock geochemical data available in the literature, we demonstrate that fractional crystallization alone is not sufficient to explain the distribution of Nb-Ta in most peraluminous granites. However, we notice that most of the granitic samples displaying evidence of interactions with fluids have Nb/Ta < 5. We propose that the decrease of the Nb/Ta ratio in evolved melts is the consequence of both fractional crystallization and sub-solidus hydrothermal alteration. We suggest that the Nb/Ta value of ~5 fingerprints the magmatic-hydrothermal transition in peraluminous granites. Furthermore, a Nb/Ta ratio of ~5 appears to be a good marker to discriminate mineralized from barren peraluminous granites.

INTRODUCTION

In granitic systems, the magmatic-hydrothermal transition separates a purely magmatic system dominated by a crystal-melt interaction from a system dominated by a crystal–melt–magmatic fluid phase interaction (Halter and Webster, 2004). Hydrothermal activity in peraluminous granites can be either localized, as evidenced by pegmatites and/or quartz veins, or pervasive, leading to significant element mobility and, in the most extreme cases, to the formation of greisens (Pirajno, 2013). These alteration events occur during the sub-solidus stage of granitic magma emplacement and may lead to the deposition of economically significant mineralization such as tin (Sn) or tungsten (W).

Niobium (Nb) and tantalum (Ta) are lithophile elements considered to be "geochemical twins" because they have the same charge and a similar ionic radius. As a result they have similar geochemical properties and should not be fractionated during most geological processes (Goldschmidt, 1937). However, Nb/Ta ratios are variable in several types of igneous rocks, more particularly in granites (<2–25; Green, 1995). Some authors have demonstrated that the Nb/Ta ratios decrease in granites during fractional crystallization (Raimbault et al., 1995; Linnen and Keppler, 1997; Stepanov et al., 2014). Other studies have suggested that Nb and Ta could be fractionated in evolved peraluminous granites during the interaction with late magmatic fluids (Dostal and Chatterjee, 2000; Tartèse and Boulvais, 2010; Ballouard et al., 2015; Dostal et al., 2015).

In order to decipher the specific role of magmatic and hydrothermal processes in the evolution of Nb/Ta ratios, we compiled the whole-rock geochemical data available in the literature for peraluminous granites having various mineralogy and geochemical properties and emplaced in various tectonic contexts at different times.

PRESENT KNOWLEDGE

Magmatic Behavior of Nb-Ta

In highly evolved granites and pegmatites, columbite [$(Fe,Mn)Nb_2O_6$] and tantalite [$(Fe,Mn)Ta_2O_6$] are the main mineral phases hosting Nb and Ta. Experimental studies have shown that the solubility of these two minerals in granitic melts increases with temperature but decreases with increasing the aluminum saturation index (ASI), a parameter related to the degree of polymerization of the melt (e.g., Linnen and Keppler, 1997).

Partial melting can produce granitic peraluminous melts with Nb/Ta ratios higher or lower than that of their source, depending on the temperature (Stepanov et al., 2014). Melts formed during high-temperature anatexis tend to have high Nb/Ta ratios, as a result of the complete consumption of biotite and the high abundance of titanium (Ti)-bearing oxides in the residue, which preferentially incorporate Ta over Nb (Stepanov et al., 2014). Conversely, low-temperature partial melting generates melts with low Nb/Ta ratios because residual biotite preferentially incorporates Nb over Ta (Stepanov et al., 2014). Because biotite and Ti-bearing minerals can also be involved during the differentiation of granitic melts, fractional crystallization also changes the Nb/Ta ratios: Nb/Ta increases during high-temperature fractional crystallization of Ti-rich melts due to the preferential saturation of Ti-oxide minerals over biotite, whereas Nb/Ta ratios decrease during low-temperature differentiation of granitic melts due to the fractionation of biotite and/or muscovite (Stepanov et al., 2014). In the most evolved peraluminous melts, the lower solubility of manganocolumbite ($MnNb_2O_6$) compared with manganotantalite ($MnTa_2O_6$) also enhances the decrease of the Nb/Ta ratio in the melt (Linnen and Keppler, 1997). In lithium-fluorine (Li-F) granites, melt inclusions indicate a separation of an immiscible F-rich hydrosaline melt that can induce a decrease of the Nb and Ta contents in the residual melt (Badanina et al., 2010).

Nb-Ta Behavior in Hydrothermal Systems

Nb and Ta are generally poorly soluble in aqueous solutions, Ta being even less soluble than Nb (Zaraisky et al., 2010). Experiments with aqueous F-rich fluids and aluminosilicate melt indicate that Nb and Ta preferentially partition into the melt (Chevychelov et al., 2005). However, the solubility and hydrothermal transfer of Ta and Nb are greatly enhanced in F-rich solutions under reducing conditions (Zaraisky et al., 2010). These experimental results are consistent with the fact that several F-rich cupolas of greisenized peraluminous granites are significantly enriched in both Nb and Ta (e.g., Zaraisky et al., 2009).

VARIATIONS OF WHOLE-ROCK Nb/Ta RATIOS IN PERALUMINOUS GRANITES

We compiled data for peraluminous granites [i.e., with an $Al_2O_3/(CaO + Na_2O + K_2O)$ ratio (A/CNK) >1; excluding aplites and pegmatites], as well as for some greisens, of different ages (Archean to Mesozoic) that were emplaced in various geodynamical contexts (see Table DR1 in the GSA Data Repository[1]).

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[1]GSA Data Repository item 2016069, synthesis of peraluminous granites reported in this study, is available online at www.geosociety.org/pubs/ft2016.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

GEOLOGY Data Repository item 2016069 | doi:10.1130/G37475.1

Nb-Ta Fractionation During Magmatic Processes

As shown in Figure 1, the Nb/Ta ratios in the compiled data are highly variable, between ~15 and ~0.1, and the lowest values are shown by whole rocks displaying the highest Nb and Ta contents. Mica fractionation in granitic melt induces a decrease of the Nb/Ta ratios (Stepanov et al., 2014). Figure 1 also shows our model of the evolution of a melt with initial Ta and Nb contents of 1.5 ppm and 12 ppm (Nb/Ta = 8), respectively. This melt undergoes extraction of a cumulate made of 80 wt% (quartz + feldspar) + 10 wt% muscovite + 10 wt% biotite, using the Rayleigh distillation law and the silicate-melt partition coefficients compiled by Stepanov et al. (2014). The modeling qualitatively reproduces the behaviors of Nb and Ta, but it requires an unrealistic amount of mineral fractionation (>90 wt%) to reach low Nb/Ta ratios of ~2 and Nb and Ta contents of ~20 and 10 ppm, respectively (Fig. 1). The addition

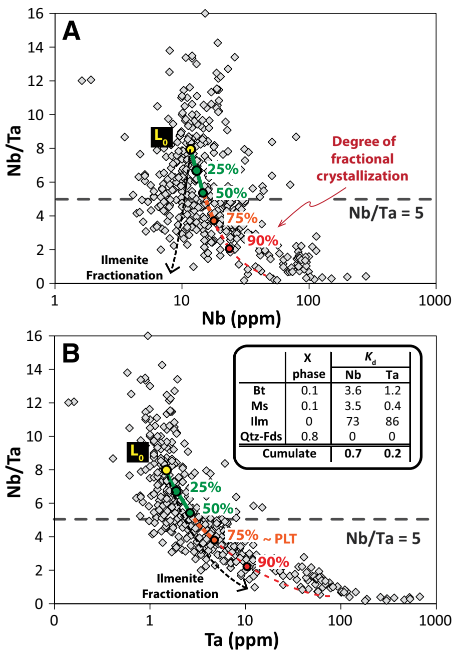

Figure 1. Nb/Ta versus Nb (A) and Ta (B) abundances for peraluminous granites. Colored curves represent model of evolution of Nb and Ta in liquid L_0 (Nb = 12 ppm, Ta = 1.5 ppm, Nb/Ta = 8) during fractionation of assemblage made of 10 wt% biotite + 10 wt% muscovite + 80 wt% (quartz + feldspar). Numbers above curves indicate amount of fractional crystallization. Black dashed line represents same model during fractionation of assemblage composed of 10 wt% biotite + 10 wt% muscovite + 0.5 wt% ilmenite + 79.5 wt% (quartz + feldspar). Bulk partition coefficient (K_d) values used and presented in inset are from Stepanov et al. (2014, and references therein). X phase—proportion of a mineral phase in the cumulate; PLT—particle locking threshold (Vigneresse et al., 1996); Bt—biotite; Ms—muscovite; Ilm—ilmenite; Qtz—quartz; Fds—feldspar.

of 0.5 wt% Fe-Ti oxide (e.g., ilmenite or rutile) in the cumulate, in which Ta and Nb are highly compatible (Stepanov et al., 2014), makes things even worse. Indeed, the fractionation of this cumulate causes a decrease of the Nb content (Fig. 1A), resulting in a trend opposite to the trend displayed by the peraluminous granites.

Crystal-melt fractionation is likely to occur during the crystallization of granitic melts in magmatic bodies (Dufek and Bachmann, 2010) and during magma ascent in dikes (Tartèse and Boulvais, 2010; Yamato et al., 2015). However, numerical modeling shows that the efficiency of crystal-melt segregation in dikes is restricted to cases where crystals represent a low percentage of the total magma volume (<45%; Yamato et al., 2015). Indeed, 70%–75% crystallization marks the particle locking threshold (PLT in Fig. 1B; Vigneresse et al., 1996) where the interstitial residual melt cannot escape from the crystal framework without deformation. The extraction of low-fraction residual melts (with an amount of fractional crystallization >75%) is thus restricted to areas affected by strong shear stress such as magmatic shear zones (Vigneresse et al., 1996) and dike walls, which represent a small percentage of the granites compiled in this study (Fig. 1). The model presented here thus suggests that fractional crystallization alone is not sufficient to explain the behaviors of Nb and Ta in most peraluminous granitic rocks.

Nb-Ta Fractionation during Magmatic-Hydrothermal Processes

Mineralogical Markers

Secondary muscovitization and greisenization occur under sub-solidus conditions during the interaction between crystallized granites and acidic late magmatic fluids (Pirajno, 2013). Figure 2 shows that the Nb/Ta ratios of whole-rock granites and greisens are anti-correlated with the average $MgO/(Na_2O + TiO_2)$ ratios of the muscovite they host (a chemical marker for secondary muscovitization; Miller et al., 1981). This observed anti-correlation suggests that the fluids involved in the secondary muscovitization processes could also be responsible for the decrease of the Nb/Ta whole-rock values. Whole-rock hydrothermal enrichment of Ta during secondary muscovitization is, for example, observed in ongonites (topaz-bearing microleucogranites), and this process is associated with the crystallization of late Ta-rich overgrowth on Nb-Ta oxides (Dostal et al., 2015).

Geochemical Markers

The whole-rock Nb/Ta ratios of peraluminous granites are anti-correlated with their Sn contents, Sn being an element highly mobilized at the magmatic-hydrothermal transition (Fig. 3A): high Sn contents (30–10,000 ppm) are only encountered in granitic samples (or

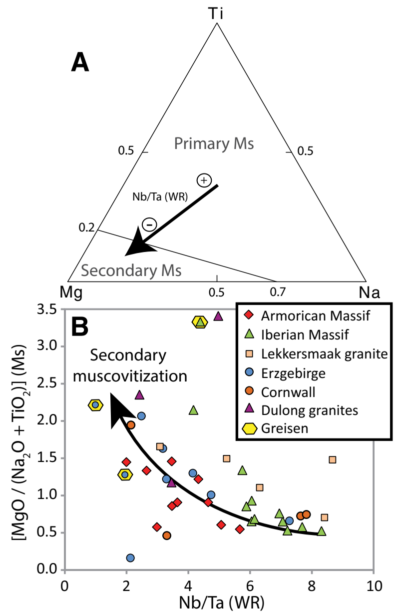

Figure 2. A: Mg-Na-Ti ternary classification diagram of muscovite (Ms) (Miller et al., 1981). B: Diagram reporting evolution of Nb/Ta ratios for whole-rock (WR) samples from different peraluminous granites against average value of $MgO/(Na_2O + TiO_2)$ ratios of their diochtaedral micas.

greisens) with low Nb/Ta (<5). These samples also display high contents of Cs (35–1000 ppm), F (>0.4%–4%), Li (250–2000 ppm), W (10–1000 ppm) and Rb (>500 ppm). Because such incompatible elements have a strong affinity for magmatic fluids, their enrichment is commonly used as a marker of a magmatic-hydrothermal alteration in highly evolved crustal granites. In Figure 3A, the Sn content of granites increases from ~10 to ~1000 ppm. During fractional crystallization, an increase by two orders of magnitude of highly incompatible elements, with a bulk partition coefficient K_d between the mineral phases and the melt close to 0, requires a degree of fractionation of up to 99 wt%. This unrealistic degree of fractionation suggests that hydrothermal processes are also involved. Such enrichments in highly incompatible elements, attributed to interaction with magmatic fluids, have been noticed in the Erzgebirge (Germany and the Czech Republic; Förster et al., 1999), in the South Mountain batholith (Nova Scotia, Canada) (e.g., Dostal and Chatterjee, 2000), and in the Armorican Massif (France; Tartèse and Boulvais, 2010; Ballouard et al., 2015).

Also, the Nb/Ta ratios correlate with the K/Rb ratios (Fig. 3B). Most granites with low Nb/Ta display K/Rb values <150, characteristic of pegmatite-hydrothermal evolution (Shaw, 1968). This tendency is observed in the South Mountain batholith, where it was interpreted as evidence for a magmatic-hydrothermal alteration (Dostal and Chatterjee, 2000).

Finally, the whole-rock Nb/Ta ratios can be compared with the degree of the tetrad effect,

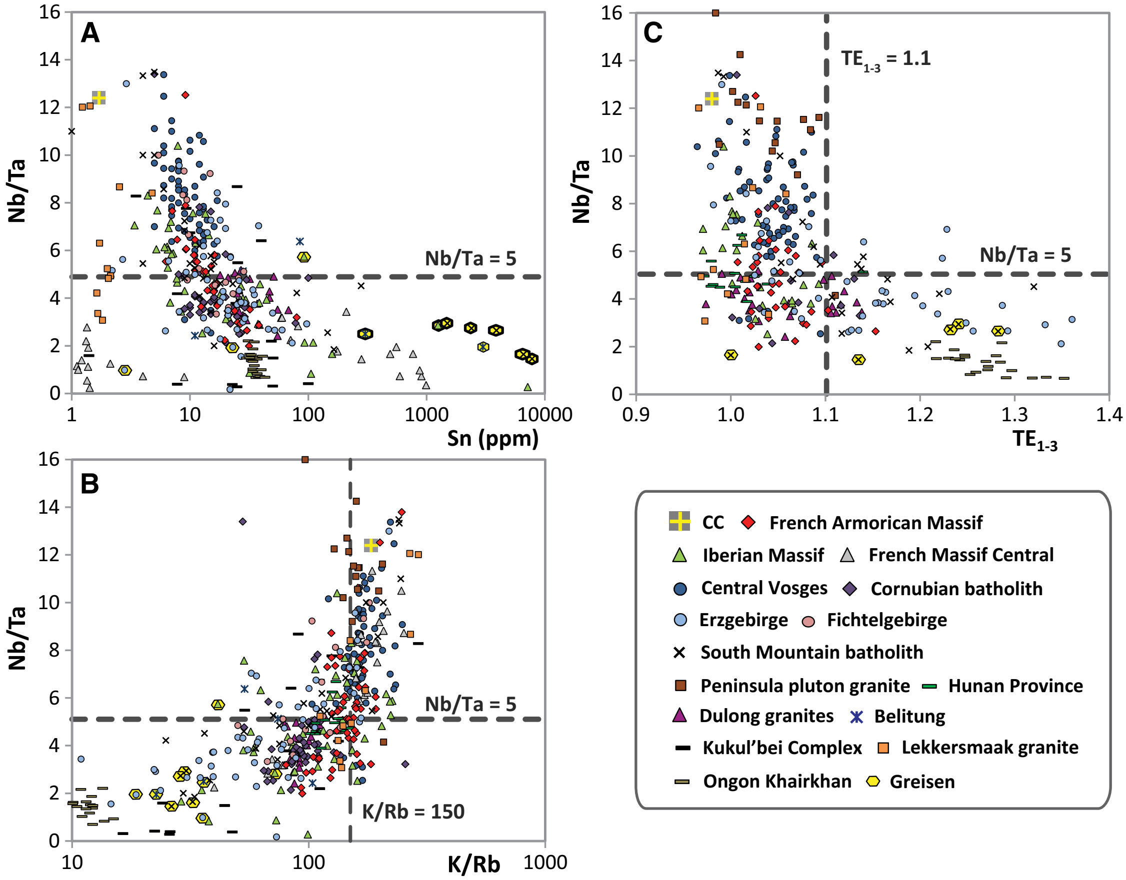

Figure 3. Evolution of Nb/Ta ratios of peraluminous granites as function of selected markers of magmatic-hydrothermal alteration. Degree of tetrad effect (TE_{1-3}) has been calculated using equation of Irber (1999). CC—continental crust composition (from Rudnick and Gao, 2005).

which corresponds to the intra-REE (rare earth element) fractionation observed in the REE patterns of highly fractionated magmatic rocks and hydrothermal precipitates (e.g., Irber, 1999). Although Duc-Tin and Keppler (2015) have recently suggested that the tetrad effect could result from monazite and xenotime fractionation, most authors have argued that such REE patterns actually reflect a selective complexation of REE during the interaction of granitic melts with F-rich and Cl-rich aqueous fluids (e.g., Bau, 1996; Irber, 1999; Monecke et al., 2007). Irber (1999) quantified the degree of tetrad effect (TE_{1-3}) by determining the deviation of the first and third tetrad of granite REE patterns from a hypothetical tetrad effect–free REE pattern. The large majority of the samples with a significant tetrad effect (TE_{1-3} > 1.1) are also characterized by low Nb/Ta ratios (<~5) (Fig. 3C).

Metallogenic Markers

The Nb/Ta ratio is commonly compared to the zirconium/hafnium (Zr/Hf) ratio, as the latter has been proposed as a marker of either magmatic-hydrothermal interactions (Bau, 1996) or fractional crystallization (Linnen and Keppler, 2002; Claiborne et al., 2006). The Zr/Hf ratio is a geochemical indicator of the fertility of granitic rocks, as a Zr/Hf ratio <~25 (corresponding to the lower limit of the charge and radius control [CHARAC] range; Bau, 1996) is expected in granites where Sn, W, Mo, Be, and Ta mineralization is described (Zaraisky et al., 2009). In a Nb/Ta versus Zr/Hf diagram (Fig. 4), most barren granites plot in the field defined by 26 < Zr/Hf < 46 (CHARAC range of Bau, 1996) and 5 < Nb/Ta < 16, whereas peraluminous granites associated with Sn, W, and/or U deposits have comparable Zr/Hf ratios between 18 and 46 and Nb/Ta ratios <5. Rare-metals granites are characterized by even lower Zr/Hf ratios (<18) with Nb/Ta ratios that are still <5.

From the diagrams presented in Figures 2, 3, and 4, we highlight significant mineralogical (secondary muscovitization), geochemical (Sn contents, K/Rb ratio, tetrad effect), and metallogenic (Sn-W-U and rare-metal mineralization) evidence that magmatic-hydrothermal processes account for the decrease of the Nb/Ta ratio in peraluminous granites. In reduced F-rich aqueous solutions, the solubility and hydrothermal transfer of Nb and Ta are greatly enhanced by up to three orders of magnitude with some fractionation of Nb over Ta, Ta being less soluble (Zaraisky et al., 2010). Therefore, the sub-solidus alteration of peraluminous granites leads to deposition of a mineral assemblage with Ta > Nb. Consequently, we suggest here that the decrease of the Nb/Ta ratios to values <~5 in peraluminous granites reflects the concomitant effect of fractional crystallization and sub-solidus hydrothermal alteration, likely by F-rich acidic reduced fluids of magmatic origin.

Nb/Ta ~5: A Critical Ratio for Granite Petrogenesis and Mineral Exploration Strategies

Peraluminous granites that show significant evidence of interaction with fluids (i.e., Sn and Cs contents >30 ppm and >35 ppm,

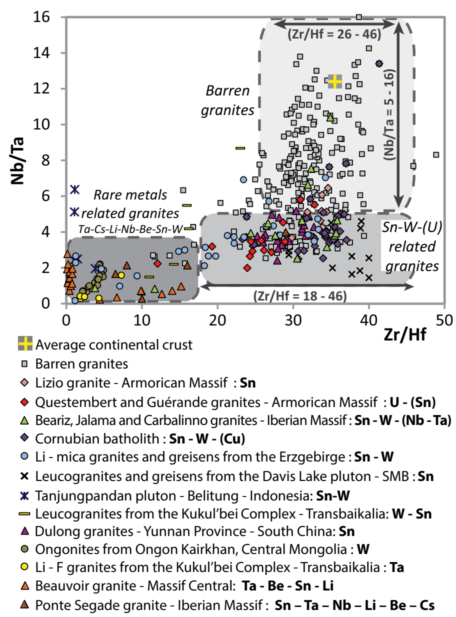

Figure 4. Nb/Ta versus Zr/Hf diagram differentiating barren and ore-bearing peraluminous granites.

respectively, K/Rb values <150, and/or TE_{1-3} > 1.1) systematically display Nb/Ta ratios <5. In such cases, we suggest that Nb/Ta of ~5 represents a threshold between a purely magmatic system (Nb/Ta > 5) and a magmatic-hydrothermal one (Nb/Ta < 5).

Finally, the use of an approximate cut-off value of 5 for the Nb/Ta ratio as a marker of the magmatic-hydrothermal transition in peraluminous granites bears some implications for exploration strategies as it can also help to define the economic potential of these granites. Figure 4 demonstrates that a Nb/Ta ratio of 5 can be used as a geochemical indicator to differentiate barren granites from granites that are spatially related to Sn-W(-U) or rare-metals mineralization. Because whole-rock trace element analyses (including Nb and Ta) are routinely performed in most laboratories around the world, the simple calculation of whole-rock Nb/Ta ratios can therefore help exploration geologists define potential targets for Sn-W(-U) and rare-metal deposits.

CONCLUSION

The mineralogical and geochemical evidence of a fluid interaction recorded in granitic whole-rock samples indicates that the value Nb/Ta of ~5 is a good marker of the magmatic-hydrothermal transition in peraluminous granites. The decrease of the Nb/Ta ratio in peraluminous granites is associated with an increase of the degree of secondary muscovitization and with geochemical and metallogenic evidence of hydrothermal interactions, suggesting that a subsolidus alteration is involved in the fractionation of Nb-Ta. To further constrain the mechanisms involved in the fractionation of the Nb/Ta ratios in peraluminous granites at the magmatic-hydrothermal transition, mineral-scale analyses would now be required. From an exploration point of view, and based on the large compilation of data presented in this study, the Nb/Ta ratio appears to be a good geochemical indicator to differentiate barren from ore-bearing peraluminous granites.

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