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Abstract:	In their late stages of evolution, peraluminous granitic melts exsolve a large amounts of fluids which can modify the chemical composition of granitic whole rocks samples. The Nb/Ta ratio is expected to decrease during 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 fluid, regardless of their age or their emplacement conditions, have Nb/Ta < 5. We propose that the decrease of the Nb/Ta ratio in highly evolved melts is the consequence of both fractional crystallization and sub-solidus magmatic-hydrothermal alteration. We suggest that the value Nb/Ta = 5 in peraluminous granite fingerprints the magmatic-hydrothermal transition. Furthermore, a Nb/Ta ratio of 5 appears to be a good marker to discriminate mineralized from barren peraluminous granites.
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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 a large amounts of fluids which can modify the chemical composition of granitic whole rocks samples. The Nb/Ta ratio is expected to decrease during 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 fluid, regardless of their age or their emplacement conditions, have $\text{Nb/Ta} < 5$. We propose that the decrease of the Nb/Ta ratio in highly evolved melts is the consequence of both fractional crystallization and sub-solidus magmatic-hydrothermal alteration. We suggest that the value $\text{Nb/Ta} = 5$ in peraluminous granite fingerprints the magmatic-hydrothermal transition.

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 crystal-melt interaction from a system dominated by crystal-melt-magmatic fluid phase interaction (Halter and Webster, 2014). 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). Such alteration events occur during the sub-solidus stage of the granitic melt emplacement and may lead to the deposition of economically significant mineralization such as Sn or W.

Nb and Ta are lithophile elements considered as “geochemical twins” because they have the same charge and similar ionic radius. As a result they have similar geochemical properties and should not be fractionated during most geological processes (Goldschmidt, 1937). However, in granitic rocks, Nb/Ta ratios are highly variable ($< 2 - 25$; 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 highly 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 the magmatic and hydrothermal processes on the evolution of the Nb/Ta ratios, we compiled whole rock geochemical data available in the literature for peraluminous granites emplaced at different times and in various tectonic contexts. Based on these data, we show that fractional crystallization of granitic melts alone is not sufficient to account for the Nb-Ta behavior observed in most peraluminous granites and that hydrothermal processes are necessarily involved.

PRESENT KNOWLEDGE

Magmatic behavior of Nb-Ta

In highly evolved granites and pegmatites, columbite ((Fe,Mn)Nb₂O₆) and tantalite ((Fe, Mn)Ta₂O₆) 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 Aluminium Saturation Index (ASI), a parameter related to the degree of polymerization of the melt (Linnen and Keppler, 1997; Aseri et al., 2015). The Li content of granitic melts also increases the solubility of columbite and tantalite (Linnen, 1998; Aseri et al., 2015). Partial melting can produce granitic peraluminous melts with Nb/Ta ratios higher or lower than their source, depending on the temperature. 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 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 incorporates preferentially Nb over Ta (Stepanov et al., 2014). Since biotite and Ti-bearing minerals can also be involved during differentiation of

granitic melts, fractional crystallization also changes 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 to manganotantalite (MnTa_2O_6) also enhances the decrease of the Nb/Ta ratio in the melt (Linnen and Keppler, 1997). Melt inclusions in Li-F granites (Orlovka massif, Eastern Transbaikalia) 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 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 in 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 a A/CNK ratio > 1) as well as for some greisens of different ages (Archean to Mesozoic) and emplaced in various geodynamical contexts (see Table DR1 in the GSA Data Repository).

Nb-Ta fractionation during magmatic processes

In Figure 1, the Nb/Ta ratios are highly variable between ~15 and ~0 when reported as a function of Nb and Ta, the lowest values being recorded 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). In Figure 1, we modeled the evolution of a melt with an initial Ta and Nb contents of 1.5 ppm and 12 ppm (Nb/Ta = 8), respectively, undergoing fractionation of a cumulate made of 80 wt.% (quartz + feldspar) + 10 wt.% muscovite + 10wt.% 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 rate of mineral fractionation (over 90 wt.%) to reach low Nb/Ta ratios around 2 and Nb and Ta contents around 20 and 10 ppm, respectively (Fig. 1). The addition of 0.5 wt.% Fe-Ti oxide (e.g. ilmenite or rutile) in the cumulate, in which Ta and Nb are highly compatibles (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.

If crystal-melt fractionation is likely to occur during the crystallization of granitic melts in magmatic bodies (Dufek and Bachmann, 2010) and during the magma ascent in dykes (Tartèse and Boulvais, 2010; Yamato et al., 2012), numerical modeling shows that the efficiency of crystal-melt segregation is restricted to cases where crystals represent a low percentage of the

total magma volume (Yamato et al., in press). Indeed, 70-75% of crystallization marks the particle locking threshold (PLT in Figure 1B, Vigneresse et al., 1996) where the liquid becomes totally locked, precluding any crystal-melt segregation. The model presented here thus suggests that fractional crystallization alone is not sufficient to explain the behaviors of Nb and Ta in 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). The Figure 2 shows that the Nb/Ta ratios of whole rock granites and greisens are anti-correlated with the average $\text{MgO}/(\text{Na}_2\text{O} + \text{TiO}_2)$ 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) from the Ongon Kairkhan (Mongolia) 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, an element highly mobilized at the magmatic-hydrothermal transition (Fig. 3A): high Sn contents above ~30 ppm are only encountered in granitic samples (or greisens) with low Nb/Ta (< 5).

These samples also display high contents in Cs, F, Li, W and Rb. Because such incompatible elements present a strong affinity for magmatic fluids, their enrichment is commonly used as a marker of a magmatic-hydrothermal alteration in highly evolved crustal granites. Indeed, increasing the abundance of highly incompatible elements, with a bulk partition coefficient K_d between the mineral phases and the melt close to 0, by two orders of magnitude, as observed in Figure 3A (from ~10 to ~1000 ppm), during fractional crystallization requires a unrealistic degree of fractional crystallization up to 99 wt.%, suggesting that hydrothermal processes are also involved. Such enrichments in highly incompatible element, attributed to interaction with magmatic fluids, have been noticed in the Erzgebirge massif (Förster et al., 1999), in the South Mountain Batholith (e.g. Dostal and Chatterjee, 2000), or in the French Armorican Massif (Tartèse and Boulvais, 2010; Ballouard et al., 2015).

The Nb/Ta ratios also correlate with the K/Rb ratios (Fig. 3B). Most granites with low Nb/Ta display K/Rb values lower than 150, characteristic of the pegmatite-hydrothermal evolution (Shaw, 1968). Such a 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 magnitude of the tetrad effect, which corresponds to the intra-REE fractionation observed in the REE patterns of highly fractionated magmatic rocks and hydrothermal precipitates (e.g. Irber, 1999). Although Duc-Tin and Kepller (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 the REE during the interaction of granitic melts with F- 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 the third tetrad of granites REE-patterns from a hypothetical tetrad effect-free REE pattern. The large majority of the samples with significant tetrad effect ($TE_{1-3} > 1.1$) are also characterized by low Nb/Ta ratios below ~5 (Fig.3C).

Metallogenic markers

The Nb/Ta ratio is commonly compared to the Zr/Hf ratio, as the latter has been proposed as either a marker of magmatic-hydrothermal interactions (Bau, 1996) or of 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 Zr/Hf ratios below ~25 (corresponding to the lower limit of the CHARGE and RADIUS Control range; Bau, 1996) are expected in granites where Sn, W, Mo, Be and Ta mineralization are described (Zaraisky et al., 2009). In a Nb/Ta vs. Zr/Hf diagram (Fig. 4), most barren granites plot in the field defined by $26 < Zr/Hf < 46$ (CHARAC range of Bau, 1996) and by $5 < Nb/Ta < 16$, whereas peraluminous granites associated with Sn, W and/or U deposits have $18 < Zr/Hf < 46$ with Nb/Ta ratio lower than 5. Rare metals granites are characterized by even lower Zr/Hf ratios (< 18) with Nb/Ta ratios that are still lower than 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. The solubility

and hydrothermal transfer of Nb and Ta are greatly enhanced, by up to three orders of magnitude, in reduced F-rich aqueous solutions (Zaraisky et al., 2010). Therefore, in peraluminous granites affected by sub-solidus alteration, the Nb/Ta ratios can be lowered by an increase of the Ta content in Ta-Nb-bearing minerals due to the lower mobility of Ta compared to Nb in aqueous solutions. As a consequence, we suggest here that the decrease of the Nb/Ta ratios to values lower than ~5 in peraluminous granites reflects the concomitant effect of fractional crystallization and sub-solidus magmatic-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

The peraluminous granite whole rock samples with Nb/Ta ratios lower than 5 show significant evidence of interaction with fluids. We suggest that Nb/Ta = 5 represents a threshold between a purely magmatic system (Nb/Ta > 5) and a magmatic-hydrothermal system (Nb/Ta < 5). Taking a 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. Indeed, Figure 4 demonstrates that a Nb/Ta ratio of 5 can be used as a geochemical indicator to differentiate barren granites from granites spatially related to Sn-W-(U) or rare metals mineralization. Since whole rock trace element analyses (including Nb and Ta) are routinely performed in most laboratories around the world, the simple calculation of whole rock sample Nb/Ta ratios can, therefore, help exploration geologists to define potential targets for Sn-W-(U) and rare metals deposits.

CONCLUSION

The mineralogical and geochemical evidence of fluid interaction recorded in granitic whole rock samples, indicate that the value $Nb/Ta = 5$ 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 sub-solidus alteration is involved in the fractionation of Nb-Ta. To further constrain the mechanisms involved in the fractionation of 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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FIGURE CAPTIONS

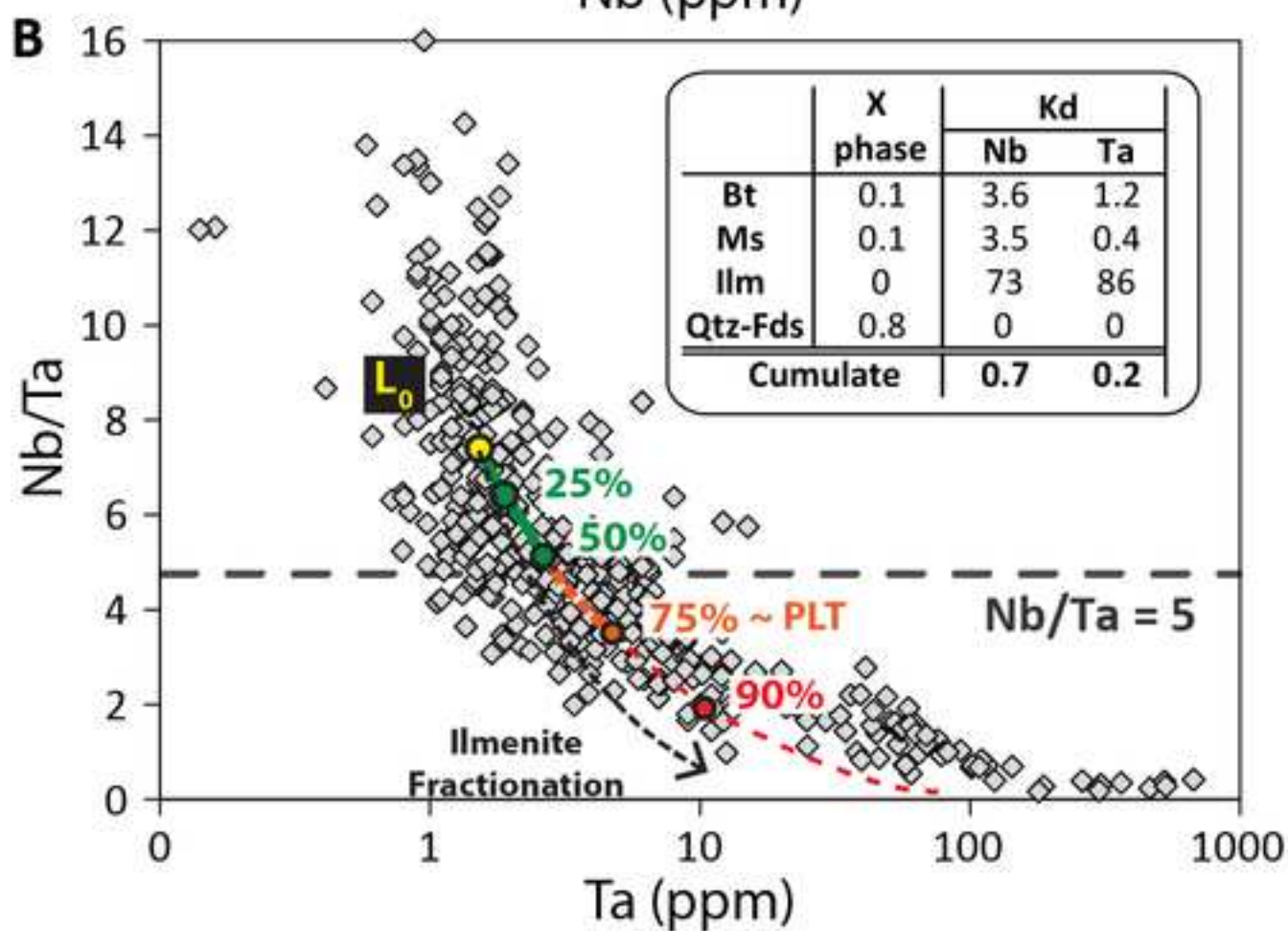
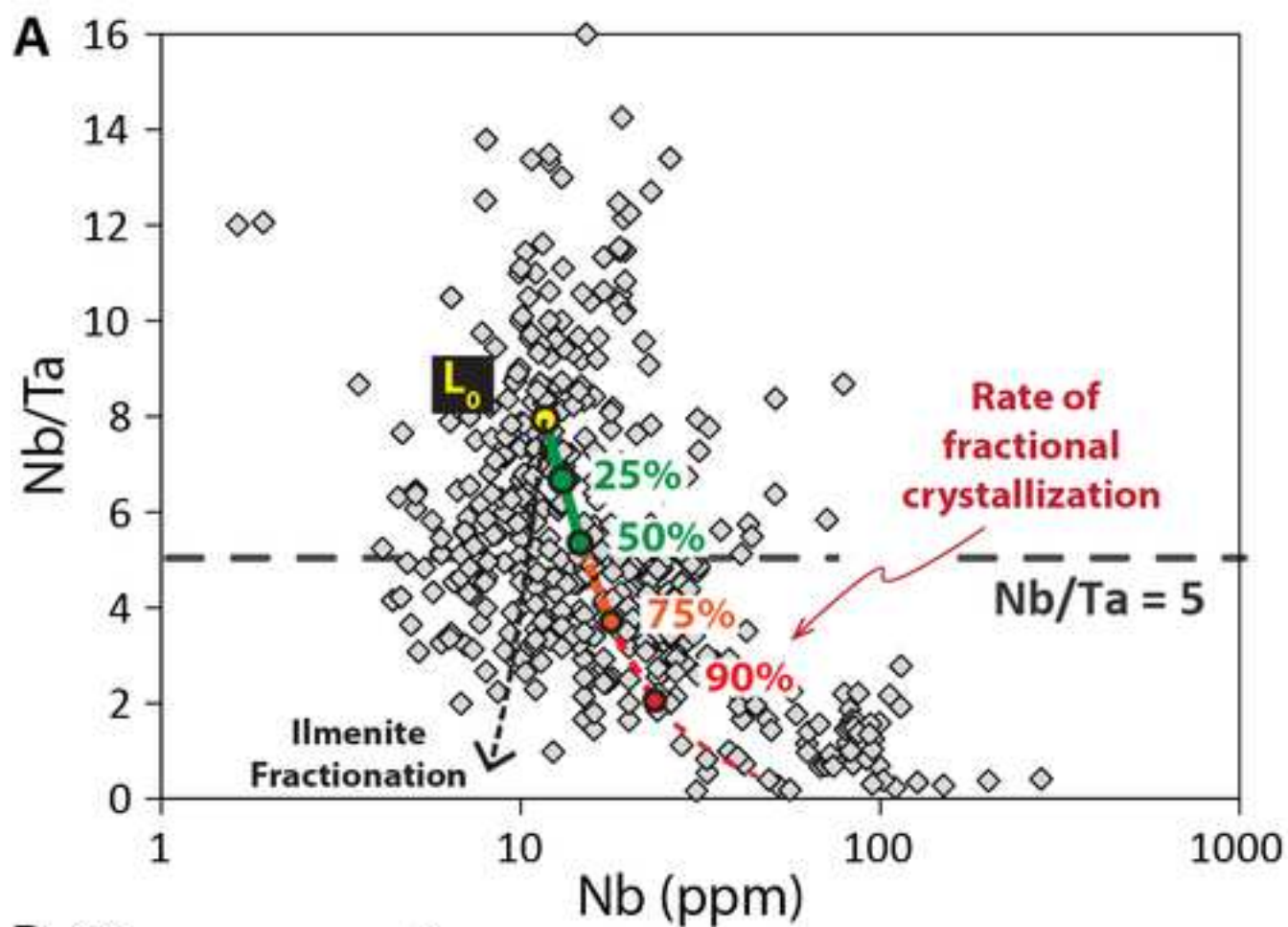
Figure 1. Nb/Ta vs. (A) Nb and (B) Ta abundances for peraluminous granites. The colored curves represent a model of evolution of Nb and Ta in a liquid L_0 (Nb = 12 ppm, Ta = 1.5 ppm, Nb/Ta = 8) during the fractionation of an assemblage made of 10 wt.% biotite + 10 wt.% muscovite + 80 wt.% (quartz + feldspar). The numbers above the curves indicate the amount of fractional crystallization. The black dashed line represents the same model during the fractionation of an assemblage composed of 10 wt.% biotite + 10 wt.% muscovite + 0.5 wt.% ilmenite + 79.5 wt.% (quartz + feldspar). The K_d used and presented in the table in inset in the diagram are from Stepanov et al. (2014) and reference therein. PLT: Particle Locking Threshold (Vigneresse et al., 1996).

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

Figure 3: Evolution of Nb/Ta ratios of peraluminous granites as a function of selected markers of magmatic-hydrothermal alteration. The degree of tetrad effect (TE_{1-3}) has been calculated using the equation of Irber (1999). CC: Continental Crust composition (from Rudnick and Gao, 2005).

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

357 ¹GSA Data Repository item 2015xxx, [[Synthesis of peraluminous crustal granites reported in](#)
358 [this study](#)], is available online at www.geosociety.org/pubs/ft2015.htm, or on request from
359 editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301,
360 USA.



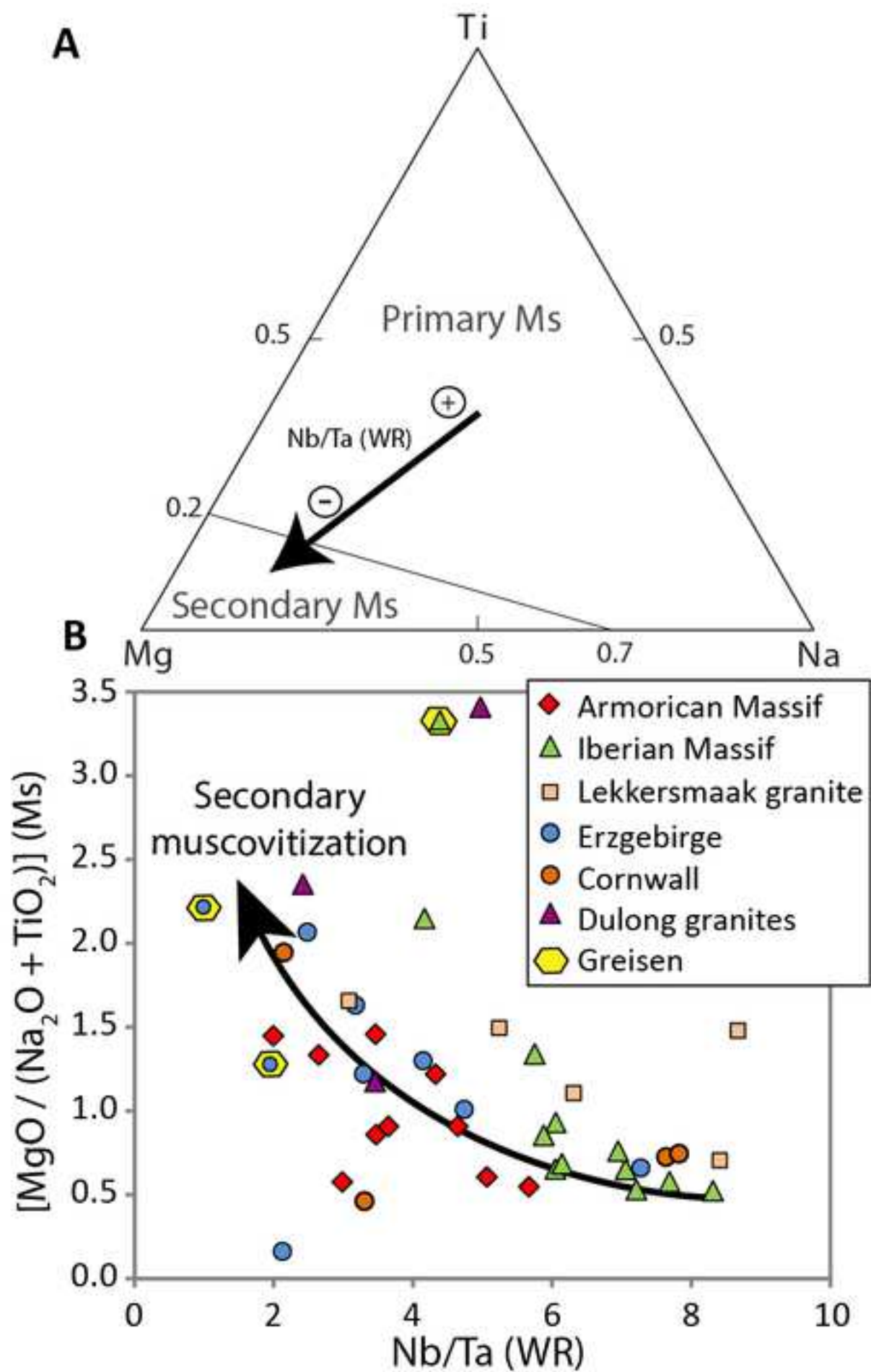
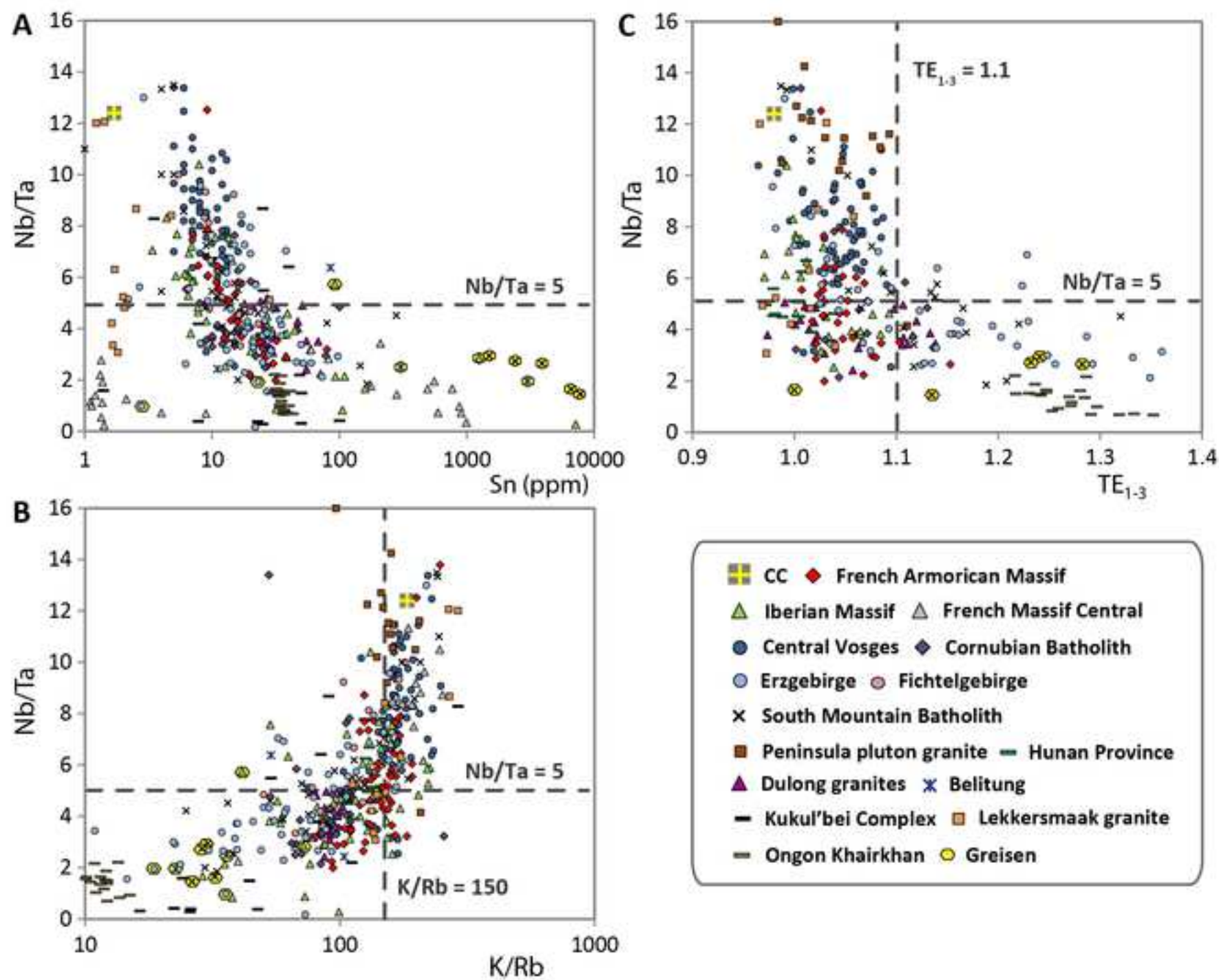
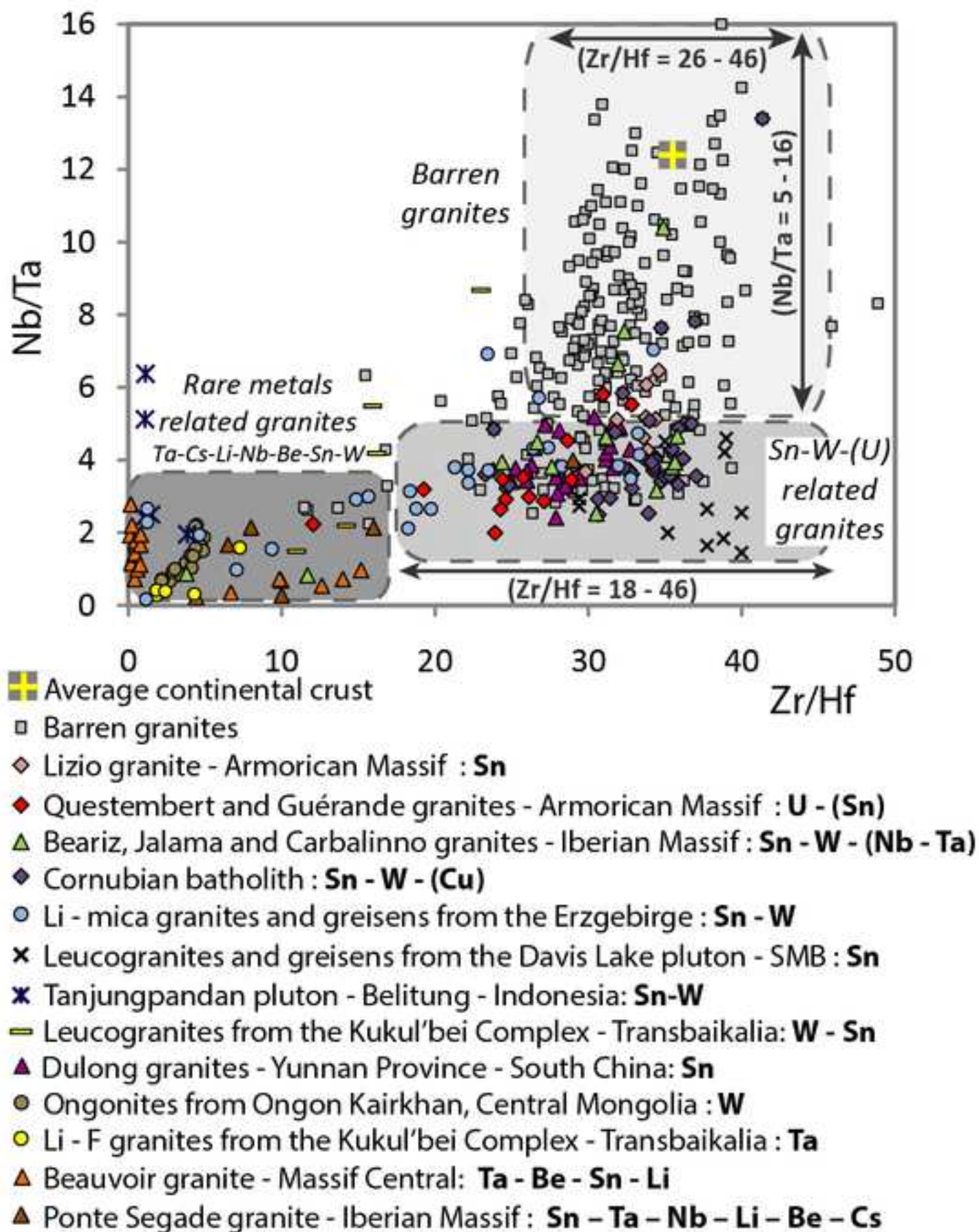


Figure 3

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Location	Igneous province	Granite	Age	Related deposit		Reference
Western Europe	French Armorican Massif	Lizio	ca. 316 Ma	Sn		Tartèse and Boulvais, 2010
		Questembert	ca. 316 Ma	(U)	U leached during hydrothermal alteration	Tartèse and Boulvais, 2010; Tartèse et al., 2013
		Guérande	ca. 310 Ma	U - Sn	Apical zone facies	Ballouard et al., 2015
		Huelgat	Late Carboniferous	-		Georget, 1986
	Iberian massif	Brignogan	Late Carboniferous	-		Georget, 1986
		Ponte Segade	Late Carboniferous	Sn - Ta - Nb -Li -Be -Cs		Canosa et al., 2012
		Jalama	Late Carboniferous	Sn-W-(Nb-Ta)		Ramírez and Grundvig, 2000
		Beariz (Avion)	Late Carboniferous	-		Gloaguen, 2006
		Beariz	Late Carboniferous	Sn -W		Gloaguen, 2006
		Boboraz	Late Carboniferous	-		Gloaguen, 2006
		Carballino	Late Carboniferous	Sn-W-(Nb-Ta)		Gloaguen, 2006
		Irixo	Late Carboniferous	-		Gloaguen, 2006
		Pedrobernardo	c.a. 300 Ma	-		Bea et al., 1994
		S. Mamede de Ribatua	Hercynian	Sn-W		Nieva, 2002
		Panasqueira	Hercynian	Sn-W		Nieva, 2002
	French Massif Central	Colette	ca. 310 Ma	-		Raimbault et al., 1995
		Beauvoir	ca. 310 Ma	Ta - Be -Sn - Li		Raimbault et al., 1995
		Guéret	ca. 350 Ma	-		Rolin et al., 2006
	Cornubian Batholith	-	295-275 Ma	Sn - W – (Cu)		Chappell and Hine, 2006; Müller et al., 2006
	Erzgebirge	-	Late Carboniferous - Early Permian	Sn - U -W	Li - mica granites and greisens	Förster et al., 1999; Breiter, 2012; Štemprok et al., 2005
	Fichtelgebirge	-	Late Carboniferous - Early Permian	?		Hecht et al., 1997
	Central Vosges	-	329 - 322 Ma	-		Tabaud et al., 2015
Nova Scotia - Canada	South Mountain Batholith	-	Late Devonian	-		MacDonald et al., 1992
		Davis Lake	Late Devonian	Sn	Topaz muscovite leucogranites and greisens	Dostal and Chatterjee, 1995
South Africa	Kaapvaal Craton	Lekkersmaak granite suite	ca. 2800 Ma	-		Jaguin, 2012
	Cape Granite Suite	Peninsula pluton	556-534 Ma	-		Farina et al., 2012
South China	Hunan Province	Indosinian granites	210 – 243 Ma	?		Wang et al., 2007
	Yunnan Province	Dulong granites	ca. 90 Ma	Sn		Xu et al., 2015
Indonesia	Belitung	Tanjungpandan pluton	ca. 215 Ma	Sn - W		Schwartz and Surjono, 1990
Eastern Transbaikalia	-	Kukul’bei complex	ca. 140 Ma	W – Sn Ta	Muscovite leucogranites (phase 2) Albite-amazonite Li-F granites (phase 3)	Zaraisky et al., 2009
Central Mongolia	-	Ongon Khairkhan	Ca. 120 Ma	W	Ongonites (topaz bearing albite-rich microleucogranites)	Dostal et al., 2015

Table DR1: Synthesis of the peraluminous granites reported in this study with their location, their age, their associated metal deposits when available and the corresponding references.

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