Geochemical Perspectives Letters

Fractionation of Nb/Ta during subduction of carbonate-rich sediments

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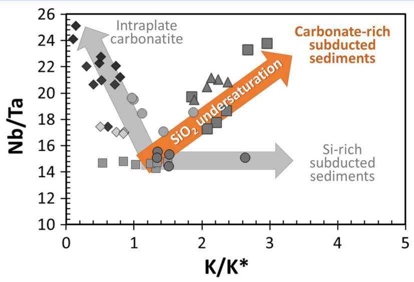
https://doi.org/10.7185/geochemlet.2410

Abstract



We report high precision high field strength element (HFSE) concentrations of Italian Plio-Quaternary mafic magmas. Silica-undersaturated rocks of the Roman magmatic province show high Nb/Ta. Instead, earlier silica-oversaturated rocks of the Tuscan magmatic province have unfractionated Nb/Ta. We show evidence that the high Nb/Ta of Roman magmas reflects subduction-derived, carbonate-rich melts. Similar melts may also account for high Nb/Ta in other silica-undersaturated magmas from the circum-Mediterranean (*e.g.*, Macedonia, Bulgaria, Turkey) and the Sunda arc, previously interpreted to reflect residual rutile. We propose a genetic link between high Nb/Ta, silica-undersaturated magmas and recycling of carbonate-rich lithologies via subduction. As such, Nb/Ta can be used to trace the recycling of subducting carbonates.

Received 21 August 2023 | Accepted 2 February 2024 | Published 5 March 2024

Introduction

The relative concentrations of Nb and Ta remain nearly constant during most magmatic processes and, thus, variations of Nb/Ta in volcanic rocks can reveal specific processes. Among geological environments, the highest Nb/Ta values are observed in carbonatites, lithosphere-derived rocks, and subduction related rocks (*e.g.*, Green, 1995; Münker *et al.*, 2003; Klemme *et al.*, 2005). The extremely high Nb/Ta of carbonatites can be used to recognise the involvement of carbonate-rich melts and fluids in different geological settings (*e.g.*, Green, 1995). For instance, the high Nb/Ta of some intraplate magmas was shown to derive from mantle metasomatism by carbonatite-like melts (Bragagni *et al.*, 2022).

The high Nb/Ta of some arc magmas was attributed to residual rutile in the subducting slab. However, it remains ambiguous why only some arc magmas show high Nb/Ta whilst the occurrence of residual rutile is rather ubiquitous, as suggested by the characteristic HFSE depletions of all subduction related magmas. Fractionation of Nb/Ta was ascribed to supercritical fluids (*e.g.*, W. Chen *et al.*, 2018; T.-N. Chen *et al.*, 2022) or melts (Klemme *et al.*, 2005; Stolz *et al.*, 1996) in equilibrium with rutile, whereas aqueous fluids are not expected to significantly influence the bulk Nb/Ta due to their low HFSE abundance (*e.g.*, Brenan *et al.*, 1994). To evaluate if Nb/Ta could be affected by carbon-rich fluids/melts released by subducted carbonate sediments, we investigated volcanic rocks from the Italian peninsula and Tyrrhenian seafloor. Here, chemical variations are well constrained and reflect different lithologies of the subducted sediments, being silicate-rich in the so called Tuscan magmatic province and carbonate-rich in the younger Roman magmatic province (*e.g.*, Conticelli and Peccerillo, 1992; Conticelli *et al.*, 2015).

Elevated Nb/Ta in Italian Silica-Undersaturated Magmas

HFSE concentrations measured by isotope dilution and $^{176}Hf/^{177}Hf$ data were obtained for representative samples of the Plio-Quaternary Italian volcanism (see Supplementary Information for analytical methods and the full data set). The new data from Tuscan and Roman magmatic provinces and IODP drill cores of the Tyrrhenian Sea (representative of mantle sources not affected by subduction) were integrated with published data from Etna, Stromboli, Vulture, and Pantelleria (Bragagni *et al.*, 2022).

The high Nb/Ta of Etna and Vulture were previously explained by mantle-derived carbonatite-like metasomatism in the subcontinental lithospheric mantle (Bragagni *et al.*, 2022). The influence of intraplate metasomatism in the subcontinental lithospheric mantle is attested by the relative deficit of K expressed as $K/K^* < 1$ (Fig. 1a). Conversely, both Tuscan and Roman lavas have elevated K/K*, typical of subduction zones, but with different Nb/Ta (Fig. 1). Tuscan and Tyrrhenian magmas have unfractionated Nb/Ta, similar to the BSE (14 ± 0.3; Münker *et al.*, 2003), whilst Roman lavas display higher ratios (up to 24).

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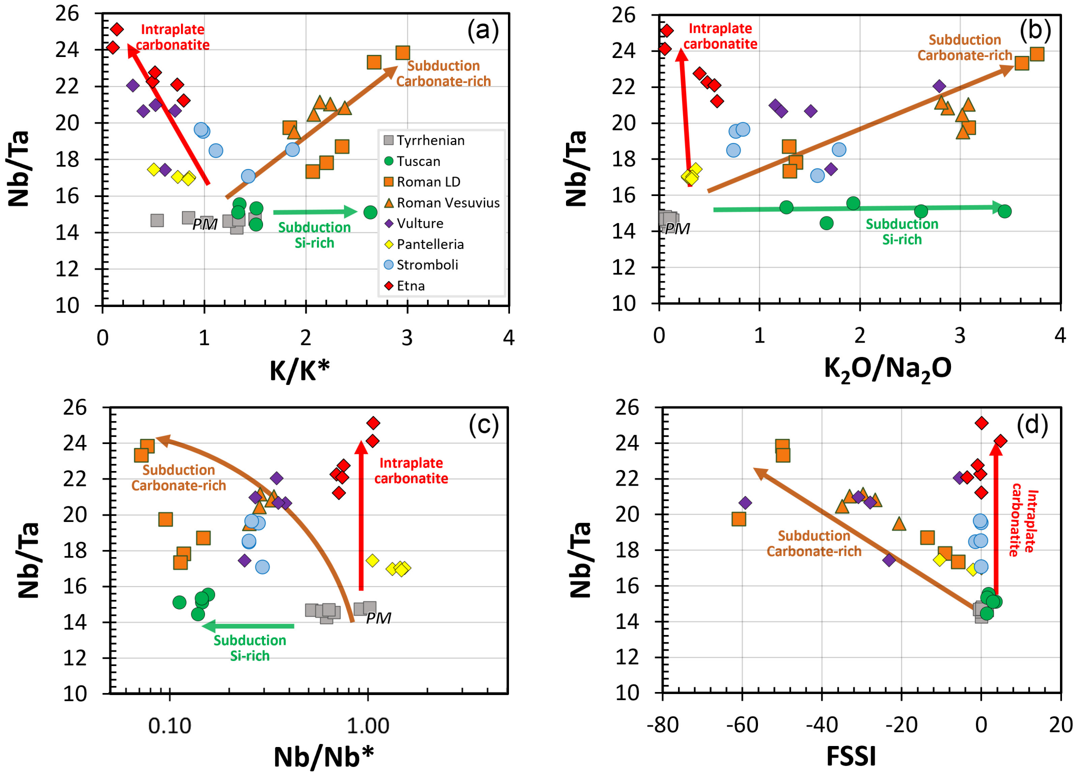

Figure 1 Variations of Nb/Ta relative to other geochemical proxies expressing intraplate metasomatism of the lithosphere (K/K*), subduction affinity (K/K* and Nb/Nb*), K-enrichment (K/K* and K_2O/Na_2O) and degree of silica saturation (FSSI; Feldspathoid Silica Saturation Index). The K* and Nb* values are calculated from the geometrical mean of PM-normalised concentrations of Nb-U and La-U, respectively. "LD" refers to "Latium District".

Both Tuscan and Roman lavas have high K content and K_2O/Na_2O (Fig. 1b), ranging in composition from shoshonitic to ultrapotassic (lamproites in the Tuscan and plagioleucitites/leucitites/kamafugites in the Roman provinces). Their trace element budget is dominated by a strong subduction signature (Conticelli and Peccerillo, 1992; Avanzinelli *et al.*, 2009; Conticelli *et al.*, 2015; Lustrino *et al.*, 2019) as shown also by the very low Nb/Nb* (Fig. 1c). Previous studies discussed the differences between magmas from the Tuscan and Roman magmatic provinces, suggesting mantle metasomatism related to subducted Si-rich metapelites, in the former, and carbonate-rich metapelites (marls) in the latter (Avanzinelli *et al.*, 2009; Frezzotti *et al.*, 2009; Conticelli *et al.*, 2015). This hypothesis is supported by the contrasting silica saturation, being saturated to oversaturated in the Tuscan and saturated to strongly undersaturated in the Roman volcanic rocks (Conticelli and Peccerillo, 1992). Other evidence for recycling of carbonates in the Roman but not in the Tuscan magma sources, includes i) $^{87}Sr/^{86}Sr$ buffered at a composition typical of carbonate-rich sediments for Roman, whilst reaching more radiogenic values for Tuscan lavas (*e.g.*, Avanzinelli *et al.*, 2009), ii) low Ni content and high Ca/Fe of high-Fo olivine within Roman lavas (Ammannati *et al.*, 2016), iii) ^{238}U-excess in Vesuvius magmas (Avanzinelli *et al.*, 2018), iv) similar trace element patterns between Roman lavas and marls (Grassi *et al.*, 2012), v) melt inclusions in the Roman lavas with high CaO (up 22 wt. %) and CaO/Al_2O_3 (Nikogosian and van Bergen, 2010) and vi) Ca isotopes of Roman leucitites (Ren *et al.*, 2024).

Subducting carbonate-rich sediments release minor CO_2-rich melts/supercritical fluids (Chen *et al.*, 2023) but in sufficient amounts to induce CO_2-excess and produce silica-undersaturated magmas upon mantle partial melting (Conticelli *et al.*, 2015; Gülmez *et al.*, 2023 and references therein). In leucite-bearing lavas, the degree of silica undersaturation shows a negative correlation with Nb/Ta (Fig. 1d). The highest Nb/Ta are recorded in leucitites, which have the strongest subduction signature (Fig. 1c) and degree of silica undersaturation (Fig. 1d). Silica-rich supercritical fluids or melts in equilibrium with residual rutile, which is usually proposed to explain the high Nb/Ta, are not expected to generate such trends, especially when compared to the degree of silica undersaturation. Therefore, we propose that elevated Nb/Ta derive from melts liberated by subducting carbonate-rich marls.

Elevated Nb/Ta from Carbonate-Rich Melts/Fluids in Subduction Zones

Since carbonates are typically HFSE poor, the silicate fraction of the marls would account for the required HFSE budget, whereas the carbonate fraction would liberate carbon-rich fluids/melts required to fractionate Nb/Ta. Recently, Gülmez *et al.* (2023) showed that the reaction of carbonate-rich sediments with peridotites at 800–850 °C forms carbonatitic and K-rich silicic melts, explaining the genesis of ultrapotassic silica-undersaturated magmas, such as the Roman ones. It is yet difficult to identify the exact nature of such melts/supercritical fluids. This is because different melts/supercritical liquids interact, mix, and exsolve as function of the physical conditions of the mantle wedge (*e.g.*, P–T–fO_2) and chromatographic effects in the slab and within veined peridotite (*e.g.*, Chen *et al.*, 2022). Moreover, the behaviour of trace elements will also depend on several unconstrained parameters describing the melting processes (*i.e.* degree of partial melting, mineralogy, partition coefficients) in the slab and in the metasomatised mantle. Two tentative simple models

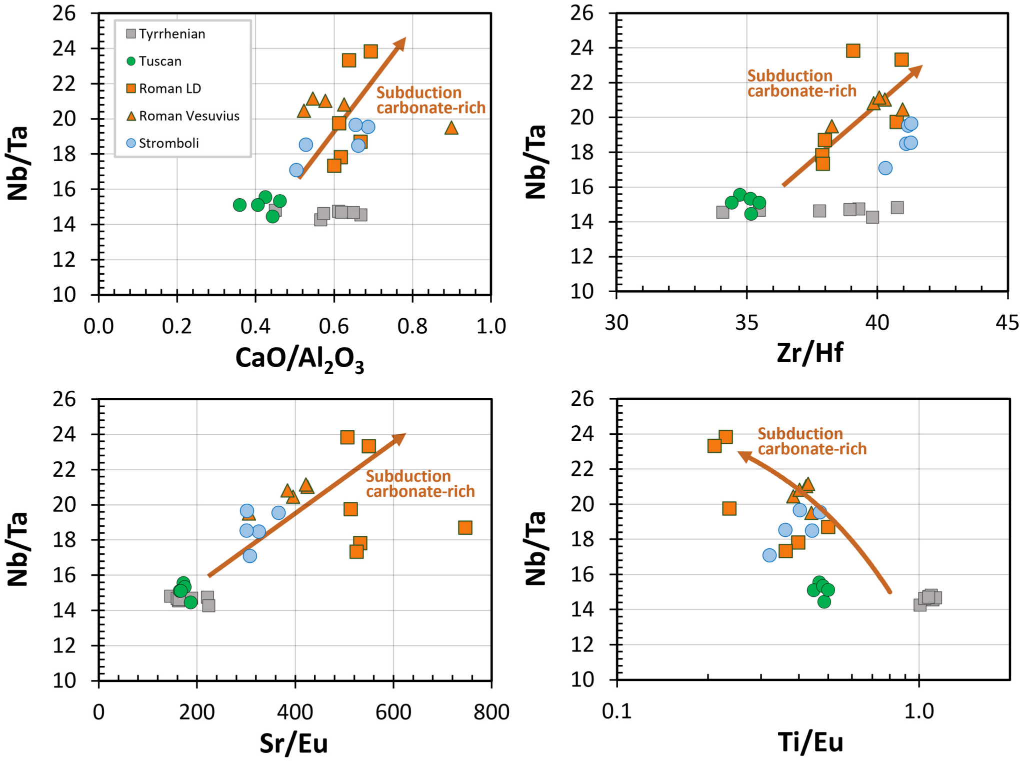

Figure 2 Nb/Ta against other proxies sensitive to carbonate-rich fluids/melts (*e.g.*, carbonatites).

are reported in the Supplementary Information to show that Roman magmas can be quantitatively explained by melting of carbonate-rich sediments. Nevertheless, there are several lines of evidence suggesting that the high Nb/Ta of Roman magmas derives from carbonate-rich sediments. 1) The Nb/Ta ratios of the Roman volcanic rocks correlate with proxies for carbonatite-like components (Fig. 2). 2) Natural melts produced from silica- and carbonate-rich lithologies, as observed in inclusions in high *P–T* metamorphic rocks, show variable enrichment in HFSE and K contents (Korsakov and Hermann, 2006). Interestingly, among these inclusions, the highest HFSE and K contents are recorded in melts with high Nb/Ta (~30). 3) Carbonatite-like melts interpreted to derive from slab melting of carbonate-rich sediments also show elevated Nb/Ta (Ravna *et al.*, 2017). 4) Rutile, which likely controls HFSE in the subducting slab, shows the lowest D_{Nb}/D_{Ta} (0.35) when in equilibrium with a carbonatite melt (Green, 2000).

Comparison with Other Potassic and Ultrapotassic Rocks in the Mediterranean Area

Zn-Mg isotope compositions in other circum-Mediterranean magmas suggests the recycling of marls (Shu *et al.*, 2023). In the area, high precision HFSE data are available for the Rhodopes (Bulgaria) and Santorini (Kirchenbaur and Münker, 2015). Among these, high Nb/Ta (19–20) was only observed in leucite-bearing absarokites from the Rhodopes. Instead, all silica-saturated volcanic rocks show lower Nb/Ta (12–16). Considering also conventional ICP-MS data, among potassic and ultrapotassic rocks of the circum-Mediterranean, the highest Nb/Ta was observed in ultrapotassic rocks from Macedonia (average of 20; Prelević *et al.*, 2008). Even if these rocks were originally classified as lamproites, they are leucite-bearing and were later classified as plagioleucitites (Lustrino *et al.*, 2019), making them comparable to Roman rocks. In the Mediterranean area, leucitites and plagioleucitites occur also in the Pontides (Turkey) and the average Nb/Ta is slightly higher than the BSE (18 in Eastern Pontides; Altherr *et al.*, 2008; 20 in Central Pontides; Gülmez *et al.*, 2016). Importantly, other silica-saturated potassic and ultrapotassic rocks from Spain, Serbia and Turkey, have lower Nb/Ta, analytically indistinguishable from the BSE value (Prelević *et al.*, 2008). High Nb/Ta in subduction-related potassic and ultrapotassic circum-Mediterranean rocks are a peculiar feature of silica-undersaturated rocks, ultimately reflecting the recycling of carbonate-bearing sedimentary lithologies.

A Common High Nb/Ta Signature in Silica-Undersaturated Magmas from Carbonate-Rich Subduction Zones

We further investigate the relationship between elevated Nb/Ta and recycled carbonate-rich sediments considering isotope dilution HFSE data from subduction-related magmas worldwide. In Figure 3a (Ba/Th *vs.* $^{143}Nd/^{144}Nd$), magmas define two trends reflecting the contribution of fluids from the subducted basaltic crust (high Ba/Th) or melts dominated by sediments (low Ba/Th).

Radiogenic isotope compositions (Sr-Nd-Hf), plotted against Nb/Ta (Fig. 3b–d), show that fluid dominated arcs (low $^{87}Sr/^{86}Sr$, high $^{143}Nd/^{144}Nd$ and $^{176}Hf/^{177}Hf$) point towards high Nb/Ta, which was previously interpreted as the effect of residual rutile in equilibrium with metasomatic fluids, possibly at the supercritical state (*e.g.*, W. Chen *et al.*, 2018; T.-N. Chen *et al.*, 2022). Instead, sediment dominated arcs (high $^{87}Sr/^{86}Sr$, low $^{143}Nd/^{144}Nd$ and $^{176}Hf/^{177}Hf$) show either BSE-like Nb/Ta (Tuscan province, Santorini, Papua New Guinea, Cyprus) or shifts towards high Nb/Ta (Roman province, Stromboli,

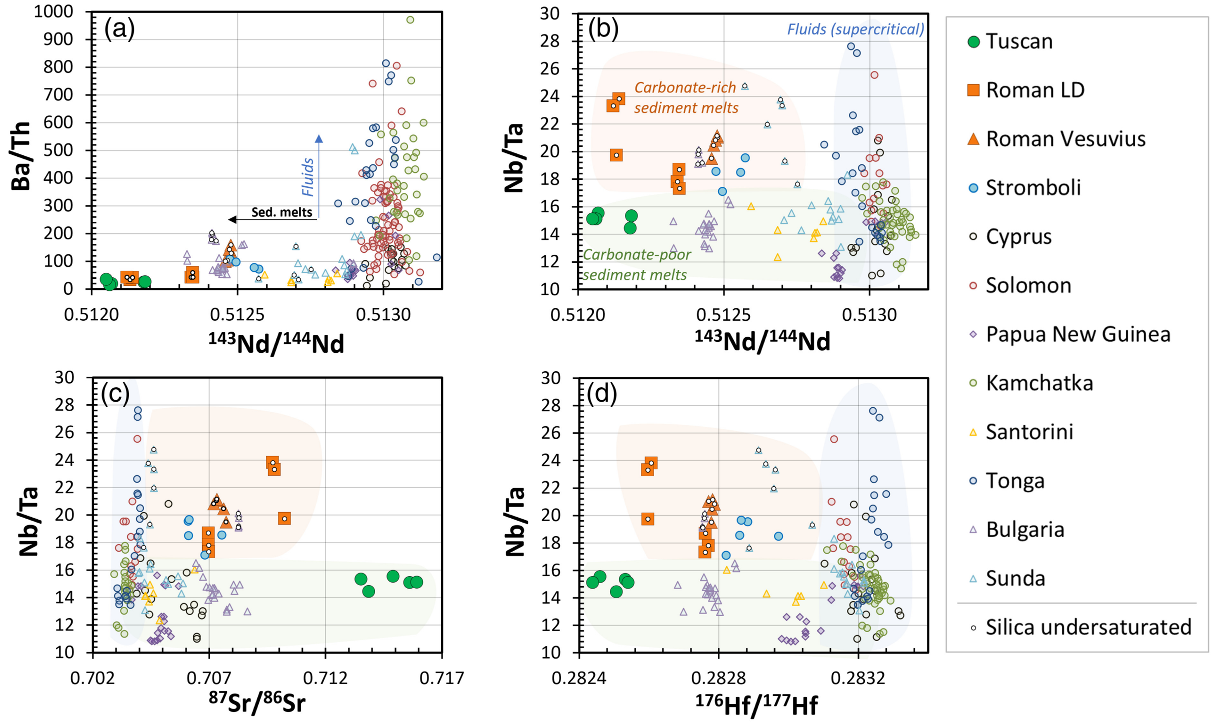

Figure 3 **(a)** Ba/Th *vs.* ^{143}Nd/^{144}Nd, showing the variable contribution of melts and (supercritical) liquids in different subduction related magmas. **(b, c, d)** Nb/Ta *vs.* Nd, Sr and Hf isotopes, respectively, in different subduction related magmas. Arc magmas dominated by sediment melts display the largest variations in radiogenic isotopes. Among them, silica-undersaturated volcanic rocks (highlighted by an open circle within the symbol) show elevated Nb/Ta due to recycling of subducting carbonate sedimentary lithologies. Only samples where Nb/Ta was determined by isotope dilution are plotted (see Supplementary Information for references).

Bulgaria, Sunda rear-arc). Similar to what is observed in Bulgaria and in Roman and Tuscan volcanic rocks, at Sunda only silica-undersaturated samples have elevated Nb/Ta, whilst silica-saturated samples have BSE-like Nb/Ta. The high Nb/Ta magmatism of Sunda is only observed in the K-rich rear arc in the Eastern sector (Stolz *et al.*, 1996; Kirchenbaur *et al.*, 2022). Importantly, at Sunda, different sediments are subducting, with a strong carbonate contribution only in the Eastern sector (House *et al.*, 2019).

In summary, in Italian collisional magmatism as well as in other melt-dominated arcs worldwide, the high Nb/Ta are associated with other evidence of recycling of carbonate-rich lithologies, such as the degrees of silica saturation. Silica saturation can also be affected by other factors, like degree and/or depth of partial melting, but which are not expected to account for the ubiquitously high Nb/Ta in such lavas. Therefore, in subduction zones affected by sediment melts, the high Nb/Ta of magmas represent a signature of recycling of carbonate-rich lithologies. Hence, Nb/Ta represents an important tool to constrain the role of subduction of recycled carbonates in the Earth's carbon cycle.

Acknowledgements

We thank Maria Kirchenbaur and Simone Tommasini for discussions and Frank Wombacher, Jonas Tusch, Josua Pakulla, and Mike Jansen for lab assistance. This research also used samples provided by the International Ocean Discovery Program (IODP). We thank the editor Horst Marschall, Dejan Prelević, and an anonymous reviewer for their valuable comments. This work was supported by UoC funding and ERC grant 669666 (to CM) and PRIN grants 20158A9CBM (to SC) and 2015EC9PJ5 (to RA).

Editor: Horst R. Marschall

Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2410.

Cite this letter as: Bragagni, A., Avanzinelli, R., Münker, C., Mastroianni, F., Conticelli, S. (2024) Fractionation of Nb/Ta during subduction of carbonate-rich sediments. *Geochem. Persp. Let.* 29, 38–42. https://doi.org/10.7185/geochemlet.2410

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