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

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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.

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 recognize 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 super-critical 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 Pecorello, 1992; Conticelli et al., 2015).

Elevated Nb/Ta in Italian Silica-Undersaturated Magmas

HFSE concentrations measured by isotope dilution and ¹⁷⁶Hf/¹⁷⁷Hf 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<sub>Si</sub> < 1 (Fig. 1a). Conversely, both Tuscan and Roman lavas have elevated K/K<sub>Si</sub>, 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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Both Tuscan and Roman lavas have high K content and K2O/Na2O (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 Pecceirillo, 1992). Other evidence for recycling of carbonates in the Roman but not in the Tuscan magma sources, includes i) 87Sr/86Sr 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) 238U-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/Al2O3 (Nikogosian and van Bergen, 2010) and vi) Ca isotopes of Roman leucitites (Ren et al., 2024).

Subducting carbonate-rich sediments release minor CO2-rich melts/supercritical fluids (Chen et al., 2023) but in sufficient amounts to induce CO2-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 leucites, which have the strongest subduction signature (Fig. 1c) and degree of silica undersaturation (Fig. 1d). 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 carbonatic 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 evolve as function of the physical conditions of the mantle wedge (e.g., P–T–fO2) 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 uncontrolled 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

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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 K2O/Na2O) 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".

**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 carbonatic 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 evolve as function of the physical conditions of the mantle wedge (e.g., P–T–fO2) 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 uncontrolled 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...
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 plagioclucitites (Lustrino et al., 2019), making them comparable to Roman rocks. In the Mediterranean area, leucitites and plagioclucitites 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; Gúmez 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 2  Nb/Ta against other proxies sensitive to carbonate-rich fluids/melts (e.g., carbonatites).
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.

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Additional Information

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

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References


Significance of carbonated pelitic vs. pelitic sediment recycling at destructive plate margins. Lithos 113, 213–227. https://doi.org/10.1016/j.lithos.2009.03.003


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