

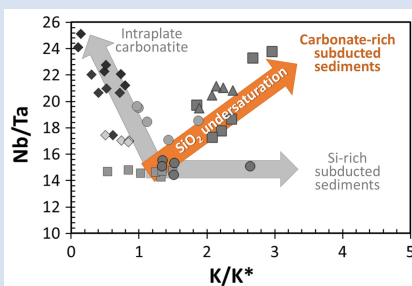
Fractionation of Nb/Ta during subduction of carbonate-rich sediments

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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.

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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.*, Brennan *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 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* < 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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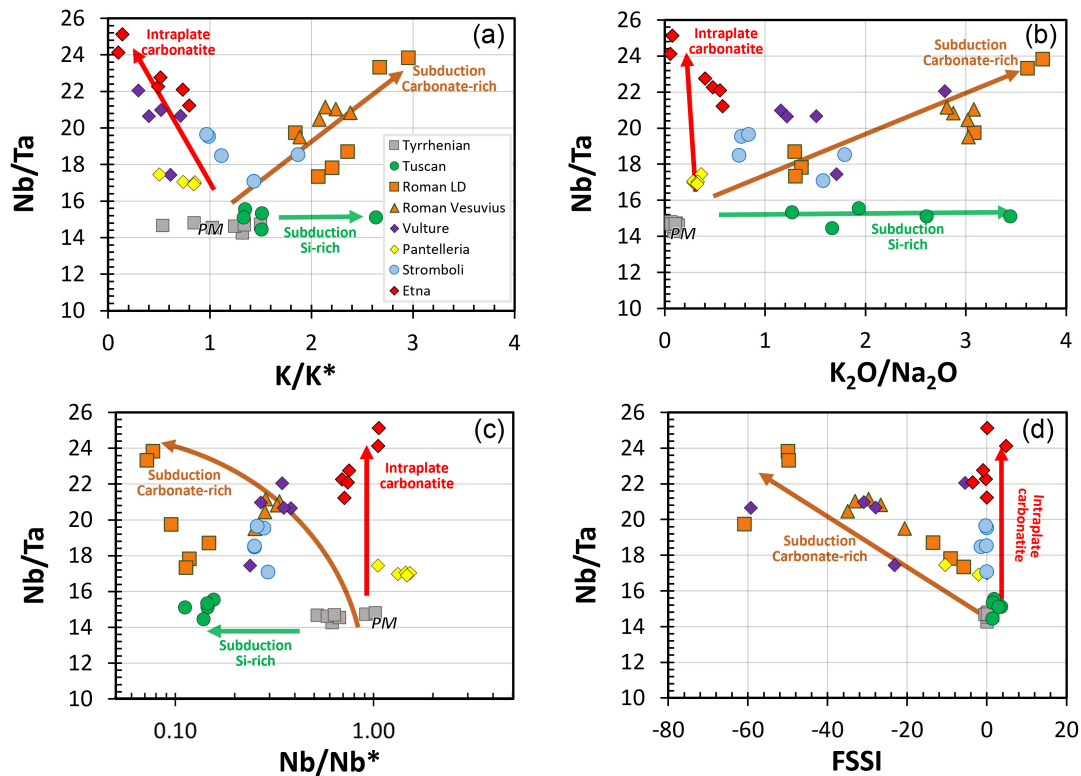


Figure 1 Variations of Nb/Ta relative to other geochemical proxies expressing intraplate metasomatism of the lithosphere (K/K^*), subduction affinity (K/K^* and Nb/Nb^*), K-enrichment (K/K^* and K_2O/Na_2O) and degree of silica saturation (FSSI; Feldspathoid Silica Saturation Index). The K^* and Nb^* 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 plagioclites/leucites/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 leucites (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 leucites, 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

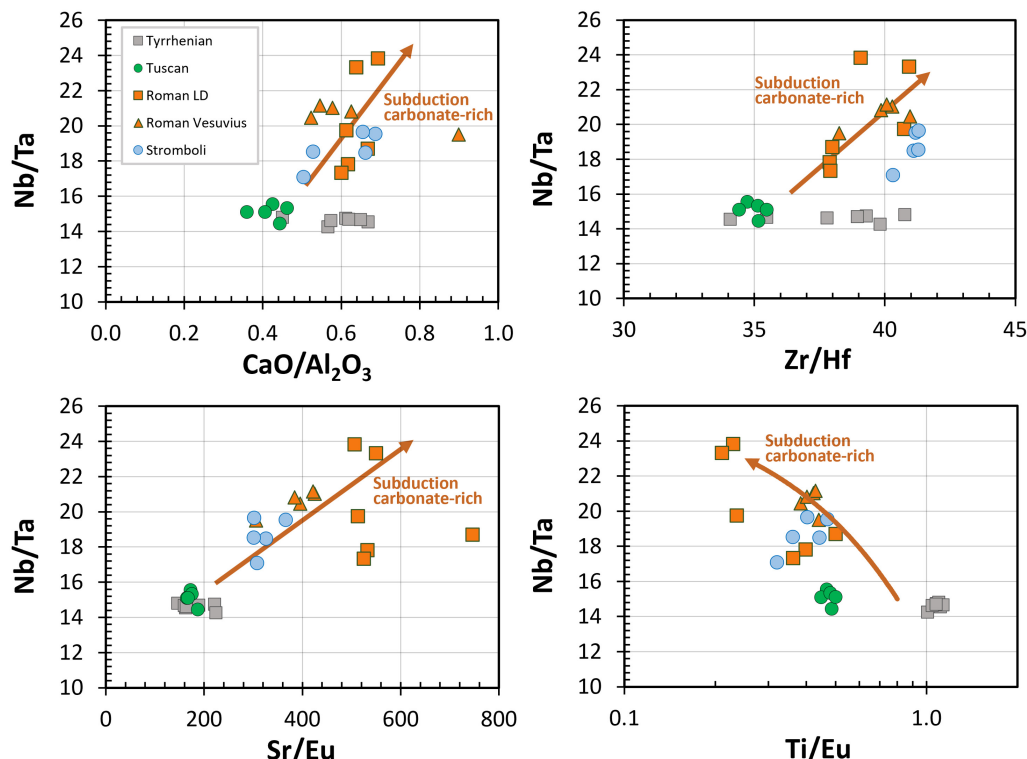


Figure 2 Nb/Ta against other proxies sensitive to carbonate-rich fluids/melts (e.g., carbonatites).

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 $D_{\text{Nb}}/D_{\text{Ta}}$ (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 plagioclitites (Lustrino *et al.*,

2019), making them comparable to Roman rocks. In the Mediterranean area, leucitites and plagioclitites 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. $^{143}\text{Nd}/^{144}\text{Nd}$), 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 $^{87}\text{Sr}/^{86}\text{Sr}$, high $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$) 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 $^{87}\text{Sr}/^{86}\text{Sr}$, low $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$) show either BSE-like Nb/Ta (Tuscan province, Santorini, Papua New Guinea, Cyprus) or shifts towards high Nb/Ta (Roman province, Stromboli,

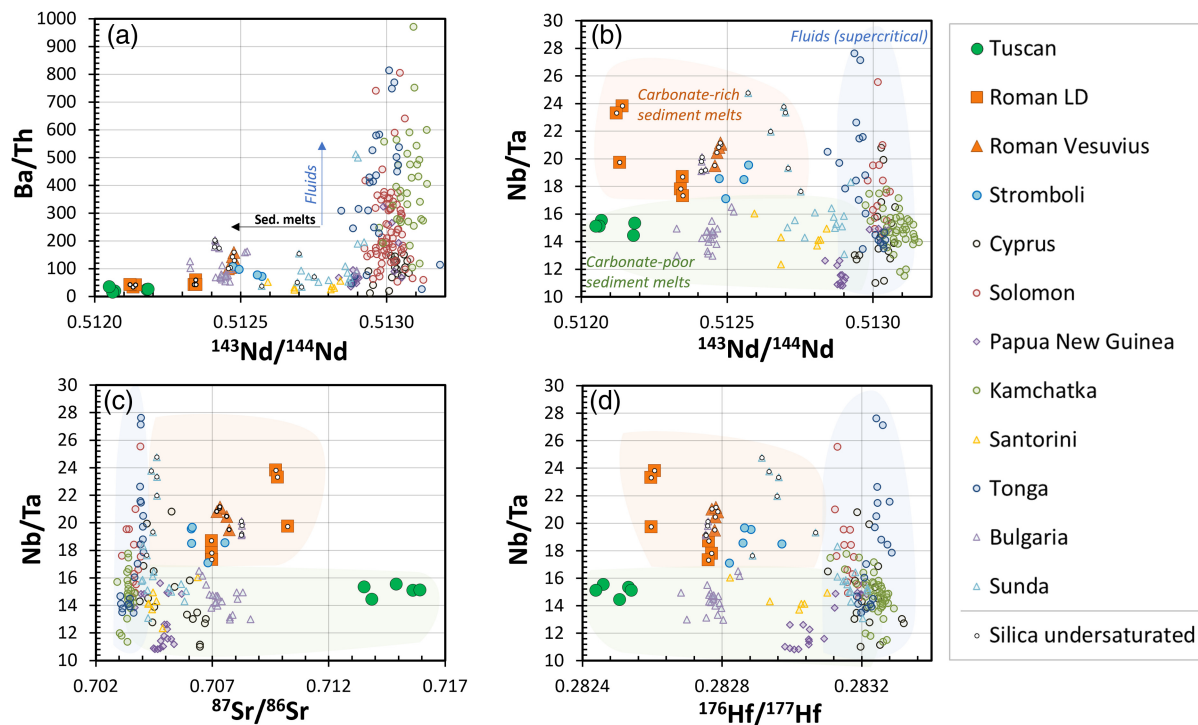


Figure 3 (a) Ba/Th vs. $^{143}\text{Nd}/^{144}\text{Nd}$, showing the variable contribution of melts and (supercritical) liquids in different subduction related magmas. (b, c, d) Nb/Ta vs. Nd, Sr and Hf isotopes, respectively, in different subduction related magmas. Arc magmas dominated by sediment melts 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.

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Additional Information

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



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Supplementary Information

The Supplementary Information includes:

- Tyrrhenian Sea Samples Description
- Analytical Methods
- Quantifying the Role of Carbonate-rich Melts in Roman Magmatic Province
- Table S-1
- Figure S-1
- References for Literature Data in Figures 2 and 3
- Supplementary Information References

Tyrrhenian Sea Samples Description

Samples from the Tyrrhenian basin were obtained from the MARUM GeoB Core Repository. They were originally collected during the Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP) in expedition 42 and 107. The samples were selected to be representative of the depleted magmatism recorded in the Tyrrhenian basin, which is thought to form in a back arc setting. In terms of composition they resemble that of transitional MORB and they are thought to derive from a depleted mantle slightly re-enriched by subduction-derived fluids (Barberi *et al.*, 1978; Beccaluva *et al.*, 1990; Dietrich *et al.*, 1977, 1978; Gasperini *et al.*, 2002; Hamelin *et al.*, 1979).

Analytical Methods

Major element concentrations of the seven samples from the Tyrrhenian basin were obtained using a Philips PW 2400 XRF at the Universität zu Köln. The trace element content was determined following the procedure of Garbe-Schönberg (1993) and using an Agilent 7500cs ICP-MS at the Universität zu Kiel. The same samples were analysed for their Sr-Nd-Pb isotopic composition at the Università degli Studi di Firenze, leaching the powders in 1 M HCl and following the procedure described in Avanzinelli *et al.* (2005) for dissolution, chemical separation and TIMS measurements.

Elemental concentrations of HFSE (Nb, Ta, Zr, Hf), Lu, W, Th, and U were obtained along with $^{176}\text{Hf}/^{177}\text{Hf}$ following the same procedure outlined in Bragagni *et al.* (2022), which is based on the methods described in Luo *et al.* (1997), Kirchenbaur *et al.* (2016), Münker *et al.* (2001), Münker (2010), Weyer *et al.* (2002), Kleine *et al.* (2004). Briefly, 100 mg of powder was weighted along with isotope tracers enriched in $^{233-236}\text{U}$ – ^{229}Th – ^{183}W – ^{180}Ta – ^{180}Hf – ^{176}Lu – ^{94}Zr . Samples were dissolved and treated as described in Bragagni *et al.* (2022). Specifically, the W fraction was separated using anion resin exchange chemistry (modified from Kleine *et al.*, 2004), the HFSE were purified in three

steps of resin exchange chemistry (LN-spec, anion, LN-spec) using a modified procedure originally developed by Münker *et al.* (2001), U and Th were separated with TRU-spec chemistry (Luo *et al.*, 1997). All measurements were performed at Universität zu Köln with a Thermo-Scientific Neptune MC-ICP-MS equipped with a Cetac Aridus II. Blanks were 36–54 pg for W, 38–163 pg for Ta, 0.7–1.4 ng for Zr, 28–57 pg for Nb, 43–123 pg for Hf, 9 pg for Th and 35 pg for U, and are all negligible with respect to the amounts of sample processed.

Quantifying the Role of Carbonate-rich Melts in Roman Magmatic Province

Quantifying the effect of silicate and carbonatitic melts in the investigated samples is not straightforward. This is due to the complexity of the involved processes and because melting parameters, such as partition coefficients, are not readily available. Green (2000) provides K_d for HFSE in rutile in equilibrium with carbonatitic magmas. However, in the case of marls, a silicate melt will also form along the carbonatite melt (*e.g.*, Gülmez *et al.*, 2023; Skora *et al.*, 2015). Therefore, to quantitatively model HFSE and other trace elements, both silicate and carbonatite partition coefficients must be considered. In the literature there are few experimental works reporting the trace element composition of melts in equilibrium with sediments at pressure and temperature relevant for mantle wedge conditions (Herman and Rubatto, 2009; Skora and Blundy, 2010; Skora *et al.*, 2015; Gülmez *et al.*, 2023). Among them, Skora *et al.* (2015) and Gülmez *et al.* (2023) investigated carbonate-rich lithologies but they do not report partition coefficients. The only experimental work with partition coefficients for sediments melt is Skora and Blundy (2010), which used a radiolarian clay lithology. These partition coefficients can be used to model melting of silicic sediments as those expected to influence the Tuscan magmatic province. Although not ideal, the same partition coefficient can be employed to reproduce the composition of a silicic melt in equilibrium with a marl, as needed to explain the Roman magmatism. As such, we assume that HFSE are controlled by rutile in equilibrium with a carbonatitic melt (partition coefficients of Green, 2000), whereas other elements are controlled by silicates in equilibrium with the silicic melt (partition coefficients of Skora and Blundy, 2010). It should be stressed that this is a simplification because also other elements can be influenced by carbonatite melts (especially REE). Moreover, also the partitioning of HFSE between rutile (and possibly other phases) and the silicate melt is not considered.

An alternative proxy of the metasomatic melt affecting the mantle wedge under the Roman magmatic province is represented by the carbonate-rich inclusions observed by Korsakov and Herman (2006) in orogenic massifs. Therefore, we model the effect of adding three different melts to a DMM, two inferred from melting silica- and carbonate-rich sediments, and one simply using the composition of a carbonate-rich inclusions of Korsakov and Herman (2006). Modelling was performed only with Nb/Ta and radiogenic isotope ratios to avoid variations of concentrations due to partial melting in the metasomatised mantle wedge. As shown in Figure S-1, mixing the DMM with silicic melt can reproduce the signature of the Tuscan magmatic province in Nb/Ta vs. Sr or Nd isotopes. The Roman magmas lie below the two mixing lines obtained for carbonate-rich metasomatic melts. This is readily explained by the concurrent occurrence of carbonate-rich metasomatic melts along with silicic melts (*i.e.* with canonical Nb/Ta) or fluids (*i.e.* negligible HFSE content but significant Sr and Nd).

References for Literature Data in Figures 2 and 3

Reference values for PM values are taken from Münker *et al.* (2003) and Palme and O'Neill (2014). Literature isotope dilution data and Sr-Nd-Hf isotopes reported in Figure 3 are from: Tonga (Beier *et al.*, 2017), Cyprus (König *et al.*, 2008), Solomon (König *et al.*, 2008; Schuth *et al.*, 2009), Papua New Guinea (PNG) (König *et al.*, 2010), Kamchatka and Aleutian arc (Churikova *et al.*, 2001; Münker *et al.*, 2004; Yogodzinski *et al.*, 1995), Santorini and Bulgaria (Kirchenbaur *et al.*, 2012; Kirchenbaur and Münker, 2015), Sunda (Kirchenbaur *et al.*, 2022), Stromboli (Bragagni *et al.*, 2022).



Supplementary Table

Table S-1 Compiled dataset with HFSE concentrations measured by isotope dilution (this work and Bragagni *et al.*, 2022) along with major-trace elements and Hf-Sr-Nd-Pb isotope data (this work and indicated literature).

Table S-1 is available for download (.xlsx) from the online version of this article at <https://doi.org/10.7185/geochemlet.2410>.

Supplementary Figure

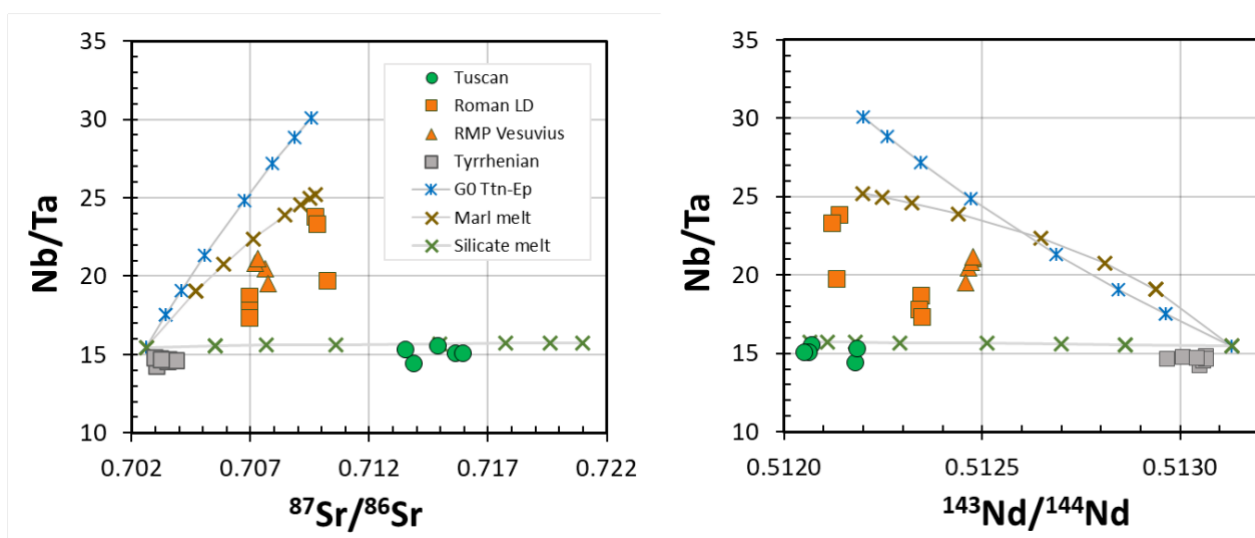


Figure S-1 Mixing models to reproduce the Nb/Ta signature of the Roman and Tuscan magmatic provinces. The blue symbols represent a mixing curve between the DMM and the carbonate-rich melt (inclusion G0 Ttn-Ep) reported by Korsakov and Herman (2006) and assuming Sr and Nd isotope composition from marl SD53 (Casalini *et al.*, 2019). The brown and green crosses display a mixing between the DMM and melts from a carbonate-rich marl (SD53 of Conticelli, 1998; Conticelli *et al.*, 2015; Casalini *et al.*, 2019) or a carbonate poor lithology (SD75 of Conticelli, 1998; Conticelli *et al.*, 2015; Casalini *et al.*, 2019), respectively. For the marl melting, we assume that HFSE are controlled only by rutile, using the partition coefficients of Green (2020) for a carbonatitic melt and imposing a 1 % modal fraction of rutile. Partition coefficients for Sr and Nd are from Skora and Blundy (2010) (900 °C). We assume an arbitrary 50 % of partial melting of the marl. Such a melt was then mixed at variable proportions with the DMM. For melting the carbonate-poor lithology, we only used the partition coefficients of Skora and Blundy (2010) (900 °C) and assume a melting degree of 50 % before mixing it with the DMM. Symbols for the mixing models are reported adding 0, 0.5, 1, 2, 5, 10, 20, 50 % of sediment melt to the DMM. In a possible scenario, the Roman magmas are explained by the double contribution of melts from carbonate-rich (*i.e.* marl melting or G0 Ttn-Ep melt) and carbonate-poor lithologies (to lesser extent). Instead, the Tuscan magmas are explained by melting only the carbonate-poor lithology. DMM values are taken from Workman and Hart (2005).

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