

Widespread slab melting in modern subduction zones

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ABSTRACT

It is still a matter of intense debate to what extent partial melting of the subducting slab contributes to arc magmatism in modern subduction zones. In particular, it is difficult to differentiate between silicate melts formed by partial melting of the slab, and aqueous fluids released during subsolidus dehydration as the main medium for slab-to-mantle wedge mass transfer. Here we use $\delta^{49/47}$Ti (the deviation in ^{49}Ti/^{47}Ti of a sample to the OL-Ti reference material) as a robust geochemical tracer of slab melting. Hydrous partial melting of subducted oceanic crust and the superjacent sedimentary layer produces silicic melts in equilibrium with residual rutile. Modelling shows that such silicic slab melts have notably higher $\delta^{49/47}$Ti (+0.24±0.06‰) than their protolith due to the strong preference of rutile for the lighter isotopes of Ti. In contrast, even highly saline fluids cannot carry Ti from the slab and hence hydrous peridotite partial melts have $\delta^{49/47}$Ti similar to mid-ocean ridge basalts (MORB; ca. 0‰).

Primitive (Mg# ≥60) arc lavas from eight subduction zones that are unaffected by fractional crystallisation of Fe-Ti oxides show a more than tenfold larger variation in $\delta^{49/47}$Ti than found in MORB. In particular, primitive arc lavas display a striking correlation between SiO_2 content and $\delta^{49/47}$Ti that ranges from island arc basalts overlapping with MORB, to primitive rhyodacites with $\delta^{49/47}$Ti up to 0.26‰ erupted in the western Aleutian arc. The elevated $\delta^{49/47}$Ti of these primitive arc lavas provides conclusive evidence for partial melts of the slab as a key medium for mass transfer in subduction zones. The Aleutian rhyodacites represent a rare example of slab melts that have traversed the mantle wedge with minimal modification. More commonly, slab melts interact with the mantle wedge to form an array of primary arc magmas that are a blend of slab- and peridotite-derived melt. We identify primitive arc lavas with a clearly resolvable slab melt signature in all eight subduction zone localities, confirming that slab melting is prevalent in modern subduction zones.

Keywords: Slab melting; Titanium isotopes; Rutile; Subduction zone; Aleutian arc

Highlights

- Global primitive arc lavas (Mg# ≥60) display notable $\delta^{49/47}$Ti heterogeneity
- Residual rutile imposes high $\delta^{49/47}$Ti of 0.24±0.06‰ on hydrous, silicic slab melts
- Primitive Aleutian rhyodacites have the same $\delta^{49/47}$Ti as predicted for slab melts
- A variably diluted signature of slab melts is found in all eight subduction zones
- A slab melt component is required to generate silicic primitive arc lavas

1. Introduction

Subduction zones are a nexus of geochemical cycles and link the crust, hydrosphere, atmosphere, and Earth's mantle. Mass transfer from subducting slabs is a likely trigger for partial melting of the overlying mantle wedge, giving rise to arc lavas with a ubiquitous geochemical signature of subducted oceanic crust and its sedimentary cover (e.g., Gill, 1981; Tera et al., 1986; White and Dupré, 1986; Plank and Langmuir, 1993; Elliott et al., 1997). Despite the key role in modulating the composition of the continental crust, deep mantle, and Earth's surface habitat, the mechanisms of mass transfer in subduction zones are still not well understood

(Spandler and Pirard, 2013; Keppler, 2017; Nielsen and Marschall, 2017; Hernández-Uribe et al., 2020; Klaver et al., 2020). A persistent question is to what extent the top of the subducting slab melts in modern subduction zones. Melts are an efficient medium to mobilise trace elements and volatiles from the slab (e.g., Johnson and Plank, 1999; Hermann et al., 2006), and the latest generation of slab thermal models (Syracuse et al., 2010; van Keken et al., 2011; van Keken et al., 2018) and geochemical slab-top thermometers (Cooper et al., 2012) suggest that the hydrous solidus of sediments and altered oceanic crust can be reached in most modern subduction zones. Conversely, saline aqueous fluids might also be capable of carrying a significant budget of trace elements to the mantle wedge source of arc magmas without the need to invoke slab melting (Tatsumi, 1989; Keppler, 2017; Rustioni et al., 2021).

The trace element and radiogenic isotopic signature of primitive arc lavas unquestionably supports slab-to-mantle wedge mass transfer, but does not provide a conclusive discrimination between slab melting and transport by saline fluids (cf., Rustioni et al., 2021; Li et al., 2022; Turner and Langmuir, 2022b). For instance, either model explains the characteristic relative depletion in Ti, Nb, and Ta displayed by primitive arc lavas. In the sediment melting scenario, this depletion is imposed by the accessory mineral rutile (TiO_2) present in the residue during hydrous melting of eclogite-facies slab lithologies (e.g., Ryerson and Watson, 1987; Yogodzinski et al., 1995; Elliott et al., 1997), whereas in the saline fluid model the relative depletion in Ti, Nb, and Ta results from the negligible solubility of these elements in fluids. Here, we demonstrate that the isotopic composition of Ti in primitive arc lavas is a uniquely diagnostic tracer of the presence of a slab melt component in primitive arc magmas. This approach hinges on the distinct bonding environment of Ti in Fe-Ti oxides. Rutile has a strong preference for the lighter isotopes of Ti compared to silicate minerals and melts (Aarons et al., 2021; Hoare et al., 2022; Rzehak et al., 2022). As a result, partial melts in equilibrium with residual rutile will display the characteristic relative depletion in Ti, Nb, and Ta, as well as distinctly heavier Ti isotope compositions than their protolith. In contrast, experimental studies indicate that aqueous fluids cannot mobilise Ti even at high salinities (e.g., Kessel et al., 2005a; Keppler, 2017; Rustioni et al., 2021), and as rutile is not a stable residual phase during hydrous peridotite melting (Grove et al., 2006; Till et al., 2012), mass transfer by saline fluids alone does not have the capability to impose a distinct Ti isotope signature on primitive arc lavas.

We test this hypothesis by combining quantitative Ti isotope fractionation modelling of slab melting with high-precision Ti isotope composition measurements of a comprehensive suite of global primitive arc lavas.

This shows that slab melting occurs in all eight subduction zones for which Ti isotope data are available, irrespective of slab age and temperature, and therefore is a widespread feature of modern subduction

2. Samples and analytical techniques

We present new Ti isotope composition data for 52 extrusive volcanic samples from six subduction zone localities. These comprise the Aegean arc (Nisyros and Santorini), Aleutian arc (Adak and dredge samples from the Komandorsky Straits and Western Cones area), Lesser Antilles arc (Bequia, Grenada, Saba, and St. Vincent), Philippines arc (Surigao Peninsula, Mindanao), Solander Islands (New Zealand), and Cook Island (Austral Volcanic Zone, Chile). A detailed description of these localities and the samples is provided in the supplementary material. The new data greatly expand on previously published data (26 samples) for arc lavas from the New Britain arc (Millet and Dauphas, 2014), Mariana arc (Millet et al., 2016), Kermadec arc (Monowai; Hoare et al., 2020), and Aegean arc (Santorini, Kos; Hoare et al., 2020; Greber et al., 2021). Taken together, these localities cover a wide range of subduction zone parameters such as the age of subducted crust (10 to ca. 200 Ma), slab dip (30–70°), and subduction angle (straight versus oblique; see supplementary Table S4). All samples have a minimum of major- and trace element characterisation, in most cases complemented with radiogenic isotope data (compiled in supplementary Dataset 2).

For the selection of the new samples, emphasis was placed on primitive lavas that are least affected by magmatic differentiation. We use Mg# (molar 100×Mg/[Mg+Fe]) as discriminant and designate samples with Mg# ≥60 as primitive, and samples with Mg# <60 as evolved. In addition, we specifically targeted primitive arc lavas with a geochemical signature often ascribed to slab melts, such as elevated Sr/Y, fractionated rare earth element patterns, and high SiO_2 content (e.g., Defant and Drummond, 1990). Although such primitive andesites, dacites, and rhyodacites are a volumetrically minor fraction of global arc magmas (Kelemen et al., 2014), they are well-suited to test the sensitivity of Ti isotopes to slab melting. In particular, we include seafloor rhyodacites with high Mg# (64–73) erupted on thin oceanic crust in the western Aleutian arc, which are proposed to be nearly unmodified melts of the subducting Pacific oceanic crust (Yogodzinski et al., 2015; Yogodzinski et al., 2017).

Titanium isotope composition measurements were carried out following a well-established protocol described in detail elsewhere (e.g., Millet and Dauphas, 2014; Hoare et al., 2020; Klaver et al., 2021). Briefly, aliquots of dissolved sample corresponding to ca. 5 µg Ti were equilibrated with a ^{47}Ti–^{49}Ti double spike prior to Ti purification with Eichrom DGA resin. Measurements were performed using a ThermoScientific Neptune Plus (at Durham University) and Nu Plasma II (at Cardiff University) multi-collector inductively-coupled plasma mass spectrometer (MC-ICP-MS) operated in medium resolution mode. Titanium isotope composition data are reported in the conventional delta-notation relative the Origins Laboratory Ti reference material (OL-Ti) as $\delta^{49/47}Ti_{OL-Ti}$ (hereafter abbreviated to $\delta^{49/47}Ti$). Repeat measurements of geological and Ti solution reference materials indicates an intermediate precision of 0.020‰ (2s) for the individual measurements made in Durham (Millet et al., 2016) and 0.030‰ (2s) for those made in Cardiff (supplementary Figure S3). For most samples measured in Cardiff, 2–4 repeat measurements were made (see supplementary Dataset 2). See the supplementary material for more discussion of measurement uncertainties.

3. Results

The primitive arc lavas (whole rock Mg# ≥60) in this study vary in major element composition from (picritic) basalts with 46 wt.% SiO_2 and up to 15.5 wt.% MgO (e.g., St. Vincent, Lesser Antilles arc) to high-Mg# rhyodacites (70 wt.% SiO_2, 2.1 wt.% MgO) erupted as submarine lavas on oceanic crust in the western Aleutian arc. Despite the large range in silica content, their high Mg# indicates that these arc lavas are primitive melts that are in or very close to equilibrium with mantle olivine and/or orthopyroxene. As shown in Figure 1, primitive arc lavas display notably heterogeneous $\delta^{49/47}Ti$ (ca. 0.3‰ variation) compared to normal mid ocean ridge basalts (N-MORB), which have homogeneous $\delta^{49/47}Ti$ of 0.001±0.015‰ (Millet et al., 2016; Deng et al., 2018). Basaltic primitive arc lavas overlap in $\delta^{49/47}Ti$ with N-MORB but more silica-rich varieties have progressively higher $\delta^{49/47}Ti$. The high-Mg# rhyodacites from the Aleutian arc have the most extreme $\delta^{49/47}Ti$ at 0.21–0.26‰, but also high-Mg# andesites from the Aegean arc, Philippines arc, Solander Islands, and Cook Island have $\delta^{49/47}Ti$ clearly elevated relative to N-MORB.

4. Modelling Ti isotope fractionation during slab melting

The contrasting bonding environment of Ti in Fe-Ti oxides compared to silicate minerals and melts is the fundamental parameter that introduces Ti isotope heterogeneity during magmatic processes (e.g., Millet et al., 2016; Deng et al., 2019; Hoare et al., 2020). Titanium isotope fractionation between silicate minerals (e.g., pyroxene, garnet) and silicate melt is negligible and, as a result, partial melting of peridotite produces melts with essentially the same $\delta^{49/47}Ti$ as their protolith (Figure 2; Hoare et al., 2022). Conversely, Fe-Ti oxide minerals, notably rutile, have a strong preference for the lighter isotopes of Ti relative to silicates (Aarons et al., 2021; Hoare et al., 2022; Rzehak et al., 2022). As a result, the presence of rutile in the residue during partial melting will aid the retention of Ti and impose an isotopically heavy Ti isotope signature on the partial melt.

Rutile is a stable residual phase during hydrous partial melting of eclogite-facies metabasite and metasediment due to the low solubility of TiO_2 in the silicic partial melts produced at 750–1000 °C (Ryerson and Watson, 1987; Gaetani et al., 2008; Xiong et al., 2009). We use experimentally determined melting reactions of such slab lithologies coupled with mineral–melt Ti isotope fractionation factors to model the magnitude of Ti isotope fractionation that occurs during melting in the presence of residual rutile. Rutile is the main repository of Ti in the melting residua of metabasite and metasediment, and the rutile–melt Ti isotope fractionation factor therefore exerts the dominant control on the magnitude of Ti isotope fractionation during melting. We employ an average rutile–melt Ti isotope fractionation factor of $10^3\ln\alpha_{rt\text{–}melt} = -0.444\pm0.028 \times 10^6/T^2$ compiled from two recent studies (Hoare et al., 2022; Rzehak et al., 2022). The difference in Ti isotope composition between the partial melt and the protolith ($\Delta^{49/47}Ti_{melt\text{–}protolith}$) can then be calculated through isotopic mass balance as described in detail in the supplementary material. Subsequently, the absolute $\delta^{49/47}$Ti of slab melts can be derived by adding $\Delta^{49/47}Ti_{melt\text{–}protolith}$ as shown in Figure 2 to the $\delta^{49/47}$Ti of the protolith ($\delta^{49/47}Ti_{slab\ melt} = \Delta^{49/47}Ti_{melt\text{–}protolith} + \delta^{49/47}Ti_{protolith}$).

The water-saturated solidus of eclogite with a composition akin to pristine to altered MORB (0–1.0 wt.% K_2O, 1.2–2.0 wt.% TiO_2) at sub-arc depths (2.6-4.5 GPa) lies between 750 and 800 °C (Schmidt et al., 2004; Kessel et al., 2005b; Carter et al., 2015; Martin and Hermann, 2018; Sisson and Kelemen, 2018). These studies find rutile as a residual phase up to at least 900 °C or 25% melting. As a result of the residual rutile, hydrous, silicic metabasite partial melts (73–79 wt.% SiO_2 on an anhydrous basis) have notably higher $\delta^{49/47}$Ti than their protolith, in clear contrast with the negligible Ti isotope fractionation during partial melting of rutile-free peridotite (Figure 2a). Metabasite melts formed at 750–800 °C show the largest Ti isotope fractionation ($\Delta^{49/47}Ti_{melt\text{–}protolith}$ = 0.21–0.29‰; Figure 2a). At higher temperature, the diminishing proportion of rutile in the residue leads to progressively lower $\Delta^{49/47}Ti_{melt\text{–}protolith}$. The MORB protolith of the metabasite has $\delta^{49/47}$Ti around zero (Figure 1; Millet et al., 2016; Deng et al., 2018); hence the absolute $\delta^{49/47}$Ti of metabasite partial melts at 750–800 °C is 0.24±0.06‰.

Low-degree hydrous partial melts of eclogite-facies metasediments at 750–950 °C and 3–6 GPa are also in equilibrium with residual rutile (Skora and Blundy, 2010; Martindale et al., 2013; Mann and

Schmidt, 2015; Skora et al., 2015) and therefore have higher $\delta^{49/47}Ti$ than their protolith (Figure 2b), unlike what was assumed by Kommescher et al. (2023). Given the lower TiO_2 content of the sedimentary protoliths, the proportion of rutile in the residue is generally smaller and the Ti isotope fractionation effect is more subdued compared to metabasite melting. In several cases, however, titanomagnetite joins rutile as a residual phase. Titanomagnetite has an even stronger preference for the lighter isotopes of Ti than rutile (Hoare et al., 2022) and hence its presence leads to higher $\Delta^{49/47}Ti_{melt\text{–}protolith}$ (0.3–0.4‰; Figure 2b). As a result, metasediment partial melts have highly variable $\Delta^{49/47}Ti_{melt\text{–}protolith}$, but are always positively fractionated relative to their protolith. Modern terrigenous sediments have $\delta^{49/47}Ti$ in the range of 0.16–0.24‰ (Greber et al., 2017; Klaver et al., 2021), meaning that hydrous metasediment partial melts have $\delta^{49/47}Ti$ ranging from 0.25‰ up to 0.6‰.

5. Discussion

5.1. Negligible influence of magmatic differentiation on $\delta^{49/47}Ti$ of primitive arc lavas

Differentiation of arc magmas in the crust modifies their composition and can obscure a mantle source signature. In case of Ti, magma mixing and fractional crystallization cause large $\delta^{49/47}Ti$ variation in evolved arc lavas (Millet et al., 2016; Hoare et al., 2020; Greber et al., 2021). Several lines of evidence confirm, however, that the variations recorded in our primitive arc lavas represent a primary feature of their source rather result from magmatic differentiation. The removal of isotopically light Fe-Ti oxides, mainly titanomagnetite, during fractional crystallization drives arc magmas to higher $\delta^{49/47}Ti$ (Deng et al., 2019; Hoare et al., 2020; Hoare et al., 2022) and evolved, low-Mg# rhyodacites from the Aegean arc display $\delta^{49/47}Ti$ up to 0.7‰ (Figure 3a). Hoare et al. (2020) found that the saturation point of titanomagnetite may be dependent on the water content of arc magmas but generally occurs around Mg# 30–40. The onset of titanomagnetite fractionation causes a notable inflection in both TiO_2 content and $\delta^{49/47}Ti$ versus Mg# (Figure 3a; Hoare et al., 2022). At higher Mg#, Ti is incompatible with only a small fraction hosted in clinopyroxene during fractional crystallization, which does not cause significant Ti isotope fractionation (Figure 3a). As a result, $\delta^{49/47}Ti$ of primitive arc lavas (Mg# ≥60) is not affected by low-pressure fractional crystallization of Fe-Ti oxides.

Crystallisation of garnet at the base of thick crust or in the upper mantle is another mechanism that can generate silicic magmas with a geochemical signature similar to slab melts (e.g., high Sr/Y; Defant and Drummond, 1990), as proposed for instance by Macpherson et al. (2006). High-pressure fractional crystallisation, however, cannot explain the high $\delta^{49/47}$Ti as garnet, like other silicate minerals (see supplementary Figure S1), does not fractionate Ti isotopes relative to the melt. Furthermore, studies indicate that, just as found for low-pressure fractional crystallisation (Figure 3a), Fe-Ti oxides are absent in early stages of high-pressure crystallisation (Alonso-Perez et al., 2009; Coldwell et al., 2011) and thus cannot drive an increase in $\delta^{49/47}$Ti at Mg# ≥60.

The high Mg# of primitive arc lavas also precludes significant modification by mixing with evolved magmas with low Mg# and elevated $\delta^{49/47}$Ti (Figure 3b). Binary mixing between a basaltic components with $\delta^{49/47}$Ti of ca. 0‰ and an evolved Aegean arc andesite (61 wt.% SiO_2, $\delta^{49/47}$Ti = 0.19‰), dacite (65 wt.% SiO_2, $\delta^{49/47}$Ti = 0.43‰), or rhyodacite (70 wt.% SiO_2, $\delta^{49/47}$Ti = 0.69‰) forms a much steeper array in $\delta^{49/47}$Ti *versus* SiO_2 space than the primitive arc lavas (Figure 3b). Furthermore, andesites and dacites from Kos (Aegean arc) that formed through extensive hybridization of mafic and felsic melts may have similar $\delta^{49/47}$Ti to the primitive arc lavas, but they also have Mg# <60 (Greber et al., 2021). In general, there does not exist a mixing solution that can reproduce the combined SiO_2–$\delta^{49/47}$Ti signature of the primitive arc lavas at Mg# ≥60.

The primitive rhyodacites from western Aleutian arc with $\delta^{49/47}$Ti of 0.21–0.26‰ are the most extreme arc lavas in this study and therefore deserve special consideration. The absence of Fe-Ti oxide phenocrysts suggests that these magmas are undersaturated with respect to Fe-Ti oxides. In general, the geochemical variability of lavas from the western Aleutian arc is inconsistent with any plausible fractional crystallisation process, and the complete absence of evolved (Mg# <55) samples further attests to the negligible role that intracrustal differentiation plays in this locality (Yogodzinski et al., 2015). Extensive fractional crystallisation of hydrous basaltic magmas in the mantle wedge, including removal of a Fe-Ti oxide phase and concomitant Ti isotope fractionation, followed by re-equilibration with mantle wedge peridotite to re-establish Mg# ≥60 (Macpherson et al., 2006) is therefore also unlikely. Furthermore, in such a scenario it would be expected that a broad spectrum of primitive lavas ranging from basalts to rhyodacites are erupted, but only primitive rhyodacites are recovered from the Western Cones area and there is no trace of lavas with lower Mg# or SiO_2 (Yogodzinski et al., 2015). Hence, the unusual Ti isotope variation observed in the western Aleutian rhyodacites and other primitive arc lavas in this study does not result from crustal processes but reflects a primary signature that informs on the mode of slab-to-mantle wedge mass transfer in subduction zones.

5.2. Bulk addition of sediments

Recycled sediments form a key component of arc magmas and could contribute to the elevated $\delta^{49/47}$Ti of primitive arc lavas. Phanerozoic marine sediments have higher $\delta^{49/47}$Ti (0.16–0.24‰; Greber et al., 2017; Klaver et al., 2021) than N-MORB, but only barely reach the $\delta^{49/47}$Ti of primitive rhyodacites from the Aleutian arc (Figure 4). We investigate the role of sediments by combining $\delta^{49/47}$Ti with radiogenic Nd isotopes (^{143}Nd/^{144}Nd) that act as a sensitive proxy for recycled sediment. For the Aegean arc there are direct constraints on $\delta^{49/47}$Ti of subducting sediments, which are homogeneous at 0.172±0.012‰ and have ^{143}Nd/^{144}Nd of 0.5125 (Klaver et al., 2021). Bulk mixing of depleted mantle wedge peridotite with Aegean sediment causes a rapid decrease in ^{143}Nd/^{144}Nd but only a subdued increase in $\delta^{49/47}$Ti in the peridotite (Figure 4a). Mixing with sediment that has lower ^{143}Nd/^{144}Nd, such as the global subducting sediment average (GLOSS; Plank and Langmuir, 1998), has an even smaller influence on $\delta^{49/47}$Ti. Hence, bulk mixing with subducting sediment can only cause a resolvable Ti isotope effect in primitive arc lavas with highly unradiogenic Nd isotope compositions. Moreover, partial melting of physical mixtures of sediment and mantle wedge peridotite, as proposed in the mélange model (e.g., Nielsen and Marschall, 2017), does not leave residual rutile or another Fe-Ti oxide phase (Codillo et al., 2018), and is hence not accompanied by Ti isotope fractionation. Two samples from the Lesser Antilles arc and one from the Aegean arc with ^{143}Nd/^{144}Nd <0.5129 show combined Ti–Nd isotope compositions that can be consistent with bulk sediment mixing. A group of samples (predominantly from the Lesser Antilles) have $\delta^{49/47}$Ti and ^{143}Nd/^{144}Nd similar to MORB, but the majority of the primitive arc lavas have rather radiogenic Nd isotope compositions (^{143}Nd/^{144}Nd >0.5129) coupled with much higher $\delta^{49/47}$Ti than sediment–peridotite mixtures, indicating that bulk sediment addition cannot account for the observed Ti isotope heterogeneity of primitive arc lavas.

5.3. Partial melts in equilibrium with rutile

The only viable agent that can impose elevated $\delta^{49/47}$Ti on primitive arc lavas is a partial melt generated in the presence of residual rutile. The stability of rutile in a melting residue is an interplay between the Ti content of the protolith and the solubility of TiO_2 in the partial melt. Rutile solubility increases with temperature and is much higher in mafic melts than in silicic, alkali-rich melts (Ryerson and Watson, 1987; Gaetani et al., 2008; Xiong et al., 2009). As such, rutile is not a residual phase during melting of sediment–peridotite mixtures (mélanges) as the TiO_2 solubility in such high-temperature (>1200 °C) mafic partial melts exceeds the TiO_2 content of the mélange protolith (Codillo et al., 2018). Furthermore, experimental studies indicate that Ti is highly insoluble in aqueous fluids; even highly saline fluids cannot liberate Ti from the slab (Rustioni et al., 2021) and hence do not have the capability to drastically alter the $\delta^{49/47}$Ti of the mantle wedge. When an influx of aqueous fluids causes hydrous melting of mantle wedge peridotite, the Ti content of the peridotite protolith is too low to retain rutile in the residue (e.g., Grove et al., 2006; Till et al., 2012; Pirard and Hermann, 2015). As a result, $\delta^{49/47}$Ti of hydrous partial melting of mantle wedge peridotite does not cause Ti isotope fractionation and the resultant melts are therefore expected to have the same $\delta^{49/47}$Ti as N-MORB (Figure 5).

The oceanic crust and its sedimentary cover provide the only suitable protolith for partial melts in equilibrium with rutile. The Ti content of the protolith is sufficiently high (typically 1–2 wt.% TiO_2 in MORB and 0.5–1 wt.% TiO_2 in sediments), and hydrous partial melting at low temperature produces silicic partial melts in which the solubility of TiO_2 is low but still at least an order of magnitude higher than in fluids. Hence, rutile is retained in the residue up to at least 900 °C and our modelling (see section 4 and Figure 2) shows that partial melts of (altered) oceanic crust formed at 750–800 °C have fractionated $\delta^{49/47}$Ti (0.24±0.06‰). Partial melts of the subducting slab are therefore the only plausible medium to impart the diagnostic $\delta^{49/47}$Ti signature on arc magmas.

Moreover, slab melts in equilibrium with residual rutile can adequately explain the characteristic relative depletion in Nb and Ta of global arc magmas (e.g., Ryerson and Watson, 1987; Yogodzinski et al., 1995; Elliott et al., 1997; Turner and Langmuir, 2022a). Negative Nb anomalies by themselves, however, do not provide unambiguous evidence for slab melting. Slab-to-mantle wedge mass transfer by aqueous fluids can also impose a negative Nb anomaly on arc magmas due to the low solubility of Nb and Ta in fluids compared to other incompatible elements (Rustioni et al., 2021), but cannot impose elevated $\delta^{49/47}$Ti on primitive arc lavas due to the lack of Ti mobility in such fluids. The difference between fluid- and partial melt-dominated mass transfer is clearly demonstrated by the samples in this study. All primitive arc lavas display clear relative depletions in Nb, but in several basaltic samples with $\delta^{49/47}$Ti similar to N-MORB, including the majority of the Lesser Antilles samples (Figure 4), negative Nb anomalies are not associated with a fractionated Ti isotope signature (supplementary Figure S6). The lack of elevated $\delta^{49/47}$Ti suggests fluid-dominated mass transfer in these Lesser Antilles samples, whereas the combination of relative Nb–Ta depletion and elevated $\delta^{49/47}$Ti as seen in other primitive arc lavas in this study is uniquely attributable to slab melting.

Metabasite partial melts will have the same ^{143}Nd/^{144}Nd as their protolith (MORB; Figure 4b). Primitive Aleutian rhyodacites overlap with metabasite partial melts in Ti–Nd isotope space, in agreement with other geochemical data that suggest a strong slab melt signature in these samples (e.g., Yogodzinski et al., 1995; Yogodzinski et al., 2015; Yogodzinski et al., 2017). Samples from the other localities have lower $\delta^{49/47}$Ti, which suggests that they are not pure slab melts, but these lavas do require a variable contribution of a slab melt to explain their fractionated Ti isotope compositions. In general, Nd isotopes indicate that the slab melt component recorded in the primitive arc lavas is predominantly derived from the (altered) oceanic crust with a subordinate contribution from the superjacent sedimentary veneer. Aegean arc lavas show the strongest metasediment melt signature, consistent with the thick subducted sediment package that is clearly expressed in the radiogenic isotope composition of Aegean arc lavas (e.g., Elburg et al., 2014; Klaver et al., 2016).

5.4. How slab melts contribute to arc magmatism

Hydrous, silicic slab melts are in chemical disequilibrium with mantle wedge peridotite and will react to form orthopyroxene once released from the slab (e.g., Rapp et al., 1999; Pirard and Hermann, 2015). This reaction consumes some SiO_2 from the slab melt and leads to an increase in Mg# and compatible element contents (Cr, Ni) in the reacted melt while incompatible trace element patterns are preserved (e.g., Pirard and Hermann, 2015; Sisson and Kelemen, 2018; Lara and Dasgupta, 2020). Once formed, such orthopyroxene veins can act as pathways for subsequent batches of slab melt, leading to equilibration of melt Mg# with wall-rock orthopyroxene but otherwise leaving the major- and trace element signature of the slab melt unaffected (Rebaza et al., 2023).

The reaction that forms orthopyroxene veins will have little effect on the $\delta^{49/47}$Ti of the percolating slab melt. Titanium is incompatible in orthopyroxene and hence the extraction of orthopyroxene from the melt will increase melt Ti content (Sisson and Kelemen, 2018). Equilibrium Ti isotope fractionation between silicate melt and orthopyroxene is negligible (Rzehak et al., 2021; see supplementary Figure S1). Hence, newly formed orthopyroxene is predicted to have a Ti isotope composition that mirrors that of the melt and does drive the melt to notably higher or lower $\delta^{49/47}$Ti. Even after substantive orthopyroxene formation $\delta^{49/47}$Ti of the slab melt will be thus conserved.

The primitive rhyodacites from the Aleutian arc with $\delta^{49/47}$Ti of 0.24±0.03‰ (Figures 4 and 5) are a rare example of such a process where silicic slab melts have traversed the mantle wedge with little modification besides Mg# equilibration and have erupted at the surface. This probably reflects the tectonic setting of western Aleutian rhyodacite volcanoes (Yogodzinski et al., 2015), which lie only 40–50 km above the top of the slab and just east of a physical opening in the subducting plate (Levin et al., 2005; Hayes et al., 2018). In this setting significant melt production is expected because the temperature of the subducting oceanic crust must be well above the hydrous basalt solidus. The shallow depth means that, in turn, any melt that escapes the slab will have a relatively short pathway to the surface, thus limiting thermal and chemical exchange between the silicic melt and ambient mantle peridotite.

More commonly, however, ascending hydrous slab melts will trigger partial melting of the mantle wedge when the wet peridotite solidus is exceeded (Kelemen, 1995; Pirard and Hermann, 2015). Mixing with peridotite melts will attenuate the trace element and $\delta^{49/47}$Ti slab melt signature and produce a wide array of primary arc magma compositions that are blends of slab- and peridotite-derived melt. Nevertheless, elevated $\delta^{49/47}$Ti compared to N-MORB remains a uniquely sensitive tracer for the involvement of a slab melt even when this is diluted with peridotite melt in transit through the mantle wedge (Figure 4b).

Furthermore, the striking correlation between $\delta^{49/47}$Ti and SiO_2 content of primitive arc lavas (Figure 5) suggests that the elevated silica content of primitive (Mg# ≥60) andesites and (rhyo)dacites found worldwide (e.g., Kelemen et al., 2014) is a direct consequence of slab melting. We reiterate that although fluid-fluxed melting of mantle wedge peridotite can produce andesitic melts with high Mg# (e.g., Kushiro, 1972; Till et al., 2012), the lack of Ti mobility in fluids means that such partial melts do not have the elevated $\delta^{49/47}$Ti found in primitive andesites and (rhyo)dacites (Figure 5). Hence, Ti isotope systematics of primitive arc lavas provide strong support for slab melts as a key medium for mass transfer in subduction zones.

5.5. A recipe for widespread slab melting

The specific sensitivity of Ti isotopes to slab melting allows us to identify at least one sample with a slab melt component in all eight subduction zones for which $\delta^{49/47}$Ti compositions of primitive arc lavas are available (Figure 5). Primitive andesites and rhyodacites from the Aleutian arc, Cook Island, and Solander Islands have previously been interpreted in the light of a significant slab melt contribution (e.g., Kay, 1978; Yogodzinski et al., 1995; Stern and Kilian, 1996; Foley et al., 2014; Yogodzinski et al., 2017; see supplementary material), which is confirmed by the new Ti isotope data, but also arcs where primitive silicic magmas are rare show evidence for slab melting. For example, a reappraisal of previously published $\delta^{49/47}$Ti data for the New Britain arc and Mariana arc (Millet and Dauphas, 2014; Millet et al., 2016) leads us to recognize that one out of two New Britain, and two out of three Mariana primitive lavas show a combination of elevated SiO_2 content and $\delta^{49/47}$Ti (ca. 0.05‰) relative to N-MORB (Figure 5) that could be indicative of a modest but clearly resolvable slab melt contribution, though a more systematic study of Mariana and New Britain arc lavas is needed to substantiate this. Moreover, primitive basaltic andesites from the Aegean arc show clear Ti isotope evidence for an important role for slab melting ($\delta^{49/47}$Ti = ca. 0.10‰) whereas this had hitherto not been explicitly demonstrated. In the Lesser Antilles arc, there is no unambiguous Ti isotope evidence for slab melting in the southern islands (Grenada, St. Vincent, Bequia). The single sample from Saba, the northernmost active volcanic centre of the Lesser Antilles arc, does display elevated $\delta^{49/47}$Ti (0.06‰; Figure 4). The combined SiO_2–$\delta^{49/47}$Ti signature of this samples falls on the primitive arc lava array in Figure 5, consistent with a slab melt contribution, but lavas from Saba show evidence for magma mixing (Defant et al., 2001) and this process cannot be completely ruled out. In general, however, slab melting seems to be a widespread phenomenon in modern subduction zones.

The prevalence of slab melting in modern subduction zones raises the question of which conditions are required to allow melting of the subducted slab. Slab melting has often been related to the subduction of young and warm oceanic crust (e.g., Defant and Drummond, 1990). Recent dynamic models (Syracuse et al., 2010; van Keken et al., 2011; van Keken et al., 2018) and geochemical thermometry (Cooper et al., 2012), however, suggest that the temperature required for slab melting can be met in the majority of modern subduction zones. Based on the Ti isotope evidence for widespread slab melting, it appears that slab age is not the defining parameter that dictates whether the slab can melt. For example, the Aegean arc has the oldest (ca. 200 Ma) and therefore coldest subducting oceanic crust globally, yet lavas with a strong slab melt signature are erupted. Rather than slab age, the three-dimensional structure of the slab likely plays a pivotal role in providing additional sources of heat. In particular, tearing of the slab allows the inflow of asthenospheric mantle that can heat the torn edge of the slab. This explanation has been invoked for the melting of the 50–60 Ma Pacific slab in the western Aleutian arc (Yogodzinski et al., 2001; Levin et al., 2005; Yogodzinski et al., 2017) and can also apply to the Aegean arc where lavas from Nisyros display Pb isotope evidence for toroidal mantle flow through a slab tear (Klaver et al., 2016).

Another prerequisite for slab melting is the presence of aqueous fluids to lower the solidus of the metabasite and metasediment. Insufficient water is probably present in the protolith at sub-arc depths to allow dehydration melting (e.g., Spandler and Pirard, 2013), and hence an external fluid source is required. Strontium isotope constraints suggest breakdown of serpentinite in the lithospheric mantle of the slab as an important source of aqueous fluids (Yogodzinski et al., 2017; Klaver et al., 2020). These fluids will travel up a temperature gradient in the slab and initiate hydrous partial melting when the wet solidus of metabasite and/or metasediment is crossed. In cold subduction zones where the temperature does not exceed the wet solidus of the slab, solute-rich aqueous fluids may still play an important role of slab-to-mantle wedge mass transfer (e.g., Keppler, 2017; Rustioni et al., 2021) and contribute to island arc basalt generation, but only slab melts can deliver fractionated Ti to the mantle wedge and produce silicic primitive arc magmas.

6. Conclusions

A comprehensive study of the Ti isotope composition of primitive arc lavas (Mg# ≥60) from eight global subduction zones indicates that primitive arc lavas display pronounced Ti isotope heterogeneity compared to basalts erupted at oceanic spreading centres (MORB) and within-plate settings. Normal MORB has homogeneous $\delta^{49/47}$Ti (0.001±0.015‰), consistent with an absence of Ti isotope fractionation during peridotite melting. In contrast, primitive arc lavas have strongly correlated $\delta^{49/47}$Ti and SiO_2 contents with the highest $\delta^{49/47}$Ti (0.24±0.03‰) recorded in primitive rhyodacites from the western Aleutian arc. The fractionated Ti isotope signature reflects melting in the presence of residual rutile, which can only plausibly take place in the subducted oceanic crust and its sedimentary cover. Hence, $\delta^{49/47}$Ti is a robust tracer of slab melting even when slab melts are diluted during interaction with the mantle wedge. The conclusions from this study can furthermore be summarised as follows:

- The modelled $\delta^{49/47}$Ti of hydrous metabasite partial melts at 750–800 °C and 2.6–4.5 GPa (0.24±0.06‰) matches that of primitive Aleutian rhyodacites (0.24±0.03‰), indicating that these

Aleutian rhyodacites are slab melts that have traversed the mantle wedge with only little modification in the form of Mg# equilibration.

- The elevated $\delta^{49/47}$Ti of primitive andesites and rhyodacites rules out their generation through hydrous peridotite melting as the fractionated Ti signature cannot be carried to the mantle wedge by aqueous fluids and rutile is not stable in peridotite melting residua.
- In addition to the Aleutian arc, all other studied subduction zones also display evidence for slab melting, but in a more diluted form. Hydrous, silicic slab melts in transit through the mantle wedge promote additional peridotite melting, which dilutes the original slab melt signature and generates a wide spectrum of primary arc magmas that are blends of slab- and peridotite-derived melt.
- Slab melting therefore appears to be a common, widespread phenomenon in modern subduction zones, irrespective of slab age. Rather, three-dimensional effects such as the presence of slab tears can help raise the temperature of subducting slabs above their wet solidus. The influx of fluids released by serpentinite breakdown will then trigger hydrous melting of the oceanic crust and superjacent sediments.

Acknowledgements

This manuscript greatly benefitted from discussions with Pierre Bouilhol, Ben Maunder, Jeroen van Hunen, Tim Elliott, Julie Prytulak, and Nikitha Saji. Jon Blundy and Richard Robertson are thanked for providing some of the Lesser Antilles samples; Felix Genske and Heidi Beier are thanked for their assistance with Sr–Nd isotope measurements made in Münster. Comments made by Steve Turner and an anonymous reviewer helped to improve this work. Rosemary Hickey-Vargas is thanked for editorial handling. This work was supported by NERC project NIIICE (NE/R001332/1) and a Royal Society Research Grant (RG150693) to MAM, as well as U.S. National Science Foundation grants to GY (OCE-1551640, EAR-1753518).

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Martijn Klaver: Conceptualization, Formal Analysis, Investigation, Writing – Original Draft; **Gene Yogodzinski**: Conceptualization, Resources, Writing – Review & Editing, Funding Acquisition; **Capucine Albert**: Investigation; **Michal Camejo-Harry**: Resources; **Marlina Elburg**: Resources; **Kaj Hoernle**: Resources; **Colin Macpherson**: Resources, Writing – Review & Editing; **Geoff Nowell**: Resources; **Tracy Rushmer**: Resources, Writing – Review

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FIGURE CAPTIONS

Figure 1. Kernel density diagram for primitive arc lavas (Mg# ≥60) compared to normal mid ocean ridge basalts (N-MORB; Millet et al., 2016; Deng et al., 2018) and ocean island basalts (OIB) pus enriched MORB (Millet et al., 2016; Deng et al., 2018; Deng et al., 2019; Hoare et al., 2020; Deng et al., 2023). See supplementary Dataset 2 for all data. The field for the bulk silicate Earth (BSE) is from Millet et al. (2016). Primitive arc lavas have $\delta^{49/47}$Ti that extends to higher values than MORB.

Figure 2. The modelled magnitude of Ti isotope fractionation during hydrous melting of (altered) MORB (A) and various sediment lithologies (B) at 2.6–6 GPa, expressed as $\Delta^{49/47}Ti_{melt–protolith}$, which is the difference in $\delta^{49/47}$Ti between the partial melt and the protolith. Experimental studies (Schmidt et al., 2004; Kessel et al., 2005b; Skora and Blundy, 2010; Martindale et al., 2013; Carter et al., 2015; Mann and Schmidt, 2015; Skora et al., 2015; Martin and Hermann, 2018; Sisson and Kelemen, 2018) yield the phase proportions and Ti content of the partial melt and residual minerals after which $\Delta^{49/47}Ti_{melt–protolith}$ is calculated by isotopic mass balance using Ti isotope mineral–melt fractionation factors (supplementary Tables S1 and 2). Rutile is invariably present as a residual phase during hydrous melting of metabasite and metasediment, which imposes an isotopically heavy Ti isotope signature on the partial melt. Some symbols are shifted slightly to higher or lower temperature (≤5 °C unless indicated) to prevent cluttering of the datapoints. The open symbols in panel B denote experiments where both titanomagnetite (≥0.5 wt.% abundance) and rutile are present as residual phase. The grey field

shows the Ti isotope fractionation of 2–25% anhydrous partial melts of a fertile peridotite at 1–2.5 GPa. See supplementary material for a detailed description of the modelling approach and parameters used; the melting models are provided in supplementary Dataset 1. A corresponding figure for the fractionation of the melting residua relative to the protolith ($\Delta^{49/47}Ti_{residue–protolith}$) is provided in the supplementary material (Figure S2).

Figure 3. Effects of magmatic differentiation on the Ti isotope composition of arc lavas. (A) Fractional crystallization of isotopically light titanomagnetite (Ti-mag) drives arc lavas to high $\delta^{49/47}Ti$. Two arc differentiation suites are shown: a tholeiitic Kermadec and New Britain arcs trend, and a calc-alkaline trend displayed by Santorini lavas (Aegean arc). Both suites show a clear inflection in $\delta^{49/47}Ti$ upon saturation of the melt with titanomagnetite at Mg# 30–40. At higher Mg#, fractional crystallization of silicate minerals has negligible effect on $\delta^{49/47}Ti$ and hence primitive arc lavas (PAL; Mg# ≥60) retain a primary Ti isotope signature. (B) Titanium isotope effects of magma mixing. Two sets of mixing lines are shown between primitive lavas (St. Vincent picrite RSV52, New Britain basalt 116852-5) and either evolved andesite (AAS-036), dacite (AAS-041), or rhyodacite (AAS-033) from Santorini (Aegean arc). The mixing lines are dashed where Mg# <60. Magma mixing cannot account for the $\delta^{49/47}Ti$ variation seen in global primitive arc lavas.

Figure 4. Variation in $\delta^{49/47}Ti$ of primitive arc lavas (Mg# ≥60) versus $^{143}Nd/^{144}Nd$; see supplementary Dataset 2 for all data shown in the figure. (A) Model curves showing binary mixing between a depleted mantle (DM) source (0.05 wt.% TiO_2, 0.4 µg/g Nd) and bulk sediment subducting in the Aegean arc (Klaver et al., 2021) or global subducting sediment (GLOSS; Plank and Langmuir, 1998) with $\delta^{49/47}Ti$ estimated at 0.24‰ (i.e., the maximum of modern marine sediments; Greber et al., 2017). The compositions of N-MORB and OIB+E-MORB are shown for comparison – see Figure 1 for data sources. (B) Model curves for mixing between a depleted mantle (DM) source and hydrous partial melts of metabasite and metasediment. The composition of the metabasite partial melt ($\delta^{49/47}Ti$ = 0.24‰, 0.24 wt.% TiO_2) is the average $\Delta^{49/47}Ti_{melt–protolith}$ for metabasite at 750–800 °C (0.244‰; see Figure 2a) added to the average $\delta^{49/47}Ti$ of N-MORB (0.001‰; see Figure 1). The metasediment partial melt ($\delta^{49/47}Ti$ = 0.34‰, 0.17 wt.% TiO_2) is the average $\Delta^{49/47}Ti_{melt–protolith}$ for metasediment (without titanomagnetite) at 750–800 °C (0.171‰; see Figure 2b) added to the average $\delta^{49/47}Ti$ of sediment subducting in the Aegean arc (0.172‰; Klaver et al., 2021). Both metabasite and metasediment partial melt

are assumed to have Ti/Nd of 55 (Martindale et al., 2013; Skora et al., 2015; Sisson and Kelemen, 2018). Aleutian arc rhyodacites for which no Nd isotope data are available are plotted at the average $^{143}Nd/^{144}Nd$ of similar samples from the Western Cones area where $^{143}Nd/^{144}Nd$ is homogeneous at 0.51312±0.00004. Sample location abbreviations: Aeg – Aegean arc; Ale – Aleutian arc; LAn – Lesser Antilles arc; Mar – Mariana arc; NBr – New Britain arc; Phi – Philippines arc; CI – Cook Island (Austral Volcanic Zone, Chile); SI – Solander Islands (New Zealand).

Figure 5. Primitive arc lavas (Mg# ≥60) display a strong correlation between $\delta^{49/47}Ti$ and SiO_2 content. The composition of the metabasite partial melts at 750–800 °C (grey squares) is their $\Delta^{49/47}Ti_{melt–protolith}$ (Figure 2a) added to the average $\delta^{49/47}Ti$ of N-MORB (0.001‰; see Figure 1). The composition of hydrous peridotite melts is from experimental studies for peridotite+H_2O (Grove et al., 2006; Till et al., 2012) where $\delta^{49/47}Ti$ is calculated though an isotopic mass balance (as in Figure 2; see supplementary material for details), assuming that no Ti is transported to the mantle wedge by aqueous fluids (Rustioni et al., 2021) and mantle peridotite has $\delta^{49/47}Ti$ = 0. Sample location abbreviations: Aeg – Aegean arc; Ale – Aleutian arc; LAn – Lesser Antilles arc; Mar – Mariana arc; NBr – New Britain arc; Phi – Philippines arc; CI – Cook Island (Austral Volcanic Zone, Chile); SI – Solander Islands (New Zealand).

Figure 1

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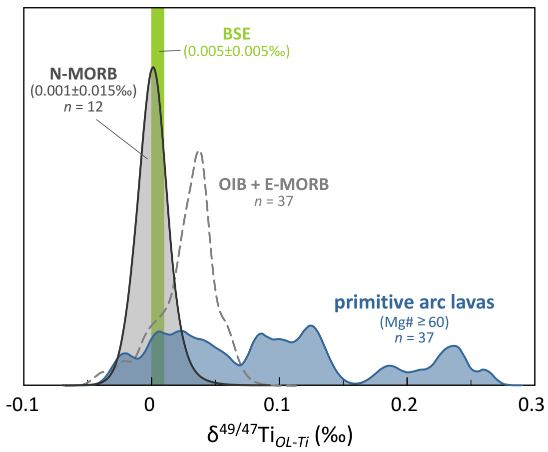
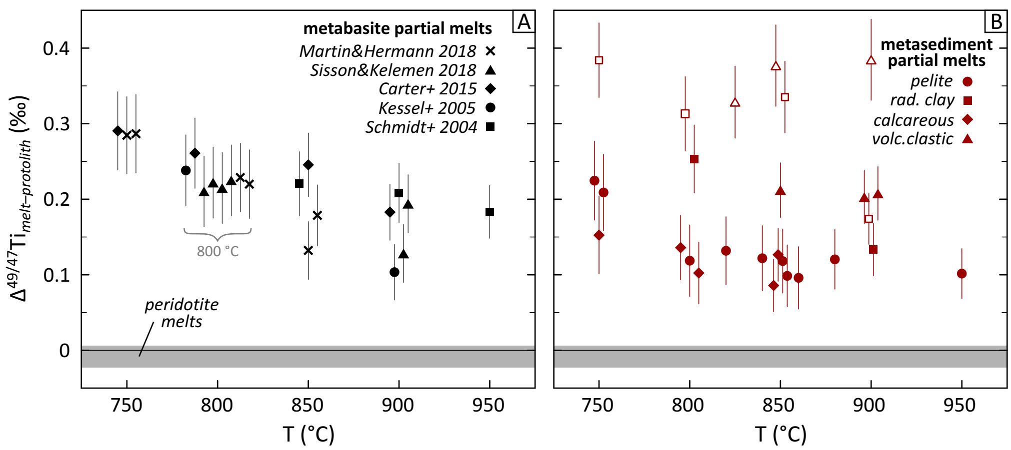


Figure 2



A
metabasite partial melts
Martin&Hermann 2018
Sisson&Kelemen 2018
Carter+ 2015
Kessel+ 2005
Schmidt+ 2004
800 °C
peridotite melts
$\Delta^{49/47}Ti_{melt-protolith}$ (‰)
0.4
0.3
0.2
0.1
0
750
800
850
900
950
T (°C)
B
metasediment partial melts
pelite
rad. clay
calcareous
volc.clastic
750
800
850
900
950
T (°C)

Figure 3

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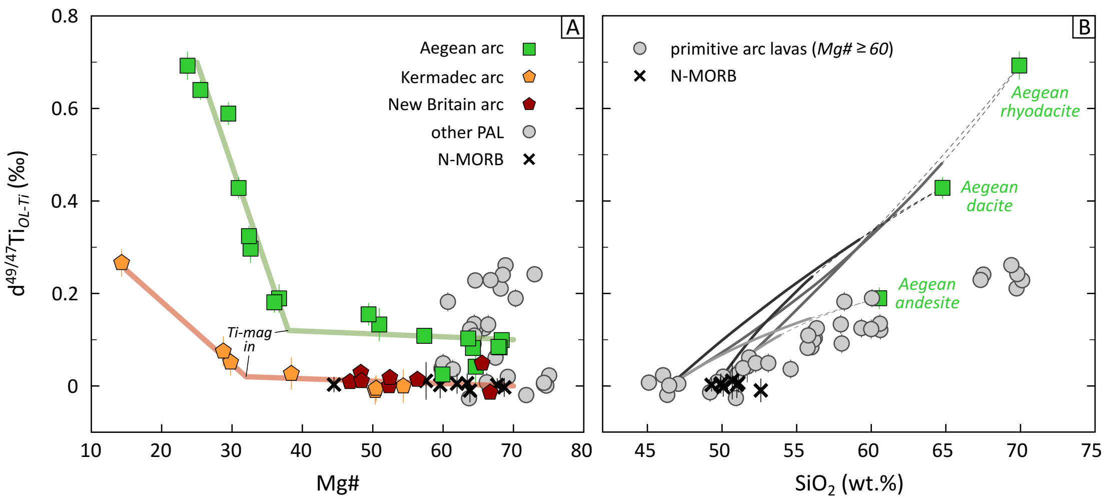


Figure 4

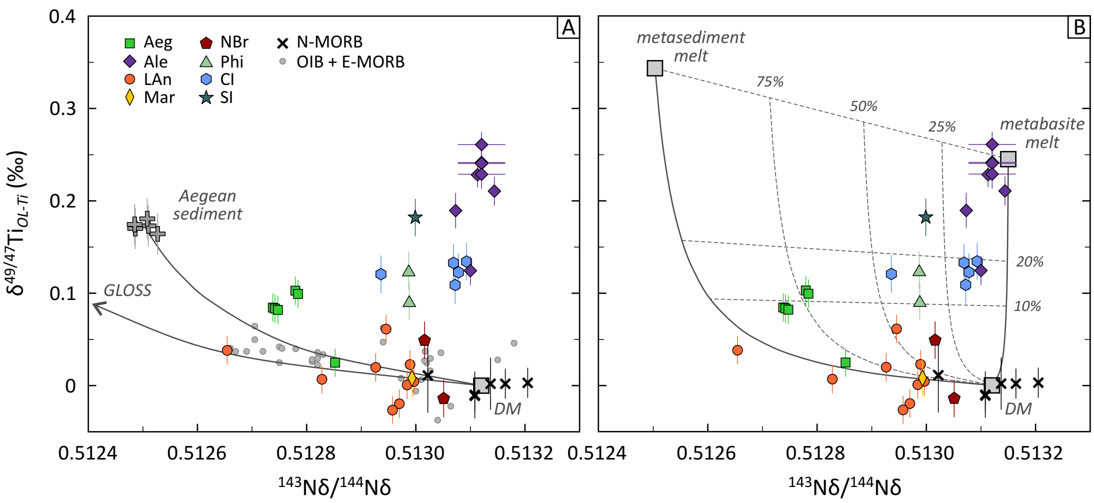
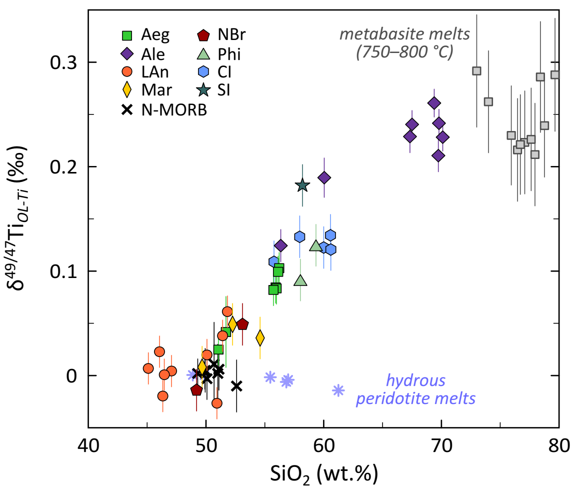

A
Aeg
Ale
LAn
Mar
NBr
Phi
CI
SI
N-MORB
OIB + E-MORB
Aegean sediment
GLOSS
DM
0.4
0.3
0.2
0.1
0
0.5124
0.5126
0.5128
0.5130
0.5132
δ49/47TiOL-Ti (‰)
143Nd/144Nd
B
metasediment melt
metabasite melt
75%
50%
25%
20%
10%
DM
0.5124
0.5126
0.5128
0.5130
0.5132
143Nd/144Nd

Figure 5



Aeg
Ale
LAn
Mar
N-MORB
NBr
Phi
CI
SI
metabasite melts
(750–800 °C)
hydrous
peridotite melts
0.3
0.2
0.1
0
40
50
60
70
80
$\delta^{49/47}Ti_{OL-Ti}$ (‰)
SiO_2 (wt.%)

Dataset 1

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Supplementary material for online publication only

Supplementary Dataset 1_melting models.xlsx

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Supplementary material for online publication only
Supplementary Dataset 2_Ti isotope data.xlsx

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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