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Titanium isotope constraints on the mafic sources and geodynamic origins of Archean crust

L. Hoare[1*], **L.J.A. Rzehak**[1], **S. Kommescher**[1], **M. Jansen**[2], **M.T. Rosing**[3], **T. Nagel**[4], **M.-A. Millet**[5], **J.E. Hoffmann**[6], **R.O.C. Fonseca**[1]

Abstract

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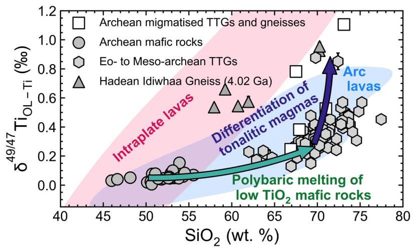

The timing and formation of Earth's first continents during the Archean are subjects of significant debate. By examining titanium isotope variations in Archean Tonalite-Trondhjemite-Granodiorite (TTG) rocks and using advanced thermodynamic modelling, we can narrow down the processes involved and emphasise the role of mafic precursor compositions. In our study of Eoarchean Isua metabasalts and Itsaq tonalites in southern West Greenland, we observed a pattern of increasing Ti isotope enrichment with higher SiO_2 content, resembling the compositions found in modern subduction zone rocks. Our modelling suggests that the Ti isotope variations in TTGs can be best explained by a combination of partial melting of low TiO_2 metabasalts and subsequent crystallisation of tonalitic magmas, resulting in heavier Ti isotopes. This means that Ti isotopes help us distinguish the contributions of various mafic sources and fractional crystallisation during TTG formation. In the case of Itsaq tonalites and many other Eoarchean TTGs, low TiO_2 tholeiitic metabasalts with arc-like characteristics likely represent the mafic source rocks, suggesting the formation of some of Earth's earliest continental crust within a proto-subduction zone setting.

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Introduction

Remnants of Archean juvenile continental crust are preserved in the form of sodic granitoids collectively known as Tonalite-Trondhjemite-Granodiorites (TTG). There is ongoing debate about the origin of these incomplete remnants, leading to varying interpretations over the responsible tectonic regime. TTG formation hypotheses are broadly divided between two end members that involve partial melting of thickened, hydrated mafic crust in 1) a horizontal tectonic regime, possibly analogous to modern subduction (*e.g.*, Foley *et al.*, 2002), or 2) a non-uniformitarian regime such as oceanic plateaux (*e.g.*, Nair and Chacko, 2008). Furthermore, despite extensive geochemical and experimental evidence supporting polybaric dehydration melting of hydrated mafic crust as a formation mechanism of juvenile TTG magmas (*e.g.*, Barker and Arth, 1976; Rapp *et al.*, 1991), many TTGs have undergone subsequent fractional crystallisation (*e.g.*, Laurent *et al.*, 2020), obscuring the nature of their mafic protolith.

Mass dependent isotope variations of titanium (expressed as $\delta^{49/47}$Ti) have recently been utilised as a novel tool to investigate magmatic differentiation (Millet *et al.*, 2016; Greber *et al.*, 2017; Deng *et al.*, 2019; Aarons *et al.*, 2020; Hoare *et al.*, 2020), and can be applied to test petrogenetic models of TTG formation. Based on these studies it has been postulated that titanium isotope fractionation is mainly driven by the sequestration of light isotopes into Fe-Ti oxides (ilmenite, magnetite, and rutile) where Ti occupies VI-fold coordination (*e.g.*, Hoare *et al.*, 2022; Johnson *et al.*, 2023). Consequently, melts in equilibrium with these phases are enriched in heavy Ti isotopes, which occupy lower coordination (VI- and V-fold). Furthermore, $\delta^{49/47}$Ti variations of evolved magmas from different geodynamic settings show differences (Fig. 1). Silicic melts from reduced, H_2O-poor, Ti-rich intra-plate magmas have higher $\delta^{49/47}$Ti relative to arc magmas at a given SiO_2 content (Fig. 1; Deng *et al.*, 2019; Hoare *et al.*, 2020). In alkaline intra-plate magmas, larger Ti isotope fractionation is driven by significant Fe-Ti oxide crystallisation, in contrast to hydrous subduction zone magmas where only low Ti magnetite is present (Hoare *et al.*, 2022; Johnson *et al.*, 2023). The uniform Ti isotope composition in Archean shales and comparable fractionation patterns in Archean TTGs have sparked the hypothesis that substantial felsic crust has existed since 3.5 billion years ago, potentially indicating past plate tectonics (Greber *et al.*, 2017; Zhang *et al.*, 2023). Conversely, non-subduction related magmatism also produces felsic rocks with heavy Ti isotope compositions (Deng *et al.*, 2019) and the Ti isotope composition of

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1. Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, 150 Universitätsstraße, 44801 Bochum, Germany
2. Deutsches Bergbau-Museum Bochum, Leibniz-Research Museum for Georesources, Herner Str. 45, 44787 Bochum, Germany
3. Globe Institute, University of Copenhagen, Øster Voldgade 5-7, 1350 København, Denmark
4. Institut für Geologie, Technische Universität Bergakademie Freiberg, Bernhard-von-Cotta-Str. 209599 Freiberg, Germany
5. School of Earth and Environmental Sciences, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK
6. Institut für Geologische Wissenschaften, Freie Universität Berlin, Malteserstraße 74-100, 12249 Berlin, Germany
* Corresponding author (email: liam.hoare@rub.de)

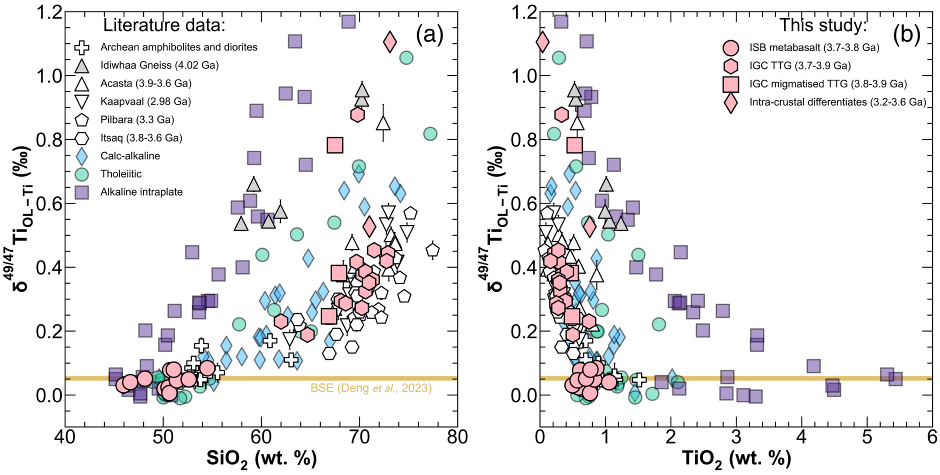

Figure 1 $\delta^{49/47}$Ti compositions of ISB metabasalts, IGC tonalites and intra-crustal differentiates, with other Hadean-Archean rocks, compared to Phanerozoic lavas from different tectonic settings *versus* **(a)** SiO_2 and **(b)** TiO_2. Literature sources are given in the Supplementary Information, Table S-11.

sedimentary archives may be biased *via* mechanical processes (Klaver *et al.*, 2021; Saji *et al.*, 2023). These factors challenge the reliability of Archean sediments as Ti isotope archives of the continental crust. A subsequent study by Aarons *et al.* (2020) observed that SiO_2 *vs.* $\delta^{49/47}$Ti covariations within 4.02 Ga Idiwhaa gneisses from the Acasta Gneiss Complex, Slave craton, Canada (Fig. 1a), mirror the trend of alkaline intra-plate magmas, whereas post-4.02 Ga TTGs exhibit $\delta^{49/47}$Ti variations comparable to modern calc-alkaline magmas (Aarons *et al.*, 2020). This dichotomy may imply a transition to subduction style tectonics at the Hadean-Archean boundary (Aarons *et al.*, 2020). The usefulness of Ti isotopes in understanding early Earth geodynamics is challenging due to the lack of information about Hadean mafic crust composition (Nebel *et al.*, 2014) and differing opinions on the ideal mafic protolith for Archean TTG magmas (Smithies *et al.*, 2009; Nagel *et al.*, 2012). Accurate knowledge of mafic protoliths is crucial because the early Archean mantle had a distinct Ti isotope composition from today (Deng *et al.*, 2023), and the composition of the parental melt significantly influences Ti isotope fractionation during magmatic processes (Deng *et al.*, 2019; Hoare *et al.*, 2020). Elucidating the composition of the mafic protolith may thus provide tighter constraints of the geodynamic setting of TTG formation.

Here we present $\delta^{49/47}$Ti data of well characterised Eoarchean (3.8–3.7 Ga) tholeiitic metabasalts from the Isua supracrustal belt (ISB) and Palaeo- to Eoarchean (3.9–3.2 Ga) tonalites and intra-crustal differentiates (pegmatites and augen gneisses) from the adjacent Itsaq Gneiss Complex (IGC) of southern West Greenland. The Itsaq meta-tonalites are found within low-strain zones in the IGC as almost undeformed, single phase tonalites with partially preserved primary magmatic textures and mineral assemblages (Nutman *et al.*, 1999) making these samples ideal to investigate early crustal formation. These rocks are interpreted to originate from polybaric partial melting of thickened, arc-like mafic crust followed by fractional crystallisation of pooled melts in mid-crustal plutons, within a geodynamic regime analogous to a modern subduction setting (Nagel *et al.*, 2012; Hoffmann *et al.*, 2014). Others argue against such an origin, favouring non-uniformitarian processes (Rollinson, 2022). We use Ti isotope variations in ISB and IGC rocks, and detailed thermodynamic modelling, to unravel the influence of mafic source composition and the effects of partial melting and crystallisation processes on the geochemistry of Archean TTGs.

Results

Titanium isotope measurements are reported as $\delta^{49/47}Ti_{OL-Ti}$ (‰) = $[^{49/47}Ti_{sample}/^{49/47}Ti_{OL-Ti} - 1] * 10^3$, which is the deviation in parts *per* thousand of the ^{49}Ti/^{47}Ti ratio relative to Origins Laboratory Ti (OL-Ti), the recognised Ti reference material. The $\delta^{49/47}$Ti values of ISB tholeiitic metabasalts show limited variation (+0.01 to +0.09 ‰). Non-gneissic IGC tonalites display $\delta^{49/47}$Ti compositions between +0.18 and +0.88 ‰ (Fig. 1). Migmatised tonalites and intra-crustal differentiates (augen and pegmatitic gneisses) also show substantial variability in δ^{49}Ti; +0.25 to +0.78 ‰, and +0.55 to +1.11 ‰, respectively. To assess the extent of Ti isotope fractionation during partial melting of different mafic source compositions and magmatic differentiation we utilise constraints from thermodynamic phase equilibria modelling combined with relevant mineral-melt Ti isotope fractionation factors. A detailed summary of our results and modelling are provided in the Supplementary Information.

Ti Isotope Fractionation During Partial Melting of Different Mafic Protoliths

Polybaric melting of a single mafic source has been invoked to explain the chemical diversity of TTG magmas. However, given the sensitivity of Ti isotope fractionation to parental melt composition (Deng *et al.*, 2019; Hoare *et al.*, 2020), partial melting of diverse mafic sources of differing TiO_2 contents will likely generate melts with contrasting Ti isotope compositions. Polybaric melting of both TiO_2-poor (~0.6–0.7 wt. %) Isua tholeiitic metabasalts, and intermediate TiO_2 (~1 wt. %) plateau basalts produce tonalitic melts ($SiO_2 > 60$ wt. %) with $\delta^{49/47}$Ti between ~+0.10 to +0.26 ‰ (Fig. 2). The partial melt compositions in these scenarios define shallow trends of increasing $\delta^{49/47}$Ti with increasing SiO_2 and decreasing TiO_2 (Fig. 2a). For low Al metabasalts, the absence of residual plagioclase means that, at a given melt fraction and $\delta^{49/47}$Ti, melt compositions are shifted to lower SiO_2 (Fig. 2a). Low pressure (0.8 GPa) melting of E-MORB (~1.5 wt. % TiO_2), produces a steep trend with elevated $\delta^{49/47}$Ti at lower SiO_2 and higher TiO_2 (Fig. 2b). Melting E-MORB at higher pressure (1.3 GPa) produces a notably shallower trend. However, irrespective of melting pressure, higher TiO_2 mafic sources produce melt compositions that are generally too TiO_2-rich at a given SiO_2 content (Fig. 2b,d). Conversely, the

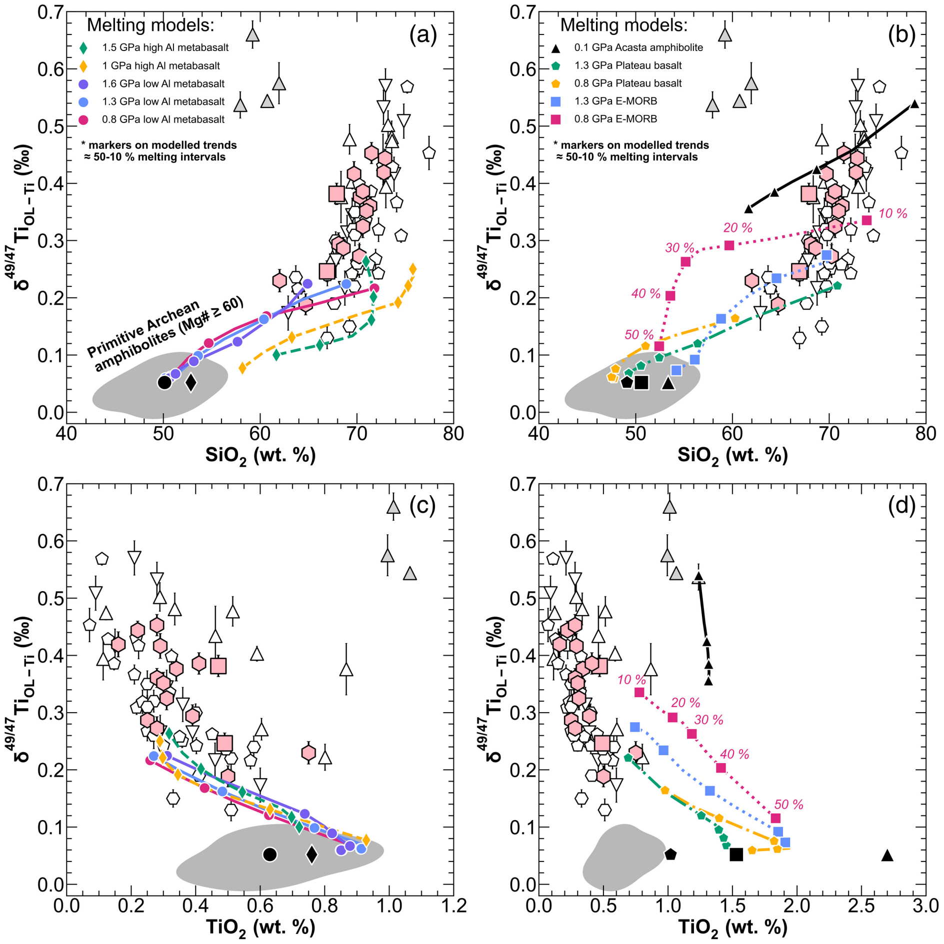

Figure 2 $\delta^{49/47}$Ti *versus* SiO$_2$ and TiO$_2$ for partial melting of high and low Al Isua metabasalts at 0.8–1.6 GPa **(a and c)**; and partial melting of E-MORB and primitive plateau basalt at 0.8–1.3 GPa **(b and d)** superimposed on to $\delta^{49/47}$Ti data for Hadean-Archean TTGs (pink, white and grey symbols; see Fig. 1 for the legend). Shaded grey field represents $\delta^{49/47}$Ti range of primitive Archean amphibolites (Mg# > 60) defined by a 0.95 probability density contour. Black symbols indicate the starting composition for each model. Symbols on modelled trends represent melting intervals between 50–10 %. Modelling details are given in the Supplementary Information.

impact melt scenario of Johnson *et al.* (2018) for the Hadean Idiwhaa gneisses, would involve low pressure (0.1 GPa) melting of a TiO$_2$-rich protolith (~2.7 wt. %) producing amphibole-free residues and high SiO$_2$-TiO$_2$ melts with significantly higher $\delta^{49/47}$Ti (~+0.36 to +0.54 ‰) relative to the other melting scenarios (Fig. 2b,d). However, it is noteworthy that this model produces, at best, an imperfect match to the Idiwhaa data (Fig. 2b,d). The varying magnitude of Ti isotope fractionation during partial melting is largely driven by competition between amphibole and Fe-Ti oxides for the elemental budget of Ti (Fig. S-1; Supplementary Information). Amphibole is the dominant Ti-bearing phase during melting of low to intermediate Ti mafic sources, whereas Fe-Ti oxides, which possess larger Ti isotope fractionation factors, are mostly absent (Fig. S-1; Supplementary Information). Higher parental melt TiO$_2$ contents enable greater abundances of Fe-Ti oxides in the melting residues (Fig. S-1). This results in a greater magnitude of Ti isotope fractionation (Fig. 2), with reduced fractionation at higher pressure as rutile possesses a smaller fractionation factor relative to ilmenite (Hoare *et al.*, 2022; Rzehak *et al.*, 2022). Therefore, the shallow positive correlation between $\delta^{49/47}$Ti and SiO$_2$ shared by modern calc-alkaline lavas and Archean TTGs (Fig. 1a) could be largely coincidental, with the modest fractionation in TTGs reflecting the dominance of amphibole on the Ti budget during partial melting. Furthermore, the dominant role of amphibole likely precludes a TiO$_2$ -rich (>1 wt. %) mafic source for Itsaq tonalites and other Eoarchean TTGs or requires very low or high melting pressures if TiO$_2$-rich mafic sources are invoked (Fig. 2). Nevertheless, polybaric melting of low-TiO$_2$ metabasalts can only reproduce the $\delta^{49/47}$Ti variation for TTGs with $\delta^{49/47}$Ti up to ~+0.3 ‰ (Fig. 2a,c), suggesting that an additional process is required to explain $\delta^{49/47}$Ti above that value.

Ti Isotope Fractionation During Magmatic Differentiation and Crustal Re-Working

While partial melting of tholeiitic metabasalts accounts for many major and trace element characteristics of IGC tonalites (cf. Hoffmann *et al.*, 2014), our modelling reveals that partial melting alone cannot reproduce the complete range of $\delta^{49/47}$Ti in TTGs (Fig. 2). The differentiation of intermediate tonalitic/andesitic liquids is fundamental to generating evolved magmas within the Earth's crust (*e.g.*, Marxer and Ulmer, 2019), and similar processes have been invoked to explain the compositional diversity of TTG magmas (*e.g.*, Laurent *et al.*, 2020).

Equilibrium crystallisation models of tonalitic magmas (~62–66 wt. % SiO$_2$) at 0.5 GPa with an initial $\delta^{49/47}$Ti ranging between ~+0.2 to +0.3 ‰ produces evolved melts (>70 wt. % SiO$_2$) with $\delta^{49/47}$Ti values up to ~+0.6 ‰ (Fig. 3). Fractional crystallisation at the same pressure produces TTG melts with heavier

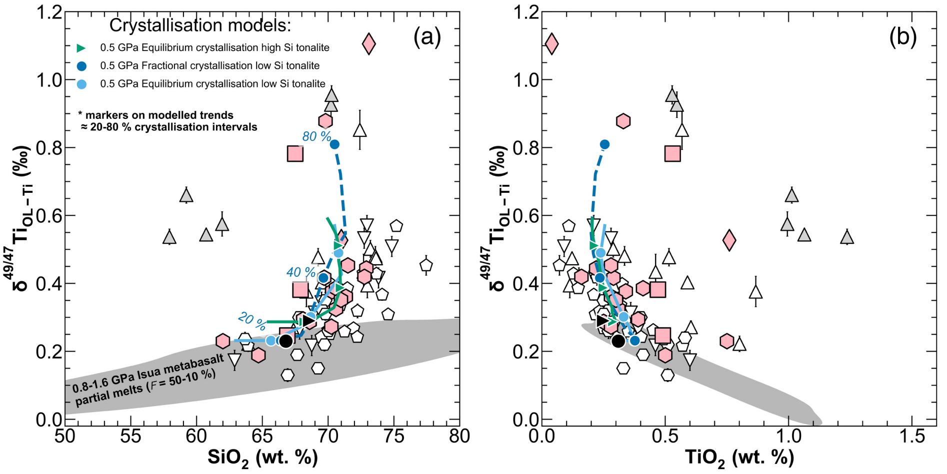

Figure 3 $\delta^{49/47}$Ti *versus* **(a)** SiO_2 and **(b)** TiO_2 for equilibrium (solid lines) and fractional crystallisation (dashed line) of tonalitic melts at 0.5 GPa compared to $\delta^{49/47}$Ti of Hadean-Archean TTGs (pink, white and grey symbols; see Fig. 1 for legend). Shaded grey field represents the $\delta^{49/47}$Ti range of modelled 50–10 % partial melts of Isua metabasalts from Figure 2 defined by a 0.95 probability density contour. Black symbols indicate the starting composition for each model. Symbols on modelled trends represent crystallisation intervals between 20–80 %. Modelling details are given in the Supplementary Information.

$\delta^{49/47}$Ti up to +0.8 ‰ (Fig. 3). Titanium isotope fractionation during differentiation of tonalitic magmas is largely controlled by ilmenite, and to a lesser extent, amphibole, and biotite. Consequently, at a given temperature, the bulk Ti solid-melt fractionation factor ($\alpha_{\text{solid-melt}}$) is larger for crystallisation compared to partial melting, where amphibole has a greater influence on $\alpha_{\text{solid-melt}}$ (Supplementary Information). Equilibrium crystallisation is responsible for most of the $\delta^{49/47}$Ti variation in IGC tonalites and other Archean TTGs, spanning approximately +0.3 to +0.6 ‰ (as seen in Fig. 2d). This process likely occurred within upper crustal crystal mushes, as suggested by Laurent *et al.* (2020). The scatter of some TTGs with $\delta^{49/47}\text{Ti} > +0.3$ ‰ (Fig. 3) can be explained by differentiation of tonalitic magmas of differing initial SiO_2 and TiO_2 contents, themselves the products of variable polybaric melting (Fig. 2).

There is an additional complication that migmatised IGC tonalites and intra-crustal differentiates generally exhibit more scatter in their $\delta^{49/47}$Ti compositions compared to non-gneissic tonalites, with elevated $\delta^{49/47}$Ti at lower SiO_2 and higher TiO_2 (Figs. 2, 3). Furthermore, intra-crustal differentiates display significantly heavier Ti isotope compositions above +1 ‰ (Figs. 2, 3). These samples are characterised by superchondritic Nb/Ta (21–37), suggesting the fractionation of Ti-bearing phases like rutile, titanite or ilmenite (Hoffmann *et al.*, 2011). Moreover, these samples were identified in the field as being amphibolite facies rocks that had previously experienced prior modification by melts or fluids (Nutman and Bridgwater, 1986). Given that intra-crustal differentiates are ~200 Myr younger than the majority of Istaq TTGs, the scatter in $\delta^{49/47}$Ti could result from a subsequent intra-crustal melting event where additional Ti isotope fractionation was driven by rutile or ilmenite. Intra-crustal melting might have resulted from crustal thickening, causing the remelting of pre-existing felsic, likely isotopically heavy, portions of the lower continental crust. These high Nb/Ta felsic melts could have then infiltrated the mid-crust (Hoffmann *et al.* 2011).

The Influence of Source Depth on the Ti Isotope Evolution of TTG Magmas

Based on $\delta^{49/47}$Ti systematics alone it is difficult to fully establish the control of melting pressure, which dictates the stable phase assemblages during partial melting. However, the full spectrum of variations in trace element ratios (*e.g.*, Zr/Sm, Gd/Yb and Nb/Ta) in IGC tonalites implies the presence of garnet and a Ti-bearing phase (such as rutile or ilmenite) in the melting residuum, and hence polybaric melting (*e.g.*, Nagel *et al.*, 2012; Hoffmann *et al.*, 2014). Dy/Dy* is an effective discriminator for the roles of amphibole, garnet, and source LREE (Light Rare Earth Element) contents in magmatic processes (Davidson *et al.*, 2013). When combined with phase equilibria modelling it can provide quantitative estimates on source mineralogy and melting depth during TTG formation (Fig. 4). The negative correlation between Dy/Dy* and $\delta^{49/47}$Ti is evidence of the dominant role for amphibole in dictating the $\delta^{49/47}$Ti composition of TTGs (Fig. 4). The majority of Eoarchean TTGs with $\delta^{49/47}\text{Ti} < +0.3$ ‰ do not require melting pressures greater than 1.6 GPa if low TiO_2, LREE-enriched metabasalts are invoked as the source (Fig. 4a). Conversely, E-MORB or primitive plateau basalt are slightly too enriched or depleted, respectively, to fully encapsulate the natural TTG data at 0.8–1.3 GPa (Fig. 4b). The absence of a significant negative Dy/Dy* for the Idiwhaa gneisses suggests a reduced role for amphibole and thus their higher $\delta^{49/47}$Ti are primarily influenced by Fe-Ti oxides. The $\delta^{49/47}$Ti-Dy/Dy* systematics indicates that the formation of Eoarchean TTGs may not require high pressure eclogite facies conditions (≥2 GPa) for partial melting. This challenges previous proposals, such as those by Rapp *et al.* (2003), that suggested high pressure conditions were required to produce juvenile continental crust.

Geodynamic Implications of Ti Isotope Variations in TTGs

Our study reveals that the formation of most Eoarchean TTG magmas likely included low to medium pressure melting of low TiO_2, REE-enriched metabasalts, followed by differentiation of tonalitic melts within upper crustal crystal mushes, resulting in TTGs with higher $\delta^{49/47}$Ti values. The shallow positive correlation between $\delta^{49/47}$Ti and SiO_2 shared by modern calc-alkaline lavas and Archean TTGs may be coincidental, rather reflecting the dominance of amphibole over Fe-Ti oxides during partial melting. Partial melts of TiO_2-rich mafic protoliths result in melts with elevated $\delta^{49/47}$Ti at a given SiO_2 and TiO_2 compared to most Eoarchean TTGs, unless melting occurs at either very low (0.1 GPa) or higher pressures (>1.3 GPa). Consequently, this

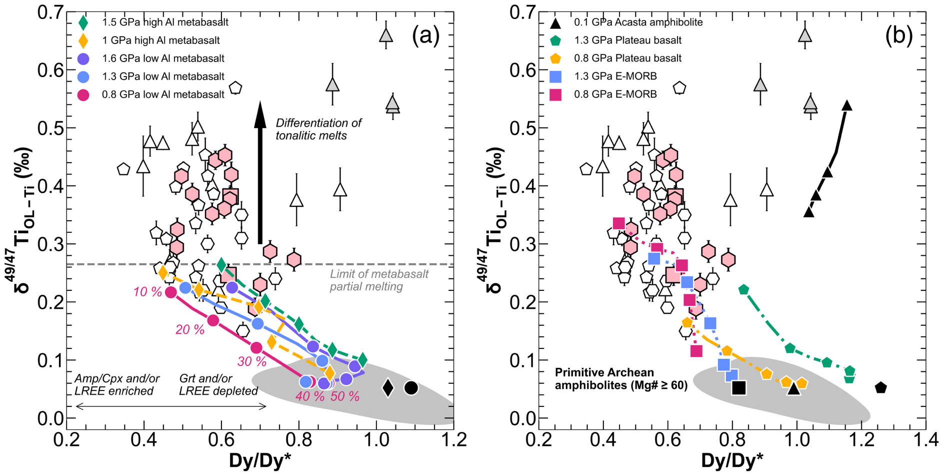

Figure 4 $\delta^{49/47}$Ti *versus* Dy/Dy* (after Davidson *et al.*, 2013) for partial melting of **(a)** high and low Al Isua metabasalts at 0.8–1.6 GPa, and **(b)** partial melting of E-MORB and primitive plateau basalt at 0.8–1.3 GPa superimposed on to $\delta^{49/47}$Ti data for Hadean-Archean TTGs (pink, white and grey symbols, refer to Fig. 1 for the symbol legend). Shaded grey field represents the $\delta^{49/47}$Ti range of primitive Archean amphibolites (Mg# > 60) defined by a 0.95 probability density contour. Black symbols indicate the starting composition for each model. Symbols on modelled trends represent melting intervals between 50–10 %. Modelling details are given in the Supplementary Information.

rules out a TiO_2-rich mafic source and a plume origin for most Eoarchean TTGs. The $\delta^{49/47}$Ti systematics of the Hadean Idiwhaa gneisses necessitate a TiO_2-rich source and potentially an intraplate origin (Aarons *et al.*, 2020); however, the mechanism responsible for their heavy Ti compositions could have plausibly resulted from a combination of very low pressure melting (Johnson *et al.*, 2018) and fractional crystallisation (Aarons *et al.*, 2020). In the case of the Eoarchean Itsaq tonalites, the chemistry of their mafic sources resembles modern tholeiitic arc basalts, suggesting a potential subduction origin (*e.g.*, Jenner *et al.*, 2009). If subduction did indeed occur in the Eoarchean, it is likely not comparable to the present day (Sizova *et al.*, 2015), and was mostly at or below garnet-amphibolite facies conditions (~1–1.5 GPa; *e.g.*, Zhang *et al.*, 2013). The Ti isotope systematics of Eoarchean Itsaq tonalites are consistent with formation within a 'proto-subduction zone' (*e.g.*, Hoffmann *et al.*, 2014). In this scenario, low to medium pressure melting of hydrated low TiO_2 arc-like mafic crust is triggered *via* crustal thickening due to successive tholeiitic intrusions, which results in destabilisation and overturn of crustal fragments (*e.g.*, Sizova *et al.*, 2015). It is worth noting that Ti isotopes are better suited to distinguish between mafic sources and petrogenetic processes during crustal formation rather than direct proxies for tectonic settings. For instance, it cannot be ruled out that melting of low TiO_2 basalts may have occurred within subducted or thickened oceanic plateaus (Nair and Chacko, 2008; Johnson *et al.*, 2017). Thus, the sentiment that the full spectrum of Archean TTGs may have formed from various geodynamic settings and mafic sources cannot be completely discounted, and any such inferences need to be made on a more regional scale.

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Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2342.

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