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

L. Hoare1*, L.J.A. Rzehak1, S. Kommescher1, M. Jansen2, M.T. Rosing3, T. Nagel4, M.-A. Millet5, J.E. Hoffmann6, R.O.C. Fonseca1

Abstract

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 SiO2 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 TiO2 metabasalts and subsequent crystallisation of tonalitic magmas, resulting in heavier Ti isotope compositions.

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, or 2) a non-subduction setting, such as oceanic plateaux.

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 (V- and IV-fold). The uniformitarian regime such as oceanic plateaux (e.g., Nair and Chacko, 2008), and the presence of significant H2O-poor, Ti-rich intra-plate magmas have higher δ49/47Ti relative to arc magmas at a given SiO2 content (Fig. 1).

Mass dependent isotope variations of titanium (expressed as δ49/47Ti) 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.

1. Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, 150 Universitätsstraße, 44801 Bochum, Germany
2. Deutsches Bergbau-Museum Bochum, Lehrstuhl-Research-Museum für Georesources, Herren Str. 45, 44787 Bochum, Germany
3. Globe Institute, University of Copenhagen, Øster Voldgade 5-7, 1500 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 74-108, 12249 Berlin, Germany

* Corresponding author (email: liam.hoare@rub.de)
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 $\delta^{49/47}$Ti covariations within 4.02 Ga Oldsagaa gneisses from the Acasta Gneiss Complex, Slave craton, Canada (Fig. 1a), mirror the trend of alkaline intra-plate magmas, whereas post-4.02 Ga TIGs 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 protolith 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) tonalities and intra-crustal differentiates (pegmatites and augen gneisses) from the adjacent Isua Gneiss Complex (IGC) of southern West Greenland. The Isua meta-tonalities are found within low-strain zones in the IGC as almost undeformed, single phase tonalities 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 relative to 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 $\delta^{49/47}$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 1](https://doi.org/10.7185/geochemlet.2342)

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.
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 (\(\sim\)2.7 wt. %) producing amphibole-free residues and high SiO$_2$-TiO$_2$ melts with significantly higher $\delta^{49/47}$Ti (\(\sim\)þ0.36 to þ0.54 ‰) 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). This results in a greater magnitude of Ti isotope fractionation during partial melting being largely driven by competition between amphibole and Fe-Ti oxides for the elemental budget of Ti (Fig. S-1; Supplementary Information). 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 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 modell trends represent melting intervals between 50–10 %. Modelling details are given in the Supplementary Information.
The Influence of Source Depth on the Ti Isotope Evolution of TTG Magmas

Based on $^{49/47}$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/Sn, 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) 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 $^{49/47}$Ti is evidence of the dominant role for amphibole in dictating the $^{49/47}$Ti composition of TTGs (Fig. 4). The majority of Eoarchean TTGs with $^{49/47}$Ti $< +0.3 \%$ do not require melting pressures greater than $1.6 \text{ GPa}$ if low TiO$_2$, LREE-enriched metabasalts are invoked as the source (Fig. 4a). Conversely, E-MORB or primitive plateau basalt is slightly too enriched or depleted, respectively, to fully encapsulate the natural TTG data at $0.8 \%$ to $-2.1 \%$ $^{49/47}$Ti values. The shallow positive correlation of $^{49/47}$Ti-Dy/Dy* systems indicates that the formation of Eoarchean TTGs may not require high pressure eclogite facies conditions ($\geq 2 \text{ GPa}$) 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 $^{49/47}$Ti values. The shallow positive correlation between $^{49/47}$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 $^{49/47}$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 (>1.5 GPa). Consequently, this
rules out a TiO2-rich mafic source and a plume origin for most Eoarchean TTGs. The δ^{49/47}Ti systematics of the Hadean Idiwha gneisses necessitate a TiO2-rich source and potentially an intra-plate 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 TiO2 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 TiO2 basalts may have occurred within subducted or thickened oceanic plateaux (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

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Supplementary Information

The Supplementary Information includes:

- 1. Samples
- 2. Methods
- 3. Thermodynamic Phase Equilibria Modelling
- 4. Trace Element Modelling
- 5. Modelling of Ti Isotope Fractionation
- Tables S-1 to S-11 (Tables S-2 to S-11 are available from the online version of this article at [https://doi.org/10.7185/geochemlet.2342](https://doi.org/10.7185/geochemlet.2342)).
- Figures S-1 to S-4
- Supplementary Information References

1. Samples

All samples measured in this study have previously been characterised for their petrography, major and trace element compositions, and, in some instances radiogenic isotopes. Detailed geologic context, petrography, analytical methods, and major and trace element compositions of all tonalite and intracrustal differentiates can be found in Hoffmann et al. (2011a, b, 2014). The same information for all Isua tholeiitic metabasalt samples is sourced from Polat and Hofmann, 2003; Hoffmann et al., 2011b. All geochemical data used in this study can be found in Tables S-3 to S-5 and S-9 to S-11. A brief outline of the sample petrography and major element geochemistry is provided below.

The mafic rocks analysed in this study consist of amphibolite facies tholeiitic to picritic metabasalts and metagabbros from the 3800 Ma (previously called the outer arc domain by Jenner et al., 2009) and 3700 Ma (referred to as the inner arc domain by Polat and Hofmann 2003) terranes within the Isua Supracrustal Belt (ISB) in southwest Greenland. The ISB mafic rocks exhibit low SiO$_2$ (45.9–54.5 wt. %), low TiO$_2$ (0.6–1.1 wt. %), low to moderate Al$_2$O$_3$ (7.9–14.2 wt. %), low to moderate Na$_2$O (0.3–3.7 wt. %), moderate to very high MgO (5.2–20.1 wt. %), low K$_2$O (0.01–1.40 wt. %) and Mg# from 46.1 to 75.4 (Table S-4). Igneous textures and minerals in these samples are not pre-served on the microscopic scale, and major mineral phases present include amphibole (hornblende, anthophyllite), plagioclase, chlorite, epidote, quartz, calcite, and titanite (e.g., Polat and Hofmann 2003; Hoffmann et al. 2011a, b).
All Itsaq Gneiss Complex (IGC) TTGs analysed in this study were collected in the Isukasia terrane in the southwest portion of the Isua Supracrustal Belt (ISB). The samples possess ages that range between 3650 to 3890 Ma (e.g., Næraa et al., 2012). Most IGC meta tonalite and trondhjemite samples in our study are well preserved and exhibit magmatic textures (e.g., Nutman et al., 1999; Hoffmann et al., 2014). The main mineral assemblages of these rocks comprise plagioclase, quartz, amphibole, and biotite with minor titanite, apatite and accessory Fe-Ti oxides. The IGC meta tonalites and diorites exhibit moderate to high SiO$_2$ (62.0–72.9 wt. %), low TiO$_2$ (0.2–0.8 wt. %), high Al$_2$O$_3$ (14.8–18.1 wt. %), high Na$_2$O (4.0–5.9 wt. %), low to moderate MgO (0.5–3.2 wt. %), low to moderate K$_2$O (0.9–2.5 wt. %) and Mg# from 31.9 to 49.5 (Table S-5).

2. Methods

2.1. Chemical separation of Ti

For the duration of this study sample preparation first requires digestion of 20–60 mg (amount is dependent on the TiO$_2$ concentration of the sample to achieve at least 5 μg of natural Ti) of fine-powdered silicate rock sample or geo-standard in concentrated 1:1 mixture of HNO$_3$ and HF at 130 °C for 72 hours. An additional 2 ml of concentrated HNO$_3$ is then added and evaporated to incipient dryness. Following this step, each sample is taken up in 500 μl of concentrated HNO$_3$ and dried down, this step is repeated 3 times. The sample is then taken up in 6 M HCl with the addition of ~40 mg of H$_3$BO$_3$ into the solution to ensure the removal of any fluorides that would sequester Ti out of the sample solution. Finally, an aliquot containing 5 μg of Ti is taken from the sample solution and mixed with a $^{47}$Ti-$^{49}$Ti double spike in a 48:52 ratio based on the calibration of Kommescher et al. (2020) and taken up in 5 mL 12 M HNO$_3$ prior to column chemistry.

Titanium is separated from the sample matrix using Eichrom N, N, N, N’ tetra-n-octyldiglycolamide (DGA) resin. The procedure adopted in this study is based on the method initially developed by Zhang et al. (2011) and later modified by Hoare et al. (2020) and Millet et al. (2016). The method is outlined in Table S-1. This study used a double pass chemistry. Following purification, Ti fractions are treated with a 1:1 mixture of concentrated HNO$_3$ and 30 % H$_2$O$_2$ to remove any organic material.

Table S-1 Summary of ion exchange chromatography procedure for Ti purification of samples for MC- ICP-MS analysis

<table>
<thead>
<tr>
<th>Step</th>
<th>Acid</th>
<th>Volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cleaning</td>
<td>Milli-Q</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>3M HNO$_3$</td>
<td>10</td>
</tr>
<tr>
<td>Conditioning</td>
<td>12M HNO$_3$</td>
<td>10</td>
</tr>
<tr>
<td>Introduction</td>
<td>Sample in 12M HNO$_3$</td>
<td>5</td>
</tr>
<tr>
<td>Wash</td>
<td>12M HNO$_3$</td>
<td>20</td>
</tr>
<tr>
<td>Collect Ti</td>
<td>12M HNO$_3$ + 1 wt. % H$_2$O$_2$</td>
<td>10</td>
</tr>
<tr>
<td>Cleaning</td>
<td>Milli-Q</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>3M HNO$_3$</td>
<td>10</td>
</tr>
</tbody>
</table>
2.2. Ti double spike MC-ICP-MS measurements and data reduction

Titanium isotope composition measurements of reference solutions OL-Ti and Col-Ti were carried out using a Nu Plasma II MC-ICP-MS at the Cardiff Earth Laboratory for Trace Element and Isotope Chemistry (CELTIC), School of Earth and Environmental Sciences, Cardiff University to check the double spike calibration. Samples and geo-reference materials were measured using either a Thermo Fischer Neptune XT MC-ICP-MS at the Deutsches Bergbau Museum, Bochum or a Thermo Fischer Neoma MC-ICP-MS at Freie Universität Berlin. For measurements on the Nu Plasma II samples were introduced via an Cetac Aridus II desolvating nebuliser (flushed with Ar), whereas in for sessions using a Thermo Fischer Scientific Neptune and Neoma an ESI Apex Omega was used (flushed with Ar and N₂).

Prior to measurements purified samples were diluted to concentrations of 250 ng/g (Neptune XT and Neoma) or 1000 ng/g (Nu Plasma II) of Ti Samples were taken up in 0.3 M HNO₃ + 0.005 M HF solution. All instruments were fitted with nickel (Ni) jet-sampler and Ni (H) skimmer cones. The measurements were performed in medium resolution mode, with a resolution power (5-95 % peak definition, ΔM/M) in the range of ~ 5,000 or up to ~ 8,000 when using the Thermo Fischer Neoma MC-ICP-MS. Such resolution was sufficient to clearly identify the peak shoulders of the Ti isotopes, and simultaneously to counter the effect of non-resolvable polyatomic interferences such as ²⁸Si¹⁹F and ¹⁴N¹⁶O₂H⁺ that can be introduced via the analyte solution (0.3 M HNO₃ – 0.005 M HF), which give inference on ⁴⁷Ti. The ‘peak shoulder’ is used to define an interference-free mass range on the respective mass, as polyatomic interferences are typically heavier than the respective mass. Titanium ion beam intensity ranged from 20-60 V on amplifiers with 10¹¹ Ω resistors in their feedback loop. Ca interference on ⁴⁶Ti and ⁴⁸Ti was monitored at mass 44 and corrected during data reduction if necessary. Measurements of an individual sample consisted of 60-80 cycles with an integration time of 8 s. To account for small unresolved polyatomic interferences on ⁴⁷Ti due to the presence of F from the sample solution and Si from the torch (²⁸Si¹⁹F), samples are bracketed by measurements of the double spiked OL-Ti standard solution.

The compositions of Ti reference solutions (OL-Ti and Col-Ti) and geo-reference materials (JB-2, BCR-2, AGV-1, G2) are in good agreement with previous published values (see Tables S-1 and S-2). The δ⁴⁹⁴⁷Ti value for AGV-1 reported here is heavier than the bulk of previously reported values but is within error of the recently published value of Storck et al. (2023; Table S-2) which could suggest this geo-reference standard is homogenous for Ti isotopes. Additionally, δ⁴⁹⁴⁷Ti values presented here for JA-2 and JG-2 differ from the values obtained by He et al. (2020; Table S-2). Given the lack of data for these two standards it is currently unclear if these offsets are the result of sample heterogeneity or inter laboratory bias. Further digestions and measurements of these geo reference materials will be required to confirm this. It should be noted that the samples ran on Neptune XT MC-ICP-MS at the Deutsches Bergbau Museum possess slightly larger 95 % c.i. values as during this session samples were analysed for fewer cycles (60 as opposed to 80). The 2σ internal precision of our δ⁴⁹⁴⁷Ti measurements, expressed as 95 % c.i. ssb (confidence interval; standard-sample-bracketing) is generally within ±0.020 - 0.030 ‰. The geo-reference materials and Ti reference solutions measured over the course of this study yield a pooled 2s intermediate precision of ±0.025 ‰, which we take as the best estimate of the uncertainty of our measurements. Total procedural blanks were always below 20 ng Ti, thus contributing less than 0.1% to the total processed sample Ti and are therefore negligible.
### Table S-2  Summary of Ti isotope compositions of Ti reference solutions and geologic reference materials.

<table>
<thead>
<tr>
<th>Reference solution/Geo-reference material</th>
<th>( \delta^{49}\text{Ti} (\‰) )</th>
<th>95 % c.i.</th>
<th>2 s.d.</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>OL-Ti</td>
<td>-0.010</td>
<td>0.004</td>
<td>0.025</td>
<td>32</td>
</tr>
<tr>
<td>Col-Ti</td>
<td>0.184</td>
<td>0.006</td>
<td>0.034</td>
<td>19</td>
</tr>
<tr>
<td>FUB-Ti (AA-Ti solution)</td>
<td>-0.162</td>
<td>0.006</td>
<td>0.034</td>
<td>12</td>
</tr>
<tr>
<td>BCR-2</td>
<td>-0.013</td>
<td>0.010</td>
<td>0.008</td>
<td>4</td>
</tr>
<tr>
<td>JB-2</td>
<td>-0.038</td>
<td>0.012</td>
<td>0.029</td>
<td>4</td>
</tr>
<tr>
<td>G-2</td>
<td>0.477</td>
<td>0.013</td>
<td>0.025</td>
<td>3</td>
</tr>
<tr>
<td>JA-2</td>
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<td>0.020</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>AGV-2</td>
<td>0.134</td>
<td>0.018</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>JG-2</td>
<td>1.045</td>
<td>0.020</td>
<td>-</td>
<td>1</td>
</tr>
</tbody>
</table>

### Table S-3  Summary of Ti isotope compositions of measured samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rock type</th>
<th>( \delta^{49}\text{Ti} (\‰) )</th>
<th>95 % c.i.</th>
<th>2 s.d.</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000-10</td>
<td>Metabasalt</td>
<td>0.078</td>
<td>0.017</td>
<td>0.038</td>
<td>2</td>
</tr>
<tr>
<td>2000-13</td>
<td>Metabasalt</td>
<td>0.020</td>
<td>0.012</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>2000-4</td>
<td>Metabasalt</td>
<td>0.024</td>
<td>0.020</td>
<td>-</td>
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</tr>
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<td>2000-6</td>
<td>Metabasalt</td>
<td>0.006</td>
<td>0.026</td>
<td>-</td>
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<tr>
<td>2000-7</td>
<td>Metabasalt</td>
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<td>0.027</td>
<td>-</td>
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<tr>
<td>2000-8</td>
<td>Metabasalt</td>
<td>0.046</td>
<td>0.042</td>
<td>-</td>
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<tr>
<td>jeh-2007-11</td>
<td>Metabasalt</td>
<td>0.079</td>
<td>0.019</td>
<td>-</td>
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</tr>
<tr>
<td>2007-01</td>
<td>Metagabbro</td>
<td>0.049</td>
<td>0.015</td>
<td>0.030</td>
<td>2</td>
</tr>
<tr>
<td>2007-08</td>
<td>Pillow basalt</td>
<td>0.040</td>
<td>0.016</td>
<td>0.013</td>
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</tr>
<tr>
<td>2007-14</td>
<td>Sheeted dyke</td>
<td>0.084</td>
<td>0.018</td>
<td>0.016</td>
<td>2</td>
</tr>
<tr>
<td>2007-15</td>
<td>Sheeted dyke</td>
<td>0.051</td>
<td>0.017</td>
<td>0.040</td>
<td>2</td>
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<tr>
<td>229467</td>
<td>Pegmatitic white gneiss</td>
<td>1.105</td>
<td>0.020</td>
<td>-</td>
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<tr>
<td>498033</td>
<td>Augen gneiss</td>
<td>0.527</td>
<td>0.020</td>
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<td>jeh-SG-07</td>
<td>migmatitic tonalite</td>
<td>0.246</td>
<td>0.018</td>
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<tr>
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<td>498028</td>
<td>migmatitic tonalite</td>
<td>0.382</td>
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<td>229403</td>
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<td>496430</td>
<td>non-gneissic tonalite</td>
<td>0.325</td>
<td>0.020</td>
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<td>0.444</td>
<td>0.016</td>
<td>0.040</td>
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<td>499337</td>
<td>non-gneissic tonalite</td>
<td>0.294</td>
<td>0.020</td>
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To assess the extent of elemental and Ti isotope fractionation during partial melting of metabasalts and crystallisation of tonalitic melts we employ the use of constraints from the latest generation of phase equilibria modelling. The modelling uses the Theriak algorithm (de Capitani and Brown, 1987), which is implemented via the Domino software (de Capitani and Petrakakis, 2010). The current version of the Domino software used in this study is distributed on GitHub and can be accessed using the following link https://github.com/Theriak-Domino/theriak-domino/. The complete output from the models including run conditions, the compositions and proportions of phases can be found in Table S-6. The procedure for thermodynamic modelling adopted in this study closely follows that of Nagel et al. (2012) and Hoffmann et al. (2014).

The references for the databases and solution models for all phases are outlined below:

**Database:** Holland and Powell (2011)

**Solution models:**
- Amphibole - Green et al. (2016)
- Melt, ilmenite, rutile, clinopyroxene, orthopyroxene and garnet - Holland et al. (2018)
- Plagioclase - Holland et al. (2022)
- Mica - White et al. (2014)

**Set up for Theriak-Domino:** Jørgensen et al. (2019)

These data are combined with relevant mineral-melt trace element partition coefficients (Table S-7) and Ti isotope fractionation factors (Table S-8). This will quantitatively test if these processes are viable mechanisms to explain the range of elemental and $\delta^{48/47}$Ti compositions observed in ISB metabasalts and IGC tonalites.
Figure S-1  Changes in the Titanium (Ti) budget of phases with respect to temperature and remaining melt fraction for partial melting of high-Al metabasalt sample 2007-23 at 1 GPa (a); and 1.5 GPa (b) and; low-Al metabasalt sample 2000-13 at 0.8 GPa (c); 1.3 GPa (d); and 1.6 GPa (e).
Figure S-2 Changes in the Titanium (Ti) budget of phases with respect to temperature and remaining melt fraction for partial melting of E-MORB (Gale et al., 2013) at 0.8 GPa (a) and 1.3 GPa (b); and a primitive flood basalt (Baffin island picrite; Kent et al., 2004) at 0.8 GPa (c) and 1.3 GPa (d); and (e) an average Acasta amphibolite from (Johnson et al., 2018).
Figure S-3  Changes in the Titanium (Ti) budget of phases with respect to temperature and remaining melt fraction for equilibrium (a) and fractional (b) crystallisation of low-Si IGC tonalite sample G 97/31 at 0.5 GPa; and equilibrium crystallisation of IGC high-Si tonalite sample JEH 10-38 at 0.5 GPa (c).
Phase equilibria modelling is based on three scenarios using different mafic source compositions (see Table S-6, S-9, S-10). Firstly, hydrous partial melting of two metabasalts (high and low Al) representative of average compositions of local Eoarchean Isua mafic rocks (2007-23 - Hoffmann et al., 2011b; 2000-13 - Polat and Hofmann, 2003), and then dehydration partial melting of E-MORB (Gale et al., 2013), a picritic plateau basalt (Kent et al., 2004), and an average amphibolite composition from the Acasta Gneiss complex (Johnson et al., 2018). The initial H₂O contents used for the starting compositions was 4 wt. % for Isua metabasalts, and 2 wt. % E-MORB and plateau basalt. The whole rock geochemistry of the starting compositions be found in Table S-6. Secondly, equilibrium and fractional crystallisation of two tonalite compositions (JEH 10-38 - Hoffmann et al., 2011a; G97/31 - Nutman et al., 1999). Amphibole is the dominant Ti-bearing mineral phase during partial melting of tholeiitic metabasalts (Fig. S-1, Tables S-6 and S-9), whereas depending on pressure, either ilmenite or rutile dominates during partial melting of E-MORB (Fig. S-2). Minor amounts Fe-Ti oxides only appear at low melt fraction (<10 %, Tables S-6 and S-9) for tholeiitic metabasalts (Table S-1 to 6). The distribution of Ti for low pressure (0.8 GPa) melting of a picritic plateau basalt is comparable to that of both tholeiitic metabasalts, except for minor amounts of ilmenite below 1000 °C, whereas at 1.3 GPa and below 1000 °C rutile hosts a significant portion of Ti (Figs. S-1, S-2). In stark contrast to the other partial melting models, ilmenite is the dominant Ti-bearing phase throughout the 0.1 GPa Acasta amphibolite model (Fig. S-2e, Table S-6, S-9). The appearance of amphibole and/or ilmenite causes the fraction of Ti hosted in the melt to sharply decline with decreasing melt fraction (Figs. S-1-3). Partial melting of the low-Al metabasalt produces plagioclase-free residues with clinopyroxene as the initially volumetrically dominant phases, until the appearance of amphibole below 1000 °C (Fig. S-1, Tables S-6 and S-9). Additionally, garnet is stabilised at ~1000 °C and 1050 °C at 1.3 and 1.6 GPa respectively in the low-Al metabasalt (Fig. S-1, Tables S-6, S-9) and at ~1100 °C for the high-Al metabasalt at 1.5 GPa (Fig. S-1, Table S-6, S-9). In the higher-pressure melting models garnet hosts a significant portion of Ti in the absence of amphibole or Fe-Ti oxides (Fig. S-1, S-2). Partial melting of high-Al metabasalt at 1 GPa produces plagioclase and notably less clinopyroxene compared to low-Al metabasalt (Fig. S-1, Tables S-6, S-9). Silicate melt is volumetrically dominant in the tonalite equilibrium and fractional crystallisation models, followed by plagioclase (Fig. S-3, Tables S-6, S-10). In the equilibrium models, amphibole, and biotite, along with minor amounts of ilmenite, quartz, and ortho-and clinopyroxene appear at lower temperature and melt fraction (Fig. S-3, Table S-6, S-10). In equilibrium crystallisation models, amphibole dominates the Ti budget of solid phases until the appearance of ilmenite, with biotite also sequestering a significant fraction of Ti at ~695 °C (Fig. S-3, Tables S-6, S-10). An abrupt transition occurs towards the latter stages of crystallisation (~80%) due to the appearance of biotite (Fig. S-3, Tables S-6, S-10), which dominates the Ti budget at low melt fraction (Fig. S-3, Tables S-6, S-10). The lower modal proportion of amphibole and earlier appearance of ilmenite in the fractional crystallisation model results in ilmenite being the dominant Ti-bearing phase (Fig. S-3, Table S-6, S-10). Clinopyroxene also possess a greater share of the Ti budget in comparison to the equilibrium models due to its higher modal abundance (Fig. S-3, Tables S-6, S-10).

4. Trace Element Modelling

For equilibrium partial melting and crystallisation models the trace element and Ti concentrations of the melt were calculated using the Equation S-1 (Shaw, 1970):

\[ C_L = \frac{C_0}{D + F(1 - D)} \]

where the trace-element composition of the liquid (\(C_L\)) depends on the composition of the source (\(C_0\)), the degree of partial melting (\(F\)), and the bulk distribution coefficient (\(D\)), itself a function of individual mineral partition coefficients.
and mineral-melt proportions. The degree of melting, the residual mineral assemblage, and the associated mineral abundances are all controlled by the intensive and extensive chemical parameters (bulk composition, pressure, temperature, fluid pressure, oxygen fugacity etc.). Hence, this equation can be seen as relating \( C_L \) with (1) the nature of the mafic protolith and (2) the thermodynamic conditions of crustal evolution. This concept applies to melting and to crystallisation in the same way.

In fractional crystallisation scenarios a Rayleigh fractionation approach was used (Eq. S-2):

\[
C_L = C_o D^{(1-F)} \quad \text{Eq. S-2}
\]

Trace element modelling always carries a certain degree of uncertainty, particularly in the case of TTG formation in which both amphibole and garnet are major residual phases (Foley, 2008; Qian and Hermann, 2013). The magnitude of D values in the literature for these phases varies greatly as function of pressure, temperature and melt composition, which is further compounded by the scarcity of experimental data relevant for tonalitic melts (Barth et al., 2002; Foley, 2008; Klein et al., 1997, 2000; Qian and Hermann, 2013). An effort was made to select experimentally determined mineral melt partition coefficients for tonalitic melts from the available published data at relevant pressure/temperature conditions (Barth et al., 2002; Bédard, 2006; Klein et al., 1997; Qian and Hermann, 2013). All mineral-melt partition coefficients (\( D_{\text{min-melt}} \)) used for trace element modelling are provided in Table S-7.

5. Modelling of Ti Isotope Fractionation

Equilibrium fractionation

Equilibrium isotope fraction during partial melting and crystallisation is governed by the following mass balance Equation S-3:

\[
R^* = \frac{C_{\text{melt}} F_{\text{melt}} R_{\text{melt}} \alpha_{\text{melt}} + C_{\text{amp}} F_{\text{amp}} R_{\text{amp}} \alpha_{\text{amp}} + C_{\text{cpx}} F_{\text{cpx}} R_{\text{cpx}} \alpha_{\text{cpx}} + \cdots}{C} \quad \text{Eq. S-3}
\]

In which \( R \) is an isotope ratio, \(^{49}\text{Ti}/^{47}\text{Ti} \) in this case (relative to \(^{49}\text{Ti}/^{47}\text{Ti} = 0.749766 \) for OL-Ti), with a * used to represent the bulk composition. \( C \) is the concentration of Ti in a phase, \( F \) is the proportion of a phase, and \( \alpha \) is the isotope fractionation factor between a given phase, \((i)\) and the melt as defined by Equation S-4:

\[
\alpha_i = \frac{R_i}{R_{\text{melt}}} \quad \text{Eq. S-4}
\]

The isotope mass balance equation can be rewritten as follows (Eq. S-5):

\[
R^* = \frac{R_{\text{melt}} \Sigma_i (C_i F_i \alpha_i)}{C^*} \quad \text{Eq. S-5}
\]
If using mineral-melt partition coefficients the distribution of Ti \((X_{\text{Ti}-i})\) for each phase present can be calculated using (Eq. S-6):

\[
X_{\text{Ti}-i} = \frac{F_i D_i \text{Ti}_{-\text{melt}}}{\sum (F_i D_i)}
\]

Eq. S-6

Finally, in instances where the bulk isotope composition is known, the isotope composition of the melt can be obtained using the Equation S-7:

\[
R_{\text{melt}} = \frac{R'C'}{\sum (C_i F_i \alpha_i)}
\]

Eq. S-7

This equation was used to calculate the Ti isotope composition of melts produced during equilibrium melting and crystallisation. The isotope composition is reported relative to the Origins Lab Ti standard (Eq. S-8):

\[
\delta^{49/47}\text{Ti}_{\text{melt}} = \frac{R_{\text{melt}}}{R_{\text{OL}-\text{Ti}}} - 1
\]

Eq. S-8

**Rayleigh fractionation**

Ti isotope fractionation during tonalite fractional crystallisation was obtained using a Rayleigh fractionation law. The Ti isotope composition of fractionated melts was obtained using the following Equation S-9:

\[
R_{\text{melt}} = R_0 f^{\alpha - 1}
\]

Eq. S-9

where, R is the \(^{49}\text{Ti}/^{47}\text{Ti}\) isotope ratio, \(R_0\) is the initial isotope ratio, f is the fraction of Ti remaining in the melt, and \(\alpha\) is the bulk solid-melt isotope fractionation factor between the remaining melt and the crystallizing mineral assemblage, where the mineral-melt fractionation factors are weighted by their Ti concentration at each stage of the model. All Ti mineral melt fractionation factors are reported in Table S-8. The references for each of the main Ti-bearing phases are outlined below:

- **Fe-Ti oxides (rutile, ilmenite, magnetite)** - Hoare et al. (2022); Rzehak et al. (2022)
- Amphibole, biotite and sphene - Mandl (2019)
- Clinopyroxene - Rzehak et al. (2022)
- Orthopyroxene - Rzehak et al. (2021)
- Garnet - Wang et al. (2020)

The phase proportions and Ti content of each phase are provided by the thermodynamic phase equilibria modelling for partial melting of metabasalts and tonalite crystallisation. In the case of partial melting models, the revised value of the bulk silicate Earth of \(+0.05 \pm 0.01\)‰ from the recent study of Deng et al. (2023) was used as the initial bulk Ti isotope composition, which is indistinguishable from the weighted mean of the Isua metabasalts presented in this study (\(\delta^{49/47}\text{Ti} = +0.052 \pm 0.006\)‰; 95% c.i; n = 11). For tonalite crystallisation, the Ti isotope composition of JEH 10-38 was used (Table S-5). Whereas \(\delta^{49/47}\text{Ti}\) composition of tonalite sample G97/31 was estimated via an exponential function of SiO\(_2\) vs \(\delta^{49/47}\text{Ti}\) using published data for Archean amphibolites and TTGs (n=48). The exponential function \(\delta^{49/47}\text{Ti} = 2.3*10^{-3}\)
$e^{1.04\times10^{-1}}$ ($R^2 = 0.85$) yielded a value of +0.23‰ for an SiO$_2$ content of 66.79 wt. % (Tables S-4, S-5, and S-11). This value is comparable to other TTG samples of similar SiO$_2$ contents (e.g. G91/61; Zhang et al., 2023, Table S-11).

**Supplementary Tables**

Tables S-2 to S-11 are available for download (.xls) from the online version of this article at https://doi.org/10.7185/geochemlet.2342.

**Table S-1** see page SI-2

**Table S-2** see page SI-4

**Table S-3** see pages SI-4 and SI-5

**Table S-4** Whole rock geochemistry and Ti isotope compositions of Isua supracrustal belt metabasalts measured in this study.

**Table S-5** Whole rock geochemistry and Ti isotope compositions of Itsaq Gneiss Complex samples measured in this study.

**Table S-6** Results and output of Theriak/Domino phase equilibria modelling.

**Table S-7** Mineral-melt partition coefficients and source compositions used for trace element modelling during partial melting and crystallisation.

**Table S-8** Mineral-melt titanium isotope fractionation factors used for modelling of Ti isotope fractionation during partial melting and crystallisation.

**Table S-9** Results of trace element and Ti isotope modelling for metabasalt partial melting.

**Table S-10** Results of trace element and Ti isotope modelling for tonalite differentiation.

**Table S-11** Compilation of literature whole rock geochemical data used in this study.

**Supplementary Information References**


