
Peer reviewed version
License (if available): CC BY-NC-ND
Link to published version (if available): 10.1016/j.gca.2022.02.011

Link to publication record in Explore Bristol Research
PDF-document

This is the accepted author manuscript (AAM). The final published version (version of record) is available online via Elsevier at https://doi.org/10.1016/j.gca.2022.02.011. Please refer to any applicable terms of use of the publisher.

University of Bristol - Explore Bristol Research
General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available: http://www.bristol.ac.uk/red/research-policy/pure/user-guides/ebr-terms/
The Titanium (Ti) isotope compositions of felsic rocks are heavier than their mafic counterparts, and alkaline magmas develop heavier Ti isotope compositions compared to other magma series during magmatic differentiation. Both observations are interpreted to reflect the preferential sequestration of light Ti isotopes in Fe-Ti oxides, such as rutile, ilmenite, and titanomagnetite. However, such interpretations so far rely on whole rock studies of cogenetic magmatic samples and the detailed mechanics of oxide-melt equilibrium on the Ti isotope composition of magmas is poorly constrained. To address this, we have measured the Ti isotope composition of co-existing Fe-Ti oxides and groundmass or silicate melt in both natural lavas from contrasting tectonic settings (Heard Island and Santorini), and experimental run products (rutile-melt). All Fe-Ti oxide phases are consistently isotopically lighter than their respective host groundmass or silicate melt, with the magnitude of \( \Delta^{49/47}T \) oxide-melt increasing from rutile to ilmenite, and titanomagnetite. The observed difference in Ti isotope fractionation between rutile-melt experiments and ilmenite-groundmass pairs is primarily reflective of small differences in their Ti-O bond length, with ilmenite being isotopically lighter (\( \Delta^{49/47}T \) ilmenite-melt extrapolated to 1000 K = -0.600±0.035‰) compared to rutile (\( \Delta^{49/47}T \) rutile-melt at extrapolated to 1000 K = -0.404±0.099‰) due to slightly longer Ti-O bonds in ilmenite. In contrast, the variation in \( \Delta^{49/47}T \) observed between titanomagnetite-groundmass pairs increases as a function of increasing TiO₂ content (increasing ulvöspinel component) in titanomagnetite, with \( \Delta^{49/47}T \) titanomagnetite-melt values extrapolated to 1000 K ranging from -0.811 to -1.451‰ in Ti-rich titanomagnetite (21-23 wt.% TiO₂; Usp66-73) from Heard Island compared to -0.673‰ to -0.863 in Santorini (14-15 wt.% TiO₂; Usp45-49). We interpret this to result from a weaker and distorted crystal lattice due to changes in the local cationic environment resulting from exchange of smaller Fe³⁺ ions with larger Fe²⁺ ions during magnetite-ulvöspinel solid solution. Our results are consistent with fractionation factors inferred from Ti isotopic analyses of mineral separates and ab-initio calculations. We use these fractionation factors in combination with Ti isotope fractionation factors for silicate minerals recalculated from previous studies, along with petrologic information to model the behaviour of Ti isotopes during partial melting of Earth’s mantle as well as reproducing the observed variation in \( \delta^{49/47}T \) of differentiated magmas from distinct geodynamic settings.
Empirical and Experimental Constraints on Fe-Ti Oxide-Melt 
Titanium Isotope Fractionation Factors

Liam Hoare*†[1], Martijn Klaver[1,2], Duncan D. Muir[1], Stephan Klemme[2], 
Jane Barling[3], Ian J. Parkinson[4], C. Johan Lissenberg[1], Marc-Alban Millet[1]

1School of Earth and Environmental Sciences, Cardiff University, Main Building, Park Place, Cardiff, 
CF10 3AT, UK
2Institut für Mineralogie, Westfälische Wilhelms-Universität Münster, Corrensstraße 24, 48149 
Münster, Germany
3Department of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN, UK
4School of Earth Sciences, University of Bristol, Wills Memorial Building, Queens Road, Bristol, 
BS8 1RJ, UK
† Now at: Institut für Geologie, Mineralogie und Geophysik, Ruhr 
Universität Bochum, Universitätsstr. 150, 44780 Bochum, 
Germany

Abstract

The Titanium (Ti) isotope compositions of felsic rocks are heavier than their mafic counterparts, and alkaline magmas develop heavier Ti isotope compositions compared to other magma series during magmatic differentiation. Both observations are interpreted to reflect the preferential sequestration of light Ti isotopes in Fe-Ti oxides, such as rutile, ilmenite and titanomagnetite. However, such interpretations so far rely on whole rock studies of co-genetic magmatic samples and the detailed mechanics of oxide-melt equilibrium on the Ti isotope composition of magmas is poorly constrained. To address this, we have measured the Ti isotope composition of co-existing Fe-Ti oxides and groundmass or silicate melt in both natural lavas from contrasting tectonic settings (Heard Island and Santorini), and experimental run products (rutile-melt). All Fe-Ti oxide phases are consistently isotopically lighter than their respective host groundmass or silicate melt, with the magnitude of $\Delta^{49/47}$Ti$_{oxide-melt}$ increasing from rutile to ilmenite, and titanomagnetite. The observed difference in Ti isotope fractionation between rutile-melt experiments and ilmenite-groundmass pairs is primarily reflective of small differences in their Ti-O bond length, with ilmenite being isotopically lighter ($\Delta^{49/47}$Ti$_{ilmenite-melt}$ extrapolated to 1000 K = -0.600±0.035‰) compared to rutile ($\Delta^{49/47}$Ti$_{rutile-melt}$ at extrapolated to 1000 K = -0.404±0.099‰) due to slightly longer Ti-O bonds in ilmenite. In contrast, the variation in $\Delta^{49/47}$Ti observed between titanomagnetite-groundmass pairs increases as a function of increasing TiO$_2$ content (increasing ulvöspinel component) in titanomagnetite, with $\Delta^{49/47}$Ti$_{titanomagnetite-melt}$ values extrapolated to 1000 K ranging from -0.811 to -1.451‰ in Ti-rich titanomagnetite (21-23 wt.% TiO$_2$; Usp66-73) from Heard Island compared to -0.673‰ to -0.863 in Santorini (14-15 wt.% TiO$_2$; Usp45-49). We interpret this to result from a weaker and distorted crystal lattice due to changes in the local cationic environment resulting from exchange of smaller Fe$^{3+}$ ions with larger Fe$^{2+}$ ions during magnetite-ulvöspinel solid solution. Our results are consistent with fractionation factors inferred from Ti isotopic analyses of mineral separates and ab-initio calculations. We use these fractionation factors in combination with Ti isotope fractionation factors for silicate minerals recalculated from previous studies, along with petrologic information to model the behaviour of Ti isotopes during partial melting of Earth’s mantle as well as reproducing the observed variation in $\delta^{49/47}$Ti of differentiated magmas from distinct geodynamic settings.
Studies investigating mass-dependent titanium (Ti) isotope variations have recently gained momentum, with Ti isotopes displaying great potential as a novel tool to trace terrestrial magmatic and sedimentary processes (Millet et al., 2016; Greber et al., 2017a; Greber et al., 2017b; Deng et al., 2019; Johnson et al., 2019; Hoare et al., 2020; Zhao et al., 2020; Klaver et al., 2021) as well as lunar and other extra-terrestrial magmatism (Millet et al., 2016; Greber et al., 2017b; Kommescher et al., 2020; Rzehak et al., 2021; Williams et al., 2021). Several of these studies have previously demonstrated the potency of Ti isotope variations as a tracer of Fe-Ti oxide-melt equilibria. Evolved melts invariably display higher $\delta^{49/47}$Ti relative to primitive melts, which is likely driven by the fractional crystallisation of isotopically light Fe-Ti oxides, thereby progressively enriching the melt with heavy isotopes during fractional crystallisation (Millet et al., 2016; Deng et al., 2019; Johnson et al., 2019; Hoare et al., 2020). The empirical evidence that Fe-Ti oxides, such as rutile (TiO$_2$), ilmenite (FeTiO$_3$), and titanomagnetite (Fe$^{2+}$(Fe$^{3+}$,Ti$^{4+}$)$_2$O$_4$), appear to prefer the lighter isotopes of Ti is bolstered by the difference in coordination of Ti between oxides and silicate; Ti primarily occupies a V-fold coordination in silicate melts and VI-fold coordination in Fe-Ti oxides (Farges et al., 1996a; Farges et al., 1996b; Farges and Brown, 1997). This coordination contrast serves to drive Ti isotope fractionation between Fe-Ti oxides and silicate melt in accordance with stable isotope theory (Bigeleisen and Mayer, 1947; Urey, 1947; Schauble, 2004). Contrasts in the magnitude of $\delta^{49/47}$Ti variation have also been documented among magmas from different tectonic settings. Evolved melts from Ti-rich alkaline intraplate magmas exhibit significantly greater Ti isotope variation compared to those from tholeiitic and calc-alkaline magmas (Deng et al., 2019; Hoare et al., 2020; Zhao et al., 2020) due to the presence of both ilmenite and Ti-rich titanomagnetite in the crystal cargo of Ti-rich alkaline intraplate magmas. Hence, the magnitude of Ti isotope fractionation observed during magmatic differentiation is indirectly controlled by melt TiO$_2$ content and redox conditions, both of which influence the timing of Fe-Ti oxide crystallisation, modal abundance and composition of Fe-Ti oxides that crystallise (Toplis and Carroll, 1995; Hoare et al., 2020). Whether melt composition (e.g., SiO$_2$ content) also has a direct control on mineral-melt fractionation factors, remains unclear. As such, Ti isotopes have the potential to be utilised as a proxy for the geodynamic origins of magmas throughout geologic history (Greber et al., 2017a; Aarons et al., 2020; Hoare et al., 2020).

Measurements of bulk Fe-Ti oxides separates have confirmed they are isotopically lighter in comparison to co-existing melt, groundmass, and silicates minerals (Johnson et al., 2019; Mandl, 2019; Greber et al., 2021; Nie et al., 2021; Rzehak et al., 2021). However, studies of bulk mineral separates, while useful, are limited by the inability to separate different co-existing oxides for analysis (e.g., titanomagnetite+ilmenite) as well as by the lack of critical petrographic information pertaining to mineral-melt equilibrium. Hence, even though quantification of Fe-Ti oxide–melt Ti isotope fractionation factors is key to fully develop Ti isotopes into a mature petrological tool, such quantitative fractionation factors are currently lacking. Important aspects that require attention are the effects of mineral composition (e.g., the magnetite-ulvöspinel solid-solution; Figure 1) and the full range of Ti isotope variation in other Fe-Ti oxide phases such as ilmenite and rutile (Fig.1), which remain unconstrained.

Here we present measurements of the Ti isotope composition of individual Fe-Ti oxide phenocrysts (titanomagnetite, ilmenite, and rutile) and their co-existing silicate melt or microcrystalline groundmass. Using micro-milling, we sampled two experimental run
products (rutile-melt; Klemme et al., 2005), and six lavas (three per suite) from Heard Island (alkaline, intraplate) and Santorini (calc-alkaline, subduction zone). Measurement of individual Fe-Ti oxides from contrasting melt compositions (intraplate vs. subduction zone) enables us to further explore the controls of both melt and Fe-Ti oxide composition on the magnitude of Ti isotope fractionation during magmatic differentiation. Once the mechanics of Ti isotope fractionation are better constrained these fractionation factors can then be applied to forward modelling of igneous processes such as mantle melting and magmatic differentiation.

2. Sample petrography

A petrographic summary and modal phase assemblages for all samples used in this study are provided in Table 1. Fe-Ti oxide compositions are given in Table S2 and S3. A brief petrographic description of the natural sample sets (Heard Island and Santorini) and the rutile-melt experiments is provided in the following section.

Table 1. Modal abundances (modal %) of the main phases within Heard Island and Santorini samples selected for micro-milling.

<table>
<thead>
<tr>
<th>Suite</th>
<th>Sample</th>
<th>Modes</th>
<th>% Phenocrysts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Matrix</td>
<td>Crystals</td>
</tr>
<tr>
<td>Heard Is.</td>
<td>HB24</td>
<td>39</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>65054</td>
<td>89</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>65019</td>
<td>84</td>
<td>16</td>
</tr>
<tr>
<td>Santorini</td>
<td>AAS-021</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>AAS-027</td>
<td>65</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>AAS-028</td>
<td>72</td>
<td>28</td>
</tr>
</tbody>
</table>

2.1. Santorini

Santorini is located in the Aegean sea (Greece) and forms part of the South Aegean Volcanic Arc (e.g., Druitt et al., 1999). The three samples (Table 1) selected for use in this study are <500 ka and form part of a low pressure, medium-K calc-alkaline differentiation sequence (Nicholls, 1971; Huijsmans et al., 1988; Huijsmans and Barton, 1989; Andújar et al., 2015; Andújar et al., 2016). Sample AAS-021 is an andesite from Mt. Mikro Profitis Ilias, whereas AAS-027 and -028 are samples from the 1940–1941 and 1866 dacitic lava flows of Nea Kameni, respectively (Klaver et al., 2016a; Klaver et al., 2016b). The samples contain variable proportions of euhedral to subhedral phenocrysts (50-500 μm) of clinopyroxene, plagioclase, and magnetite, with minor orthopyroxene and apatite, set within a microcrystalline groundmass (Fig.2a, b and Fig.S1a-d). Titanomagnetite crystals are predominantly euhedral and possess relatively homogeneous compositions across the three samples (14-15 wt.% TiO₂; Usp₄₅₄₋₄₉; Table S2 and 3). No compositional zoning is observed in individual phenocrysts (Fig.2a, b and Fig.S1a-d), which indicates titanomagnetite and the melt are in equilibrium. However, some titanomagnetite crystals were observed with fine exsolution lamellae of slightly higher TiO₂ contents (19-21 wt.%), which is typically
the result of sub-solidus cooling. Of the targeted crystals, only one (AAS-021 G3-M1) exhibited these fine Ti-rich lamellae (Fig.S1d).

2.2. Heard Island

Heard Island is located on the Kerguelen Plateau in the southern Indian Ocean. The lavas included in this study are from the ≤1 Ma Mt. Dixon volcanic cone and belong to the Laurens Peninsula series (LPS) (Clarke et al., 1983; Fox et al., 2021). The samples have previously been measured for major- and trace elements contents as well as radiogenic isotopes (Barling, 1990; Barling and Goldstein, 1990; Barling, 1994; Barling et al., 1994). Whole rock δ⁴⁹/⁴⁷Ti measurements are reported in Hoare et al. (2020).

The three Heard Island samples (Table 1) selected for micro-milling are HB24 (basanite), 65054 (basaltic trachyandesite), and 65019 (trachyandesite) that fall on the liquid line of descent observed in the LPS (Barling, 1990; Barling, 1994). A common feature present across all LPS lavas is the high modal abundance of Fe-Ti oxides (ilmenite and titanomagnetite), which is reflective of the high TiO₂ contents (> 5 wt.%) of their parental magma (Barling, 1994). Sample HB24 is a basanite with ~30% phenocrysts hosted within a microcrystalline groundmass comprised of olivine, augite, plagioclase, ilmenite and titanomagnetite (Fig.2c, e). Minor amounts of apatite and sulfide are also present. The phenocryst assemblage is identical to that of the groundmass. Phenocrysts are euhedral to subhedral and range from 0.1 to 1 mm in size. Some phenocrysts also contain minor inclusions of apatite (Fig.2c, e and Fig.S1e, f). Sample 65054 is a basaltic trachyandesite with ~10-15% phenocrysts within a vesicular microcrystalline groundmass. The mineral assemblage of 65054 is like HB24, with phenocrysts of olivine, augite, plagioclase, ilmenite and titanomagnetite (Fig.2d, f and Fig.S1e, f). Sample 65019 is a trachyandesite with ~5-10% phenocrysts in a vesicular microcrystalline groundmass. The phenocryst assemblage of 65019 is comprised of augite, plagioclase, ilmenite, titanomagnetite, kaersutitic amphibole, and minor amounts of biotite. Samples 65054 and 65019 are noticeably less phryic than HB24 (Fig.2 and Fig.S1); in both samples, phenocrysts are euhedral to subhedral and range from 0.1 to 0.5 mm in size. Fe-Ti oxide compositions are relatively homogenous across all three samples, exhibiting a narrow range of variation in TiO₂ contents from 21-23 wt.% and Usp₆₆-₇₃ in titanomagnetite, and 47-49 wt.% and Ilm₆₄-₇₁ in ilmenite (Tables S3 and S4). In addition to Fe-Ti oxides, sample 65019 also possesses other Ti-bearing phases, mainly kaersutite (~6-8 wt.% TiO₂) and minor amounts of biotite (~8-10 wt.% TiO₂) (Barling, 1994). The predominantly subhedral to euhedral habit and lack of compositional zoning in Fe-Ti oxides in these Heard Island samples indicate they are in equilibrium with their host melt.

2.3. Rutile-melt experiments

The rutile-melt experimental run products MHD15_1 and HD4_4 used in this study are from Klemme et al. (2005). The experimental procedure and starting composition for these runs are given in Klemme et al. (2005), and only a short description is provided here: both experiments measured in this study were conducted on a Ti-rich, Fe-free haplo-andesitic starting composition (SKHDAN1) using the Pt wire loop technique in a 1 atmosphere gas-mixing furnace at a final run temperature of 1250°C. Redox conditions (in units of log fO₂) were controlled at -0.96 and -4.0, with run
duration times of 57 and 49 hours for MDH15_1 and HD4_4 respectively. Both experimental charges are comprised entirely of rutile crystals and quenched silicate glass (Fig.3). Rutile crystals range from ~50-600 μm (Fig.3) and exhibit no evidence of zoning or the presence of mineral inclusions (Fig.3), indicating they are equilibrium with the melt.

3. Methods

3.1. Scanning Electron Microscopy

A thorough petrographic assessment of the samples in this study was undertaken by obtaining back-scatter electron (BSE) and element maps of Fe-Ti oxide grains in polished ~2.5 cm diameter thick sections targeted as candidates for Ti isotope measurements. Back-scattered electron images were acquired at 1024-pixel resolution using a Zeiss Sigma HD Field Emission Gun SEM at the School of Earth and Environmental Sciences, Cardiff University at 15 kV using a 60 μm diameter final aperture. Element maps were acquired using two Oxford Instruments 150 mm² Energy Dispersive X-ray Spectrometry (EDS) silicon drift detectors on the same SEM. Operating conditions for element maps were set at 20 kV with a 120 μm aperture and a working distance of 8.9 mm, resulting in a nominal beam current of 4 nA. BSE images and element maps were acquired using Oxford Instruments Aztec software version 5.0. Individual grains were mapped at image resolutions of 512 by 384 or 1024 by 768 pixels. A process time of 0.5 μs was used for EDS with a pixel dwell time of 2250-4500 μs. The resulting element maps were processed using the Aztec software to perform background correction and element overlap deconvolution.

3.2. Major Element Mineral Chemistry

Major element compositions of Fe-Ti oxides and groundmass (Tables S2 and S3) were acquired using the same SEM instrument described in Section 3.1. Major element measurements were performed at 20 kV with a final aperture size of 60 μm and a 2 μs process time with a dead time around 50%, resulting in output count rates of 135,000 cps. A live time of ten seconds was used for each analysis. Checks for beam stability and analytical drift were conducted at 30-minute intervals throughout each session using a Co reference standard. A live time of ten seconds was used for each analysis. Measurements were calibrated using a suite of reference materials (Fe on ASTIMEX magnetite, Ti on Smithsonian ilmenite) and data accuracy was monitored by measuring Smithsonian magnetite and ASTIMEX rutile, and Smithsonian ilmenite as secondary standards. The precision and accuracy of mineral secondary standard measurements are reported in Table S1. Analytical procedures for the major element concentrations obtained for rutile and glass from the rutile-melt experimental run products (MHD15_1 and HD4_4) are reported in Klemme et al. (2005).

3.3. Micro-sampling

Individual Fe-Ti oxide crystals (ilmenite, titanomagnetite and rutile) and groundmass (or silicate glass in the case of the rutile-melt experimental run products) were micro-sampled at the School of Earth and Environmental Sciences, Cardiff University, using a NewWave Micro-Mill that was operated within a laminar flow hood using Horico tungsten carbide drill bits with a diameter of ~100 μm. The methodology utilised in
this study is adapted from Jansen et al. (2018), with similar techniques having been utilised successfully in previous studies (e.g. Charlier et al., 2006). Prior to drilling, drill bits were cleaned by submerging them in a clean glass beaker with Milli-Q water and washing them in an ultrasonic bath filled with Milli-Q for 15 minutes. A grid of spots was placed on targeted crystals to maximise the surface area drilled. A drop of Milli-Q was placed on the target prior to engaging the drill to capture the drilled material in suspension. At regular intervals, the Milli-Q containing the drilled material was pipetted into pre-cleaned 7 ml PFA beakers, and new drops of Milli-Q were added to ensure maximum recovery of drilled sample during drilling. Drilling speed was set at 65%, with 75-100 μm/s scan- and drill plunge speeds during drilling. The duration of micro-milling varied from 5-30 minutes per target, depending on the size and TiO₂ concentration of the target. As multiple crystals were drilled from the same sample, the sample surface was cleaned with Milli-Q and ethanol before drilling the next crystal. For each sample the phase with the lowest TiO₂ contents (i.e., groundmass or glass) was drilled first to limit the risk of contamination from drilling of TiO₂ rich phases in the same sample. The acicular habit of rutile in the experimental run products of Klemme et al. (2005) presented a challenge for precise micro-milling of pure phases as many possess a diameter of <100 μm. To circumvent this problem, we specifically targeted rutile-glass mixtures in different proportions (in addition to milling as close to the pure end member phases as possible), which we later utilise to calculate compositions via endmember unmixing.

3.4. Sample digestion and ion-exchange chromatography

The micro-milled samples were dried down and subsequently digested in 2 ml of a 1:1 mixture of concentrated HNO₃ and HF on a hotplate at 130 °C for ≥72 hours. Following evaporation to incipient dryness, samples were taken up in concentrated HNO₃ and dried down 3 times and finally dissolved in 1.5 ml concentrated HCl. To estimate precision and yield of the micro-milling, the TiO₂ content and CaO/TiO₂ of the samples was measured using the Nu Plasma II and a calibration curve consisting of reference materials JB-2, BCR-2 and RGM-2 digested in tandem with the samples. Total Ti yields of the micro-milled samples varied from 0.3 to 8 μg Ti. In natural samples measured CaO/TiO₂ was used as a check to identify any contribution of groundmass or silicate material in drilled Fe-Ti oxides. Most micro-milled Fe-Ti oxides display CaO/TiO₂ values at or close to zero (Table S5) indicating precise drilling of the intended target. However, a few samples exhibit CaO/TiO₂ values of ~0.5-1 likely suggesting the incorporation of some groundmass or neighbouring silicate material. In most cases the source of the elevated CaO/TiO₂ in micro-milled oxides are likely due to the presence of small apatite inclusions (Fig.2), but due to absence of Ti in apatite this is unlikely to exert any influence on the Ti isotope composition of micro-milled oxides. In the case of the rutile-melt experiments, utilising the measured CaO/TiO₂ values enabled us to derive the Ti isotope compositions of pure rutile and glass via a weighted linear regression of δ⁴⁷/⁴⁸Ti vs. CaO/TiO₂ mixing lines which is further discussed in section 4.3.

Approximately 20 mg of H₃BO₃ was added to the sample and 40 mg to the reference materials and left to reflux at 130 °C for ≥24 hours as an extra measure to ensure that any fluorides (which can sequester Ti from solution) are re-dissolved and all Ti was in solution. For reference materials a 5 μg aliquot of Ti was equilibrated with ⁴⁷Ti-⁴⁹Ti double spike in a 48:52 proportion (Millet and Dauphas, 2014). Micro-milled samples
were also spiked in a 48:52 ratio in accordance with their total Ti concentration, with aliquots of 5 μg taken where permissible. Chemical purification of Ti was achieved following the first step of procedure outlined by Zhang et al. (2011) using TODGA resin. Following purification via ion-exchange chromatography, samples were dried down and then refluxed in 500 μl concentrated HNO₃ at 130 ºC for ≥24 hours. The samples were then dried down and the processed was repeated a further two times using a 500 μl 1:1 mixture of concentrated HNO₃ and H₂O₂ to remove any organics.

3.5. Double Spike MC-ICP-MS measurements

Titanium isotope composition measurements were carried out using a Nu Plasma II MC-ICP-MS at the Cardiff Earth Laboratory for Trace Element and Isotope Chemistry (CELTIC), at the School of Earth and Environmental Sciences, Cardiff University following the methods previously described in Hoare et al. (2020) and Klaver et al. (2021). Samples were introduced via an Aridus II de-solvating nebuliser. Isotope ratio measurements were performed in medium resolution mode to account the possibility of minor polyatomic interferences from ²⁸Si¹⁹F⁻ on ⁴⁷Ti and ⁴⁸Ti. Sample measurements were bracketed by measurements of the spiked Origins Laboratory Ti (OL-Ti) reference material (Millet and Dauphas, 2014). Raw data were then processed offline using in-house double spike deconvolution codes written in Python and based on those used in Millet and Dauphas (2014). Titanium isotope ratios are reported relative to the OL-Ti reference material expressed in δ-notation as δ⁴⁹/⁴⁷TiOL-Ti (hereafter abbreviated to δ⁴⁹/⁴⁷Ti) following Coplen (2011). Uncertainties on δ⁴⁹/⁴⁷TiOL-Ti are expressed as 95% confidence intervals (c.i. hereafter). Geologic reference materials (BCR-2, JB-2 and RGM-2; see Fig.S2 and Table S4) and Ti solution reference materials (Alfa Aesar Ti-wire and Alfa Aesar Ti-Solution; see Fig.S2 and Table S4) measured during this study are in excellent agreement with published data (Fig.S2 and Table S4) and yield a pooled 2s intermediate precision of 0.023‰.

4. Results

4.1. Fe-Ti Oxide Geothermometry and Oxygen-Barometry

Coexisting touching Fe-Ti oxide pairs (ilmenite and magnetite) were found in all three Heard Island samples, whereas all Santorini samples contain Ti-magnetite only. The ILMAT (Lepage, 2003), an excel-based worksheet, was used to calculate FeO/Fe₂O₃ for all Heard Island mineral pairs utilising the method of Carmichael (1966), and also to check stoichiometry. Providing the Fe-Ti oxide pairs showed no compositional zoning and passed the Mg/Mn equilibrium test of Bacon and Hirschmann (1988), the Fe-Ti oxide geothermometer and oxygen barometer of Ghiorsko and Evans (2008) was applied using the ENKI Cloud app front end (Ghiorsko and Prissel, 2020) to determine the temperature and oxygen fugacity (relative to the Nickel-Nickel oxide; NNO buffer). For samples 65054 and 65019, coexisting touching pairs were less common than in HB24 and thus adjacent non-touching Fe-Ti oxides were selected using the same criteria as for touching pairs to supplement the touching pairs. Here we provide the first estimates of temperature and fO₂ for Heard Island. Values obtained from both touching and non-touching pairs overlap and are in general agreement (Figs. 4 and S3). Temperatures based on the Fe-Ti oxide thermometer range from 1103 to 1227 ºC (n=11) for HB24, 1039 to 1103 ºC (n=7) for 65054, and 1003 to 1092 ºC (n=8) for 65019 (Figs.4 and S3 and supplementary Table S3). Oxygen fugacity (fO₂, expressed
as ΔNNO) ranges from +0.05 to -0.22 for HB24, -0.08 to -0.56 for 65054, and -0.33 to -0.78 for 65019 (Figs.4 and S3; supplementary Table S3). It is common for equilibrium Fe-Ti oxide pairs from a single sample to show a range of temperature and fO2 values which reflects temporal evolution in the magmatic system (Blundy and Cashman, 2008), and also potentially minor subsolidus re-equilibration. To provide temperature estimates that can be tied to Ti isotope fractionation factors for Heard Island Fe-Ti oxides, the data from the equilibrium pairs for each sample was used to calculate a mean temperature (Fig.4 and Fig.S3; 1149 ± 24 °C for HB24, 1078 ± 18 °C for 65054, and 1056 ± 26 °C for 65019. Uncertainties are reported as 2se). The 2s uncertainty on the temperature is propagated when fractionation factors are normalised to a common temperature.

4.2. Ti isotope compositions of natural samples

The raw δ49/47Ti data for the groundmass (for natural samples), silicate glass (for experimental run products), and all Fe-Ti oxide phases are given in Table S5 and shown in Figure 5. Groundmass δ49/47Ti ranges from +0.245 to +0.526 ‰ for Heard Island samples, and from +0.414 to +0.464 ‰ for Santorini samples. Ilmenite from Heard Island samples has δ49/47Ti ranging from -0.148 to +0.253 ‰, with ilmenites consistently displaying isotopically lighter compositions compared to their corresponding groundmass (Fig.5a). Titanomagnetite from Heard Island samples possesses δ49/47Ti = -0.522 to -0.124 ‰ and is isotopically lighter with respect to both groundmass and ilmenite within the same sample (Fig.5a). In Santorini samples, titanomagnetite is also isotopically lighter with respect to groundmass but displays a narrower range of δ49/47Ti (-0.141 to -0.008 ‰) compared to Heard Island (Fig.5a).

All measured Ti isotope fractionation between micro-milled Fe-Ti oxides and groundmass (or silicate glass) was calculated using the following equation and is shown in Figure 6 and Table S6:

\[
\Delta^{49/47} \text{Ti}_{\text{oxide-melt}} = \delta^{49/47} \text{Ti}_{\text{oxide}} - \delta^{49/47} \text{Ti}_{\text{groundmass}} \quad (1)
\]

Individual Δ^{49/47}Ti_{oxide-melt} values for titanomagnetite, ilmenite and rutile are provided in Table S6. Δ^{49/47}Ti_{magnetite-melt} values exhibited by Santorini samples define a relatively narrow range of -0.453 to -0.605‰, in comparison to the larger variation observed in Heard Island of -0.401 to -0.794‰ (Fig.6 and Table S6). Ilmenite-melt Ti isotope fractionation (Δ^{49/47}Ti_{ilmenite-melt}) for Heard Island samples ranges from -0.420 to -0.273‰ (Table S6). Values of Δ^{49/47}Ti obtained from mineral separates from the Kneeling Nun Tuff (KNT) by Mandl (2019) are also included for comparison (Fig.6a). The Δ^{49/47}Ti value of KNT ilmenite is in good agreement with those observed in Heard Island and the Δ^{49/47}Ti value of KNT titanomagnetite is comparable to those of Santorini (Fig.6a).

4.3. Ti isotope compositions of experimental samples

The δ49/47Ti values for micro-milled samples in the rutile-melt experiments range from -0.265 to -0.123 ‰ and are positively correlated with CaO/TiO2 (Fig.5b). Mixing lines on δ49/47Ti vs. CaO/TiO2 were utilised to calculate the δ49/47Ti value for pure rutile and silicate glass in each experimental run product. This was performed using a York regression for the linear relationship between δ49/47Ti and CaO/TiO2 of the micro-
milled samples (Fig.5b) and extrapolating the regression to the CaO/TiO\textsubscript{2} of rutile (assumed to be 0) and the composition of the silicate glass reported in Klemme et al., (2005). The $\delta^{49/47}\text{Ti}$ values calculated for pure rutile (CaO/TiO\textsubscript{2} = 0) are -0.264 ± 0.025% and -0.224 ± 0.024% for MDH15_1 and HD4_4 respectively. The $\delta^{49/47}\text{Ti}$ values calculated for pure silicate glass from extrapolation are -0.106 ± 0.035‰ and -0.002± 0.068‰ for MDH15_1 and HD4_4 respectively (see Table S5). The values of $\Delta^{49/47}\text{Ti}_{\text{rutiler-melt}}$ are -0.158 ± 0.049‰ and -0.221 ± 0.085‰ for MDH15_1 and HD4_4 respectively (see Table S6); the fractionation factors observed in both experiments are within error of each other.

4.4. Fe-Ti oxide-melt Ti isotope fractionation factors

At magmatic temperatures, isotopic fractionation factors (expressed as $10^3\ln\alpha$ where $\alpha$ is the ratio of the isotopic composition of two phases; cf. Young et al., 2015) are proportional to the inverse square of the absolute temperature. To quantify Ti isotope oxide-melt fractionation factors, we regressed our data versus temperature (as $10^6/T^2$ with T in K; Fig.7) and, in the case of titanomagnetite, its chemical composition (TiO\textsubscript{2} and the mole fraction of ulvospinel; Fig. 8a, b).

In this study we provide the first temperature (and fO\textsubscript{2}) estimates for Heard Island samples from the mean values obtained from Fe-Ti oxide geothermometry (see section 4.1), as there are no other thermometry data available in the literature. However, the temperature and fO\textsubscript{2} estimates obtained from Heard Island are comparable to other Ti-rich intraplate magmas from the Afar Rift and Ascension Island (Field et al., 2013; Chamberlain et al., 2019). Temperature estimates for Santorini samples were taken from a compilation of literature data including two-pyroxene thermometry (Barton and Huijsmans, 1986); Fe-Ti oxide thermometry (Gertisser et al., 2009; Druitt, 2014); and melt inclusion analyses (Gardner et al., 1996; Michaud et al., 2000). From these data we obtained a mean temperature estimate of 921 ± 31 ºC (n=9) for the dacites (AAS-027 and 28) and 987 ± 12 ºC (n=11) for the andesite sample AAS-021. These temperature estimates are in good agreement with optical pyrometer measurements conducted during the 1925-1926 eruption on Nea Kameni (Washington, 1926; Reck et al., 1936). For the ilmenite and titanomagnetite Ti isotope data reported by Mandl (2019) for the Kneeling Nun Tuff, we used temperature constraints from Szymanowski (2019) that suggest a mean crystallisation temperature of 775 ± 43 ºC based on combining plagioclase, amphibole, zircon and titanite thermometers.

A weighted least-squares regression of $10^3\ln\alpha_{\text{ilmenite-melt}}$ was performed against $10^6/T^2$ (K\textsuperscript{-2}) using the data from this study (Ilm\textsubscript{64-71}) and Mandl (2019) (Fig.7a). We obtained the following linear relationship for $10^3\ln\alpha_{\text{ilmenite-melt}}$ as a function of temperature, where $10^3\ln\alpha_{\text{ilmenite-melt}} = 0$ when $10^6/T^2 = 0$ (The 2s uncertainty is given in brackets):

$$10^3\ln\alpha_{\text{ilmenite-melt}} = -0.5996 (±0.0349) \times 10^6/_{T^2} (2)$$

The rutile-melt experiments measured in this study yielded the following linear relationship with respect to temperature ($10^6/T^2$; Fig. 7b):

$$10^3\ln\alpha_{\text{rutile-melt}} = -0.4039 (±0.0985) \times 10^6/_{T^2} (3)$$
The 2s uncertainty is given in brackets. From equations 2 and 3 we derive a $10^3\ln{\alpha_{\text{titanomagnetite}}}$ of $0.159 \pm 0.103$ at 1000 K.

In contrast to the ilmenite data ($\text{Ilm}_{4-71}$), there is large variation in TiO$_2$ content between titanomagnetite from Santorini and Heard Island (Fig.8), hence all $10^3\ln{\alpha_{\text{titanomagnetite}}}$ (after normalisation to a common temperature of 1000K) were regressed using a weighted least-squares approach, as a function of both titanomagnetite TiO$_2$ content and the mole fraction of the Ti-rich endmember ulvöspinel ($\text{Fe}^{2+}_{-2}\text{TiO}_4; X_{\text{ulvöspinel}}$), as well as temperature ($10^6/T^2$; Fig. 7c and Fig. 8a, b) to yield:

$$10^3\ln{\alpha_{\text{titanomagnetite}}}=\frac{[-0.0482(\pm0.0069) * TiO_2 + -0.0530(\pm0.1203)] * 10^6}{T^2},$$

$$\sigma_{xy} = -0.0002$$ (4)

$$[-1.4906(\pm0.2187) * X_{\text{ulvöspinel}} + -0.0607(\pm0.1221)] * 10^6/T^2,$$

$$\sigma_{xy} = -0.0065$$ (5)

The 2s uncertainties are given in brackets, along with the slope-intercept covariance term, $\sigma_{xy}$. $X_{\text{ulvöspinel}}$ was calculated by stoichiometry using the method of Stormer (1983). Given that the co-variation of $10^3\ln{\alpha}$ with respect to TiO$_2$ and $X_{\text{ulvöspinel}}$ is similar and the variety of different methods available to calculate $X_{\text{ulvöspinel}}$ (e.g. Carmichael, 1966; Anderson, 1968; Lindsley and Spencer, 1982; Stormer, 1983), in the interest of simplicity and accessibility we use Eqn. 4 for the remainder of this manuscript for discussion and modelling purposes. The results of the regression using Eqn. 4 for $10^3\ln{\alpha_{\text{titanomagnetite}}}$ using different TiO$_2$ contents (14 and 22 wt.%) as a function of temperature is shown in Fig.7c, along with $10^3\ln{\alpha_{\text{titanomagnetite}}}$ values from Heard Island, Santorini, and Kneeling Nun Tuff (KNT; Mandl, 2019). The data from Kneeling Nun Tuff (KNT; Mandl, 2019) is plotted in Figures 7 and 8 for comparison to the data presented in this study but is excluded from the regression calculations.

5. Discussion

The data presented in this study provide conclusive evidence that Fe-Ti oxides have a notably lighter Ti isotope composition than co-existing silicate melt, consistent with previous studies (Johnson et al., 2019; Mandl, 2019; Aarons et al., 2021; Greber et al., 2021; Nie et al., 2021; Rzehak et al., 2021). However, in contrast to those studies, where oxides are measured as bulk separates mixing various minerals and compositions, we the first to quantify multiple oxide-melt fractionation factors for different Fe-Ti oxide minerals. Additionally, our data show that titanomagnetite and ilmenite, the main hosts of Ti in magmatic systems, display different Ti isotope fractionation factors as hypothesised by Hoare et al. (2020) from whole rock data. In the following sections we consider what parameters control the magnitude of Ti isotope fractionation for different Fe-Ti oxides and examine applications of these fractionation factors to model magmatic processes.

5.1. Comparison to ab initio fractionation factors
We compare this result with *ab initio* studies, both inter-mineral (Leitzke et al., 2018; Wang et al., 2020) and those that used the mineral fresnoite as a melt proxy (Aarons et al., 2021). Combining the reduced partition function ratios (10^3 ln\(\alpha\)) for ilmenite from Wang et al. (2020), geikielite (MgTiO\(_3\)) and fresnoite (a melt proxy) from Aarons et al. (2021), all of which were calculated using QUANTUM ESPRESSO (Giannozzi et al., 2009) yields a 10^3 ln\(\alpha_{\text{ilmenite-fresnoite}}\) value in good agreement with the values obtained from Eqn. 2 (Fig. 7a). Both 10^3 ln\(\alpha_{\text{ilmenite-fresnoite}}\) and 10^3 ln\(\alpha_{\text{ilmenite-melt}}\) calculated in this study are more negative compared to 10^3 ln\(\alpha_{\text{geikielite-fresnoite}}\) (Fig. 7a). The value of 10^3 ln\(\alpha_{\text{rutile-ilmenite}}\) calculated by combining Eqn. 2 and 3 is different to the value of -0.070 predicted by density functional theory (DFT) models reported by Wang et al. (2020). The absolute 10^3 ln\(\alpha_{\text{rutile-melt}}\) value calculated from Eqn. 3 is smaller than that of 10^3 ln\(\alpha_{\text{anatase-fresnoite}}\) (Aarons et al., 2021), and 10^3 ln\(\alpha_{\text{rutile-fresnoite}}\) (Wang et al., 2020; Aarons et al., 2021). The predicted 10^3 ln\(\alpha\) values for titanomagnetite and ulvöspinel versus fresnoite (a melt proxy) as function temperature estimated by (Aarons et al., 2021) on the basis of average Ti-O bond length are also shown in Fig. 7c for comparison. 10^3 ln\(\alpha\) values for titanomagnetite and ulvöspinel from Aarons et al. (2021) display a marginal difference, with titanomagnetite being slightly lighter compared to ulvöspinel (without uncertainty estimates; Fig. 7c). The Aarons et al. (2021) titanomagnetite/ulvöspinel 10^3 ln\(\alpha\) estimates are comparable to 10^3 ln\(\alpha\) values calculated using Eqn. 4 with TiO\(_2\) = 14 wt%, and the 10^3 ln\(\alpha\) values of titanomagnetites from Santorini (this study) and the Kneeling Nun Tuff (Mandl, 2019). However, the data for high TiO\(_2\)/X\(_{\text{usp}}\) titanomagnetites from Heard Island possess significantly more negative 10^3 ln\(\alpha\) values at a given temperature (Fig. 7c) than the predicted by Aarons et al. (2021).

5.2. Controls on the magnitude of Fe-Ti oxide – melt Ti isotope fractionation factors

5.2.1. The role of Ti-O bond length

Stable isotope theory predicts that heavier isotopes prefer shorter bonds, which are stronger due to elevated vibrational frequencies (Bigeleisen and Mayer, 1947; Urey, 1947; Schauble, 2004). The effect of bond length on the magnitude of mass-dependent isotope fractionation factors has previously been documented for some isotope systems such as Fe (e.g. Hill and Schauble, 2008; Sossi and O’Neill, 2017), where the magnitude of Fe isotope fractionation factors were found to be inversely proportional to Fe-O bond length (Sossi and O’Neill, 2017). The ab-initio study of Wang et al. (2020) demonstrated that the reduced partition function ratio (10^3 ln\(\beta\)) of ^{49}\text{Ti}/^{47}\text{Ti} calculated for silicates, ilmenite, and rutile display a general negative correlation with average Ti-O bond lengths. Available published data on the crystal structure of Fe-Ti oxide minerals indicates that rutile possesses a slightly shorter average Ti-O bond length (0.196±0.001 nm; Samat et al., 2016 and references therein) compared to compared to ilmenite (0.198±0.001 nm; Wechsler et al., 1984; Wechsler and Prewitt, 1984). For the magnetite- ulvöspinel solid solution, Bosi et al. (2009) observed a marginal decrease in the Ti-O bond length from 0.206 to 0.205 nm over a range 16 to 23 wt. % TiO\(_2\), similar to the range of TiO\(_2\) contents observed for the Santorini and Heard Island samples presented in this study. Thus, on the inference from Ti-O bond length alone, titanomagnetite would be predicted to possess the greatest affinity for lighter isotopes, which is corroborated by our new data. Figure 9 shows that Ti-O bond...
length generally correlates with $10^3 \ln a_{\text{oil-melt}}$, which slightly decreases from rutile to titanomagnetite at 1000 K. However, there are inconsistencies between our data and those of Wang et al. (2020). In the ab-initio modelling by Wang et al. (2020) $10^3 \ln \beta$ for rutile is lower than that of ilmenite-geikielite solid solution despite the longer Ti-O bond length of ilmenite-geikielite. However, it is difficult to precisely quantify this difference due to the lack of uncertainty estimates on the $10^3 \ln \beta$ values from Wang et al. (2020).

The magnitude of $10^3 \ln a$ between different oxide species generally correlates with Ti-O bond length (Fig.9). However, the large variation in the magnitude of $10^3 \ln a_{\text{titanomagnetite-melt}}$ observed between titanomagnetites of different Ti contents suggests the presence of another control on the value $10^3 \ln a_{\text{titanomagnetite-melt}}$ (Fig.8), particularly as Ti-O bond length in titanomagnetite shows a subtle decrease with increasing Ti content (Bosi et al., 2009). This is supported by a recent study from Rabin et al. (2021) in which the variations observed between Fe and Si isotope fractionation of various silicate minerals could not be explained solely by differences in average Fe- or Si-O bond lengths. Rabin et al. (2021) propose that the local composition of mineral phases, in particular the nature of the nearest atomic neighbours, determines the magnitude of isotope fractionation.

5.2.2. The role of Fe-Ti oxide solid-solution

It has been well documented that the chemical composition of a mineral affects its crystal structure and consequently also elemental partitioning between minerals and their host melt (e.g. Lundstrom et al., 1998; Hill et al., 2000). More recently, studies have begun to consider the implications for mass-dependent isotope fractionation (Huang et al., 2010; Feng et al., 2014; Roskosz et al., 2015; Wang et al., 2017; Wu et al., 2017; Rabin et al., 2021). Using first principles calculations, Feng et al. (2014) observed that mass-dependent Ca isotope fractionation between orthopyroxene (opx) and clinopyroxene (cpx) was not solely controlled by temperature, but also a function of Ca contents as the average Ca-O bond length in orthopyroxene is strongly effected by its Ca content. Feng et al. (2014) observed that $10^3 \ln a_{\text{opx-cpx}}$ increased substantially with decreasing Ca content in orthopyroxene, (Huang et al., 2010; Wang et al., 2017).

Titanomagnetite (Fe$_{3+}$Ti$_4$O$_{10}$) is a solid solution (Fig.1) between magnetite (Fe$^{2+}$Fe$^{3+}$O$_4$) and ulvöspinel (Fe$^{2+}$Ti$^{4+}$O$_4$; see Figure 1), which possess an ‘inverse’ spinel structure with an Fd$ar{3}$m space group (Barth and Posnjak, 1932). Titanium (as Ti$^{4+}$) is thought to almost exclusively occupy the octahedral site (Fujino, 1974; O’Neill and Navrotsky, 1983; Trestman- Matts et al., 1983; Wechsler et al., 1984), although some studies have postulated that minor Ti$^{4+}$ also exists in the tetrahedral site (Stout and Bayliss, 1980; Sedler et al., 1994). As the Ti content of titanomagnetite increases, the proportion of the ulvöspinel endmember increases which results in a higher proportion of Ti$^{4+}$ in the octahedral site at the expense of Fe$^{3+}$, and a concurrent increase in Fe$^{2+}$ in both the tetrahedral and octahedral sites to maintain charge balance (Akimoto et al., 1957; Bosi et al., 2009; Pearce et al., 2010; Okube et al., 2018). The ionic radii of Ti$^{4+}$ and Fe$^{3+}$ occupying VI-fold coordination are relatively similar, at 0.0605 and 0.0645 nm respectively (Shannon, 1976; O’Neill and Navrotsky, 1983). However, ferrous iron (Fe$^{2+}$) has a larger ionic radius, both in IV- and VI-fold coordination, at
0.0780 and 0.0630 nm respectively (Shannon, 1976; O’Neill and Navrotsky, 1983). Therefore, as the proportion of the ulvöspinel endmember (and hence the TiO$_2$ content) increases so does the proportion of Fe$^{2+}$ in both the VI and IV sites at the expense of smaller Fe$^{3+}$ ions. This change in the local cationic environment has the potential to impose strain on the crystal lattice and possibly weaken the bonding environment which could consequently influence isotope fractionation. Such an effect. Such a mechanism has been proposed for modifying Fe and Si isotope fractionation in some silicate minerals (Rabin et al., 2021). In titanomagnetite this is supported via crystallographic evidence of the positive correlation between increasing Ti content and the size of the unit cell parameter (a-parameter) and the oxygen fractional coordinate ($u$-parameter) of titanomagnetite (Bosi et al., 2009; Pearce et al., 2010). This imposes additional distortion on the close cubic packed (CCP) array of anions, as oxygen atoms are displaced to increase bond lengths in the tetrahedral site to accommodate larger Fe$^{2+}$ ions (Bosi et al., 2009). All these factors would make Ti-rich titanomagnetite favour lighter isotopes (Fig. 8a, b) far greater than predicted based on the marginal changes in Ti-O bond lengths (Fig. 9) of the magnetite-ulvöspinel solid solution alone. Similarly in the case of Fe isotope fractionation during forsterite-fayalite solid solution, fayalite possess a more negative $^{10}$ln$^{57}$Fe/$^{54}$Fe value as lowering Fe/Mg lowers the force constant on the central Fe ion by altering its surrounding cationic environment (Rabin et al., 2021). As it not possible to calculate estimates of Ti isotope fractionation across the full compositional spectrum of the magnetite-ulvöspinel solid-solution using DFT calculations (Wang et al., 2020; Aarons et al., 2021). The natural data presented here currently provide the only constraint on implications of the magnetite-ulvöspinel solid-solution on Ti isotope fractionation. This could be explored further by an experimental campaign to synthesise run products across the full compositional range of magnetite-
ulvöspinel solid-solution.

5.2.3. The role of melt structure

Deng et al. (2019) argued that melt structure is another parameter that can influence Ti isotope fractionation as there is a tendency for a higher proportion of Ti to occupy IV-fold coordination in more silicic melts (Farges et al., 1996a; Farges and Brown, 1997). However, (Hoare et al., 2020) observed no contrasting relationships between SiO$_2$ and NBO/T across numerous magmatic differentiation suites of both differing composition and geodynamic setting. The data presented in this study suggests that melt structure has no easily discernible influence on the titanomagnetite fractionation factor as shown by Fig. 7d and 8c, as $^{10}$ln$_{titanomagnetite-melt}$ values show no correlation with whole rock SiO$_2$ content or NBO/T. This observation holds for ilmenite, with $^{10}$ln$_{oxide-melt}$ showing no coherent variation over a large range of NBO/T values (Fig. 7d) and different melt compositions. Due to the lack of detailed quantitative data of the full range of Ti coordination in silicate melts, further experimental investigation is required to disentangle the effect of melt structure from the dominant controls of mineral and melt composition on Ti isotope fractionation.

5.3. Geologic applications of Ti isotope fractionation factors
The Ti isotope fractionation factors derived in this study provide new opportunities to utilize and develop Ti isotopes as a geochemical tool which can be applied to a variety of geologic processes. In this section we test the robustness of our new fractionation factors using forward modelling of terrestrial mantle melting and magmatic differentiation.

5.3.1. Estimating silicate-melt Ti isotope fractionation factors

Whilst the elemental and hence isotopic budget of Ti in magmatic rocks is predominantly controlled by Fe-Ti oxides, silicates could influence Ti isotopes in magmatic systems where Fe-Ti oxides are absent, such as in un-metasomatized peridotites, or in certain magmas where silicate phases such as amphibole, biotite, and titanite contain non-trivial amounts of Ti. Titanium isotope measurements of silicates are thus far limited. Mandl (2019) reported raw $\Delta^{49/47}$Ti values for amphibole- (1.5 wt.% TiO$_2$; -0.210‰), biotite- (4.8 wt.% TiO$_2$; -0.234‰), and titanite-melt (35 wt.% TiO$_2$; -0.238‰) using mineral separates from the Kneeling Nun Tuff. These silicates were observed to be isotopically lighter with respect to the groundmass. Analyses of orthopyroxene-melt experimental run products by (Rzehak et al., 2021) revealed $\Delta^{49/47}$Ti$_{orthopyroxene-melt}$ displays relatively limited fractionation at -0.002 ± 0.017‰ to +0.050 ± 0.025‰ at conditions relevant to terrestrial magmatism (fO$_2$ ≥FMQ-2). The coordination state of Ti in silicates is difficult to constrain and often non-uniform, for example in Ti-rich biotite (8-14 wt.% TiO$_2$), it has been suggested that up to 90% Ti occupies a site with VI-fold coordination (Henderson and Foland, 1996). Phases that control the Ti budget of typical of terrestrial mantle lithologies, like pyroxene, garnet and spinel, appear to host Ti predominantly in VI-fold coordination (O’Neill and Navrotsky, 1983; Waychunas, 1987). Variations of the coordination state of Ti in silicate phases have important ramifications for Ti isotopes in magmatic systems.

To provide estimates on the magnitude of various silicate-melt Ti isotope fractionation factors we combine our new ilmenite-melt fractionation factor (Eqn. 2) with the mineral-mineral fractionation factors for ilmenite and Ti-bearing silicates that are derived from the ab initio density functional theory calculations as reported by Leitzke et al. (2018; Ti in VI-fold coordination) and Wang et al. (2020; Ti in IV-fold coordination). We chose to use the ilmenite-melt fractionation factor as an anchor for the value of $\beta_{melt}$ as opposed to rutile due the availability of more data for natural ilmenite-groundmass pairs. It should be noted that the ‘melt’ for the rutile experiments is a very Ti-rich (9-11 wt% TiO$_2$), Fe-free haplogranodandesite (Klemme et al., 2005) which is necessary to crystallise rutile under experiential conditions but is clearly not directly comparable to most terrestrial rock compositions which could result in the slightly different values obtained for silicate fractionation factors shown in supplementary Figure S4. Fractionation factors for silicates when anchored to rutile-melt are provided in the supplements in Table S7 and shown in Fig.S4. Resulting mineral-melt fractionation factors for silicate minerals are listed in Table S7 and shown in Fig.10 alongside empirical data from the literature (Mandl, 2019; Rzehak et al., 2021), the oxide-fresnoite fractionation factors calculated by Aarons et al. (2021), and the complete set of Fe-Ti oxide fractionation factors from this study.
The *ab initio* models from Leitzke et al. (2018) and Wang et al. (2020) indicate that if Ti is exclusively present in IV-fold coordination, pyroxene and garnet are isotopically heavier than coexisting melt, consistent with stable isotope theory (Fig.8). Conversely, if Ti is exclusively hosted in an octahedral site (VI-fold coordinated), pyroxene and garnet show minimal fractionation, being marginally lighter than melt (Fig.10). The $10^3 \ln a$ values for amphibole-, biotite- and titanite-melt from Mandl (2019) for the Kneeling Nun Tuff (-0.231; -0.257; and -0.262 at 1000 K, respectively) are larger than those derived from *ab initio* data for clinopyroxene and garnet with Ti in VI-fold coordination and anchored to our $10^3 \ln \beta_{\text{melt}}$ value taken from Eqn.2 (-0.132 and -0.137 respectively; Fig. 10). This is consistent with the presence of longer Ti-O bonds for titanite, biotite and amphibole (Farges et al., 1996b; Henderson and Foland, 1996; Tiepolo et al., 2007). These phases, when present, also have greater influence on the Ti budget of magmatic rocks relative to pyroxene and garnet (e.g., Mandl, 2019). At oxygen fugacities of $\geq$FMQ-2 where Ti is exclusively tetravalent, the values for orthopyroxene-melt fractionation from Rzehak et al. (2021) show a narrow range of variation and are within error of the clinopyroxene-melt and garnet-melt fractionation factors calculated from the *ab initio* studies of Leitzke et al. (2018) and Wang et al. (2020) assuming Ti is exclusively in VI-fold coordination (Fig.10).

5.3.2. Ti isotope modelling during magmatic differentiation

To evaluate the robustness of our empirical and calculated Ti isotope fractionation factors, we performed forward modelling of the Ti isotope evolution during fractional crystallisation for the differentiation suites from Hoare et al., (2020). Least squares major element models (see supplementary material S9) were used to estimate modal proportions of fractionating phases and thus the bulk solid-melt Ti isotope fractionation factor. The mineral modes, compositions, and bulk solid-melt Ti isotope fractionation factors are given in Table S8 and were calculated using Eqn. 2 and 4 for ilmenite and titanomagnetite respectively. For evolved Heard Island compositions that contain both biotite and amphibole, the fractionation factors from Mandl (2019) were used. Mineral compositions are taken from the literature (see Hoare et al., 2020 and references therein). Silicate-melt fractionation factors are anchored to ilmenite-melt (Eqn. 2 and Fig.10). We modelled the Ti isotope evolution of each suite via a Rayleigh fractionation process using the following equations:

$$ R = R^o f^\alpha_{\text{bulk}}^{-1} (7) $$

$$ \alpha_{\text{bulk}} = \alpha_1 * X_1 + \ldots + \alpha_n * X_n (8) $$

where, $R$ is the $^{40}$Ti/$^{47}$Ti isotope ratio, $R^o$ is the initial ratio, $f$ is the fraction of Ti remaining in the melt, and $\alpha_{\text{bulk}}$ is the bulk fractionation factor (Eqn. 8) between the remaining melt and the crystallising mineral assemblage, where the mineral-melt fractionation factors are weighted by their Ti concentration at each stage of the model (X). The uncertainties in temperature and the fractionation factors are propagated into the calculation of the bulk solid-melt Ti isotope fractionation factor.
5.3.3. Ti isotope modelling of mantle melting

During melting of either spinel- or garnet-facies peridotite, Ti behaves as a moderately incompatible element which facilitates its efficient extraction from the mantle during basalt petrogenesis (Prytulak and Elliott, 2007; Gale et al., 2013). Consequently, previous studies have proposed that the δ\(^{49/47}\)Ti compositions of basalts is reflective of their mantle source, and hence that partial melting of the mantle produces no resolvable Ti isotope fractionation (Millet et al., 2016). This is supported by the indistinguishable δ\(^{49/47}\)Ti compositions of primitive basalts and mantle lithologies (Millet et al., 2016). However, Deng et al. (2018) observed a subtle offset between the mean δ\(^{49/47}\)Ti composition of N-MORB and E-MORB of ~+0.034‰, arguing that the former is isotopically lighter due to mantle depletion during the generation of continental crust in the Archean.

We model the batch melting of primitive mantle from 1 to 6 GPa to test the effect of mantle mineralogy and the genesis of mid ocean ridge basalts. We consider two scenarios for the melting of Ti-bearing mantle silicates i) the coordination of all Ti in clinopyroxene and garnet is VI-fold coordination (O’Neill and Navrotsky, 1983; Waychunas, 1987) and ii) all Ti is in IV-fold coordination (Wang et al., 2020).

Modelling of mantle melting was undertaken using both pMELTS (Ghiorso et al., 2002) for melting of primitive mantle (Palme and O’Neill, 2014) of which δ\(^{49/47}\)Ti = 0 at 1 GPa, and using experimental data from Walter (1998) for garnet-peridotite melting at 4 and 6 GPa. The 1 GPa pMELTS models were run in 5°C increments.
from the liquidus to solidus at $fO_2 = FMQ-1$. Ti isotope compositions of melt and residue at each increment were calculated from isotopic mass balance. Given that spinel and titanomagnetite share a common crystal structure with VI coordinated Ti (O’Neill and Navrotsky, 1983; Waychunas, 1987), the Ti isotope fractionation factor for spinel-melt is calculated using Eqn. 4 at every temperature step and using the Ti contents of spinel. The results of melting a primitive mantle composition at 1-6 GPa over the batch melting interval of 0-25% are shown in Fig.12 and are plotted relative to the BSE value of +0.005‰ from Millet et al. (2016). The same models using silicate-melt Ti isotope fractionation factors anchored to rutile-melt, as opposed to ilmenite-melt, are provided in the supplements (see Table S7 and Fig.S5).

Figure 12 demonstrates that the coordination state of Ti in typical mantle mineralogies has a significant influence on the resulting Ti isotope composition of partial melts of the mantle. If Ti is in VI-fold coordination in silicates, melting of the primitive mantle produces no significant variation in $\delta^{49/47}$Ti that is resolvable at the current limits of analytical uncertainty ($\pm$0.02-0.03 ‰), with both melt and residue being close to the BSE value (Fig.12a). However, when Ti in mantle silicates is in IV-fold coordination, partial melting produces melts that are significantly isotopically lighter and residua that are isotopically heavier relative to the BSE (Fig.12b). Previous studies (Greber et al., 2017b; Williams et al., 2021) have shown the $\delta^{49/47}$Ti compositions of chondrites are within error of primitive basalts and mantle samples (Millet et al., 2016), this observation can only be reproduced in a partial melting model in which Ti is hosted in VI-fold coordination in mantle clinopyroxenes and garnets. Furthermore, this model reproduces overlap between ultramafic to mafic rocks formed through different degrees of mantle melting, such as komatiites (Millet et al., 2016; Greber et al., 2017b; Hoare et al., 2020; Zhao et al., 2020). However, Figure 12a hints towards the possibility that extreme degrees of mantle melting (>25%) of spinel-lherzolite may have the potential to generate subtle Ti isotope fractionation in the residua.

It is notable however, that Deng et al. (2018) observed an offset between chondrites and komatiites, which was best explained by Ti isotope fractionation during extraction of the continental crust. However, this cannot be reconciled by partial melting of the mantle with Ti in IV-fold coordination as this generates residua that are significantly heavy relative to melts (up to a +0.2‰ offset; Fig.12b), causing a trend exactly opposite to that observed by Deng et al. (2018). Our fractionation factors hence clearly indicate that Ti is hosted in VI-fold coordination in mantle silicates, and this results in limited, within current analytical uncertainty, isotope fractionation during partial melting and the genesis of mid ocean ridge basalts.

6. Conclusions

In this study we present $\delta^{49/47}$Ti compositions of micro-milled Fe-Ti oxides and groundmass to derive Fe-Ti oxide-melt Ti fractionation factors. A well-constrained set of Ti isotope fractionation factors are necessary to provide further quantitative constraints on the mechanics of Ti isotope fractionation in magmatic processes and at the mineral scale.

The main conclusions of this study are as follows:

- The main conclusions of this study are as follows:
Titanomagnetite displays the largest mineral/melt $^{49}\text{Ti}/^{47}\text{Ti}$ fractionation factors, followed by ilmenite, and then rutile. This is consistent with stable isotope theory which dictates lighter isotopes prefer longer bonds, with Ti-O bond length decreasing from magnetite to ilmenite and rutile.

The titanomagnetite-melt fractionation factor shows variation greater than what can be explained by changes in bond length alone. $10^3\ln\alpha_{\text{titanomagnetite}-\text{melt}}$ increases as a function of titanomagnetite TiO$_2$ content or increasing ulvöspinel component, with titanomagnetite from Heard Island (21-23 wt.% TiO$_2$) consistently displaying larger fractionation factors compared Santorini (14-15 wt.% TiO$_2$).

We provide quantitative expressions for Fe-Ti oxide-melt fractionation factors as a function of temperature and, in the case of titanomagnetite, composition (TiO$_2$, ulvöspinel content)

We can successfully apply these fractionation factors to successfully model mantle melting and reproduce the $\delta^{49/47}\text{Ti}$ evolution of a series of magmatic differentiation suites.

Acknowledgements

The authors gratefully acknowledge Capucine Albert, Max Jansen, Laura Rzehak, and Raúl Fonseca for fruitful discussions. Max Jansen is thanked for assistance with the micro-milling technique, Felipe Leitzke for sharing ab initio data used for VI-fold clinopyroxene fractionation factors, Tony Oldroyd for assistance preparing the samples, and Lindsey Owen for support in the laboratory. The authors would also like to acknowledge detailed and constructive reviews by Sarah Aarons and Paolo Sossi which greatly improved the manuscript. Furthermore, we would like to thank Helen Williams for expert editorial handling. LH acknowledges support from a NERC GW4+ Doctoral Training Partnership studentship (NE/L002434/1). MAM acknowledges support from a NERC standard grant (NE/R001332/1) and a Royal Society Research Grant.

References


Bacon C. R. and Hirschmann M. M. (1988) Mg/Mn partitioning as a test for equilibrium


**Figure Captions**

**Figure 1.** TiO$_2$-FeO-Fe$_2$O$_3$ and TiO$_2$-MgO-FeO ternary diagrams showing the compositional diversity of different Fe-Ti oxide species. The lines denote high temperature solid solutions (ulvöspinel-magnetite, hematite-ilmenite, pseudobrookite-ferropseudobrookite, geikielite-ilmenite, and karooite-armalcolite). The boldened mineral species and highlighted solid solutions are the focus of this study.

**Figure 2.** False colour element maps of Fe-Ti oxides from Santorini and Heard Island samples. Mineral abbreviations shown in the figure are in accordance with those defined by Whitney and Evans (2010). a) Titanomagnetite phenocryst (LH 010) in rhyodacite AAS-028 from Santorini. b) Titanomagnetite phenocryst (LH 005) in rhyodacite AAS-027 from Santorini. Note the presence of minor apatite inclusions (bright blue). The groundmass includes small crystals of orthopyroxene (green) and small laths of plagioclase (purple). c) Titanomagnetite (LH 012) in basanite HB24 (Heard Island). The groundmass includes olivine (green), zoned titan-augite (pale blue to blue-green), small laths of plagioclase (purple) and small crystals of titanomagnetite (red/orange) and ilmenite (yellow/light orange). d) Titanomagnetite (LH 016) phenocryst in basaltic trachyandesite 65054 (Heard Island). e) Ilmenite phenocryst in HB24 (LH 019). f) Ilmenite (LH 012) phenocryst in 65054. Note that all the Fe-Ti oxides are compositionally un-zoned.

**Figure 3.** False colour element maps of rutile-melt experimental run products; a) MHD15_1, and b) HD4_4. Rutile (red), either appear as acicular needles or tabular euhedral crystals, surrounded by silicate glass (blue). The platinum wire is also shown (yellow).

**Figure 4.** Oxygen fugacity relative to NNO (nickel-nickel oxide) versus temperature values derived from Fe-Ti oxide pairs calculated using the method of Ghiorso and Evans (2008). Open symbols represent non-touching oxide pairs, filled symbols represent touching oxide pairs. The error bars represent the 2se of the mean values (black symbols).

**Figure 5.** a) $\delta^{49/47}$Ti versus CaO/TiO$_2$ for micro-milled Fe-Ti oxides (titanomagnetite and ilmenite) and groundmass from Heard Island and Santorini samples. b) $\delta^{49/47}$Ti versus CaO/TiO$_2$ for micro-milled rutile and silicate glass mixtures from rutile-melt experimental run products (MHD15_1 and HD4_4). Vertical coloured lines indicate the CaO/TiO$_2$ value of pure glass from Klemme et al. (2005). Dashed lines represent two component mixing lines from a york regression used to calculate the $\delta^{49/47}$Ti of pure rutile and glass. The shaded area represents the 2s of the regression.
Figure 6. a) Raw $\Delta^{49/47}$Ti values for rutile-melt, titanomagnetite-melt and ilmenite-melt as reported in this study. Fractionation factors derived from mineral separates from the Kneeling Nun Tuff (KNT; Mandl, 2019) are shown for comparison. Error bars report 2s errors.

Figure 7. Regression of Fe-Ti oxide-melt Ti isotope fractionation factors (expressed as $10^3\ln\alpha_{\text{oxide-melt}}$). a) $10^3\ln\alpha_{\text{ilmenite-melt}}$ as function of temperature (expressed as $10^6/T^2$ in units of Kelvin and degrees Celsius). b) $10^3\ln\alpha_{\text{rutile-melt}}$ as function of temperature. The shaded areas represent the 2s uncertainty accounting for the propagation of uncertainty on the linear regression for $10^3\ln\alpha_{\text{rutile-melt}}$. c) $10^3\ln\alpha_{\text{titanomagnetite-melt}}$ values for Santorini, Heard Island and KNT (Mandl, 2019) plotted at their respective temperature values and results of regressions of $10^3\ln\alpha_{\text{titanomagnetite-melt}}$ calculated for a representative TiO$_2$ content of the Santorini and Heard titanomagnetites using Eqn. 4 (14 and 22 wt.% respectively; shown as dashed black lines). d) All $10^3\ln\alpha_{\text{oxide-melt}}$ values normalised to 1000 K as a function of NBO/T. The 2s uncertainty of the regressions is indicated by the shaded areas. Where available the relevant ab-initio fractionation factors from both Wang et al. (2020; dashed blue lines) and Aarons et al. (2021; dashed red or green lines) are shown for comparison. The $10^3\ln\beta$ value of fresnoite calculated by Aarons et al. (2021) was used as a proxy for silicate melt in the case of the ab-initio mineral-melt fractionation factors. The data from Kneeling Nun Tuff (KNT; Mandl, 2019) is plotted for comparison to the data presented in this study but is excluded from the regression calculations in 7a.

Figure 8. $10^3\ln\alpha$ for titanomagnetite-melt normalised to 1000 K as a function of: a) TiO$_2$ contents; b) the proportion of the ulvöspinel endmember (Stormer, 1983); and c) whole rock SiO$_2$ contents as a function of the proportion of the ulvöspinel endmember for each mineral analyses with samples coloured with respect to the magnitude of their $10^3\ln\alpha$ value. The slope-intecept covariance term, $\sigma_{xy}$, is also provided. The data from Kneeling Nun Tuff (KNT; Mandl, 2019) is plotted for comparison to the data presented in this study but is excluded from the regression calculations in 8a and b.

Figure 9. $10^3\ln\alpha$ for rutile-, titanomagnetite- and ilmenite-melt at 1000 K versus average Ti-O bond length (in nanometres). $10^3\ln\alpha$ values were calculated from the regression of $10^3\ln\alpha_{\text{oxide-melt}}$ shown in Fig.7 a and b (Eqn. 2 and 3), and Fig.8b (Eqn. 4 for TiO$_2$ = 14 and 22 wt.%). X-axis error bars on Ti-O represent the range of bond lengths reported in the literature. Average Ti-O bond lengths for titanomagnetite were taken from Bosi et al. (2009) from analyses with representative TiO$_2$ contents comparable to those reported in this study.

Figure 10. $10^3\ln\alpha$ values between a mineral phase (i) and melt at 1000 K. Mineral-mineral fractionation factors are from first principles as reported in Leitzke et al. (2018) and Wang et al. (2020). The $10^3\alpha$ values for silicate-melt used are anchored to $\alpha$ ilmenite-melt (Eqn. 2). 2s error bars on Ti isotope fractionation factors calculated from the Leitzke et al. (2018) and Wang et al. (2020) data represent the propagated uncertainty on the $10^3\ln\alpha_{\text{ilmenite-melt}}$ regression as a function of temperature (expressed as $10^6/T^2$ in units of Kelvin; Eqn. 2). Mineral separate data from Mandl (2019) and Rzehak et al. (2021), alongside ab initio oxide-fresnoite (Aarons et al. 2021; melt proxy) fractionation factors are included for comparison.

Figure 11. $\delta^{49/47}$Ti compositions of magmatic differentiation suites (solid symbols) from Hoare et al. (2020) plotted against MgO contents. IgPet (Carr and Gazel, 2017) was used to model the fractional crystallisation of these differentiation suites via least-squares mass balance modelling (e.g. Bryan et al., 1969) using mineral compositions taken from the literature (see supplementary material S9). The $\delta^{49/47}$Ti evolution was modelled using a Rayleigh
fractionation law and a bulk $\alpha_{\text{solid-melt}}$ weighted on the proportion of Ti in each crystallising phase. Modelling was performed into two steps (S1 and S2; demarcated by the vertical grey dashed lines) from the most primitive lava to a representative intermediate composition, then from the intermediate to most evolved composition. The results of the model are shown by the solid-coloured lines. The shaded error represents the 2s uncertainty on bulk $\alpha_{\text{solid-melt}}$ with propagated uncertainty from the temperature variation at each stage of the model and the various $10^3\ln \alpha$ regressions used to calculate the Ti isotope fractionation factors. The titanomagnetite fractionation factor was calculated using Eqn. 4, whereas ilmenite-melt was calculated using Eqn. 2. The $10^3\alpha$ values for pyroxene-melt used are anchored to $\alpha$ ilmenite-melt (Eqn. 2) and taken from Leitzke et al. (2018; Ti in VI-fold coordination) and Wang et al. (2020; Ti in IV-fold coordination). The pie charts display the proportion on Ti in each phase in each step of the model (S1 and S2) along with the value of bulk $10^3\alpha_{\text{solid-melt}}$ represented by the solid-coloured lines.

Figure 12. $\Delta^{40/47}$Ti values mantle melting models relative to the BSE for melt (solid lines) and residue (dashed lines) as a function of degree of melting and pressure for; a) pMELTS modelling of a primitive mantle source (PM; Palme and O’Neill, 2014) at 1 GPa and melting of a garnet peridotite (KR4003) at 4 and 6 GPa (Walter, 1998) when Ti in silicates is in VI-fold coordination; b) Same models as panel a) but for a scenario where Ti in silicates is in IV-fold coordination. The orange field represents the mean $\Delta^{40/47}$Ti value of N-MORB relative to the BSE (-0.004 ± 0.039‰ (2sd); Millet et al., 2016, Deng et al., 2018; Hoare et al., 2020; Zhao et al., 2020). Shaded areas represent the 2s error on the models. All $\alpha$ values used are anchored to $\alpha$ ilmenite-melt (Eqn. 2). The spinel-melt fractionation factor was calculated using Eqn. 4. The $10^3\alpha$ values for pyroxene-melt used are anchored to $\alpha$ ilmenite-melt (Eqn. 2) and taken from Leitzke et al. (2018; Ti in VI-fold coordination) and Wang et al. (2020; Ti in IV-fold coordination).
Figure 3

A

MHD15_1

1mm

B

HD4_4

Pt wire

Silicate glass

Rutile

Ti

Si

Pt

500μm
Figure 4

Heard Island Oxide Pairs
NTP=Non-touching Pair, TP=Touching Pair

- HB24-NTP
- 65054-NTP
- 65019-NTP
- HB24-TP
- 65054-TP
- 65019-TP
- HB24-Mean
- 65054-Mean
- 65019-Mean
Figure 5

A

CaO/TiO$_2$ of MHD15_1 Glass
CaO/TiO$_2$ of HD4_4 Glass
MDH15_1
HD4_4

HD4_4 $\Delta^{49/47}$Ti$_{rutile}$ – melt 1250°C
= $-0.22 \pm 0.09\%$

MDH15_1 $\Delta^{49/47}$Ti$_{rutile}$ – melt 1250°C
= $-0.16 \pm 0.05\%$
\[ 10^3 \ln a_{\text{ilmenite-melt}} = a \times 10^6 / T^2 \]

\[ a = -0.5996 \pm 0.0349 \]

\[ 10^3 \ln a_{\text{rutile-melt}} = a \times 10^6 / T^2 \]

\[ a = -0.4039 \pm 0.0985 \]
The text contains equations and data related to the calculation of the order parameter $\alpha$ for titanomagnetite melt, expressed as:

\[ 10^3 \ln \alpha_{\text{titanomagnetite - melt}} = [a \cdot \text{TiO}_2 + b] \cdot 10^6 / T^2 \]

For $\text{TiO}_2$ (wt.%) in Ti-magnetite:
- $a = -0.0482 \pm 0.0069$
- $b = -0.0530 \pm 0.1203$
- $\sigma_{xy} = -0.0002$

For $X_{\text{Ulvospinel}}$:
- $a = -1.4906 \pm 0.2187$
- $b = -0.0607 \pm 0.1221$
- $\sigma_{xy} = -0.0065$

The diagrams illustrate the relationship between the order parameter and $\text{TiO}_2$ percentage, as well as $X_{\text{Ulvospinel}}$, with data points representing different samples.
Figure 9

Average Ti-O Bond Length (nm)

$10^3 \ln \alpha_{\text{oxide} - \text{melt}} 1000 K$

-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4

0.192 0.194 0.196 0.198 0.200 0.202 0.204 0.206 0.208

Average Ti-O Bond Length (nm)
1.5
1.0
0.5
0.0
0.5
1.0
10
3
ln
i melt
1000 K

Ti in [VI]
Ti in [IV]

Silicates
Fe-Ti oxides
Rutile/Anatase

Cpx - Ti [IV] (Wang et al., 2020)
Opx [IV] (Wang et al., 2020)
Ol (Wang et al., 2020)
Grt - Ti [IV] (Wang et al., 2020)
Grt - Ti [VI] (Wang et al., 2020)
Cpx - Ti [VI] (Leitzke et al., 2018)
Opx (Air-FMQ-2; Rzehak et al., 2021)
Ilmenite (Mandl, 2019)
Ti-magnetite (Mandl, 2019)
Geikielite (Aarons et al., 2021)
Ilmenite (Wang et al., 2020)
Anatase (Aarons et al., 2021)
Rutile (Wang et al., 2020)
Rutile (This study)
Ilmenite (This study)
Ti-mag (Ti-14)
Ti-mag (Ti-22)

Orthopyroxene
Garnet
Clinopyroxene
Olivine

Ti-Mag TiO₂ = 14 wt.%
Ti-Mag TiO₂ = 22 wt.%

Figure 10
Click here to access/download;Figure;Fig10_Alphas_CaltechPlt_Ilm.pdf
Figure 12

A - Ti in VI coordination (in silicates)

B - Ti IV coordination (in silicates)
Click here to access/download
Supplementary Material
Hoare_et_al_GCA_supp_mat.xlsx
Click here to access/download

Supplementary Material

Hoare_et_al_GCA_Supplementary_Figs.pdf
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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: