Clues from \textit{Ab Initio} Calculations on Titanium Isotopic Fractionation in Tholeiitic and Calc-Alkaline Magma Series

Sarah M. Aarons,* Nicolas Dauphas, Marc Blanchard, Hao Zeng, Nicole Xike Nie, Aleisha C. Johnson, Nicolas D. Greber, and Timo Hopp

\section*{ABSTRACT:} Magmatic differentiation produces positive correlations between \( \delta^{49}\text{Ti} \) and \( \text{SiO}_2 \). The equilibrium \( \text{Ti} \) isotope fractionation factors of \( \text{Ti} \)-bearing minerals are essential for understanding the mechanisms driving this isotopic fractionation. We present \textit{ab initio}-derived mean force constants of \( \text{Ti} \)-bearing minerals (barium orthotitanate, potassium titanium oxide, fresnoite, diopside, geikielite, karrooite, titanite, pseudobrookite, anatase, and titanium oxide) based on density functional theory (DFT) to calculate equilibrium isotopic fractionation factors. We find that the main driver for \( \text{Ti} \) isotopic fractionation is its coordination, with four-, five-, and sixfold-coordinated \( \text{Ti} \) characterized by mean force constants of 547, 462, and 310 N/m, respectively. The coordination number of \( \text{Ti} \) in silicate melts is thought to be lower than in minerals, driving magmas toward higher \( \delta^{49}\text{Ti} \) values by fractional crystallization. The mineral-melt fractionation factors allow modeling of the observed \( \text{Ti} \) isotope trends in tholeiitic and calc-alkaline rocks. Our model results indicate that to first order, the steeper \( \delta^{49}\text{Ti} \) trend observed in tholeiitic \textit{versus} calc-alkaline magmas is most likely due to enhanced removal of \( \text{Ti} \) into sequestered minerals at low \( \text{SiO}_2 \) concentration in tholeiitic series compared to calc-alkaline series. The \( \delta^{49}\text{Ti} \)–\( \text{SiO}_2 \) differentiation trends, however, depend on \( \text{Ti} \) coordination in the melt and the strengths of \( \text{Ti} \) bonds in diverse \( \text{Fe} \)–\( \text{Ti} \)-oxides, which are still uncertain. Our results show that \( \text{Ti} \) isotopes can be used to reconstruct the crystallization history and identify the magmatic series parentage of magmas that otherwise lack context, but further work is needed to identify the drivers behind \( \text{Ti} \) isotopic fractionation in igneous rocks.

\section*{KEYWORDS:} titanium, isotopes, fractional crystallization, isotopic fractionation, \textit{ab initio}

\section*{1. INTRODUCTION}

Arc magmatism and calc-alkaline magma differentiation are fundamental processes in the establishment of felsic continental crust.\textsuperscript{1–5} \( \text{Ti} \) isotopes provide unique insights into magmatic differentiation processes, as the \( \delta^{49}\text{Ti} \) composition of magmatic rocks increases with increasing silica content, reflecting the history of partial melting and \( \text{Fe} \)–\( \text{Ti} \) oxide crystallization.\textsuperscript{6–12} The \( \text{Ti} \) isotopic composition of fine-grained tergigenous sediments (shales) has been used to conclude that, as far back as 3.5 Ga, the composition of the crust exposed to weathering comprised a large fraction of felsic rocks, implying that subduction processes were likely operating before that time.\textsuperscript{9} Subsequent work demonstrated that \( \text{Ti} \) isotopes fractionated distinctly in plume and island arc settings,\textsuperscript{7,11,12} suggesting that \( \text{Ti} \) isotopes may provide insights into the geodynamic setting responsible for the formation of the continental crust.\textsuperscript{13}

In general, igneous rocks display a monotonically increasing trend in \( \delta^{49}\text{Ti} \) during magmatic differentiation, which is attributed to the fractionation of \( \text{Ti} \) isotopes following the saturation and crystallization of \( \text{Ti} \)-bearing oxides.\textsuperscript{6,7,10–12} However, different rock series show contrasting behaviors in \( \text{Ti} \) isotope fractionation during tholeiitic and calc-alkaline magmatic differentiation, and the process responsible for these trends is still not well understood. Modern calc-alkaline magmas occur in subduction zone environments and are characterized by enrichment in water content, higher oxygen fugacity, and \( \text{Fe} \) depletion.\textsuperscript{14–19} Tholeiitic magmas can occur in both subduction and intraplate environments and are characterized by strong \( \text{Fe} \) and \( \text{Ti} \) enrichments and lower water content and oxygen fugacity.\textsuperscript{14,15}

Several studies have focused on stable \( \text{Fe} \) isotopes in a variety of magmatic systems\textsuperscript{20–24}, and only one thus far has reported both stable \( \text{Fe} \) and \( \text{Ti} \) isotopic compositions.\textsuperscript{13} Iron isotopic variations in magmatic rocks reflect the combined effects of mineral-melt equilibrium involving silicates and oxides (modulated by \( \text{Fe} \) redox state and coordination) and kinetic effects associated with \( \text{Fe} \)–\( \text{Mg} \) interdiffusion in olivine. Due to these multiple controls, interpretation of \( \text{Fe} \) isotopic variations of bulk differentiated igneous rocks is often far from straightforward, unless individual mineral analyses are performed and a full differentiation series is studied.
The increase in \( \delta^{49}\text{Ti} \) values with increasing SiO\(_2\) in all magmatic series\(^{7,10-12}\) was hypothesized\(^{12}\) to be the result of the preferential incorporation of light Ti isotopes into sixfold coordinated Fe–Ti oxides during fractional crystallization, whereas the silicate melt hosts Ti in lower coordination averaging ∼4.5 to 5.4.\(^{7,5,26}\) Lower coordinated bonding environments are indeed associated with stronger and stiffer bonds, which promote heavy isotope enrichments at equilibrium.\(^{27}\)

During crystallization, heavy Ti isotopes preferentially remain in the low-coordination melt, while light Ti isotopes are incorporated into crystallizing sixfold-coordinated Ti-bearing mineral phases.\(^{6}\) The hypothesis that Fe–Ti oxide crystallization drives Ti isotopic fractionation during magmatic differentiation was confirmed by Johnson et al.\(^{11}\) who separated Fe–Ti oxides from Kīlauea Iki Lava Lake (primarily ilmenite and Ti-magnetite) using heavy liquid separation and then measured the Ti isotopic compositions of the oxide and glass. They found that Fe–Ti oxide separates were isotopically lighter than their glass counterparts.\(^{11}\) Several studies have since shown that a single melt-crystal equilibrium fractionation factor cannot account for the isotopic variations that have been documented in magmatic series, even when the temperature decrease in more evolved magmas is accounted for refs 7, 11, and 12. Three possible explanations for the non-constant oxide-melt isotopic fractionation factors can be calculated as a function of Ti coordination in silicate melt. These fractionation factors can be used to predict how Ti isotopes can be fractionated between co-existing phases at equilibrium. In the present contribution, we use an \textit{ab initio} DFT approach to calculate a new set of Ti equilibrium fractionation factors aimed at understanding the drivers behind Ti isotopic fractionation in igneous rocks. Wang et al.\(^{30}\) and Leitzke et al.\(^{31}\) previously calculated the equilibrium Ti isotopic fractionation factors of Ti\(^{4+}\)-bearing clinoxyroxene, orthopyroxene, olivine, pyrope, rutile, karsroite, as well as Ti\(^{3+}\)-bearing clinoxyroxene. We extend this work here to include Ti\(^{4+}\)-bearing BaTiO\(_4\), K\(_2\)Ti\(_2\)O\(_5\), Ti-diopside, geikielite, karsroite, titanite, pseudobrookite, fresnoite, anatase, and Ti\(^{3+}\)-bearing Ti oxide. Some of the minerals (fresnoites, barium orthotitanate, and the average of sixfold coordinated minerals) are used as proxies for Ti coordination in silicate melt. These fractionation factors are then used to evaluate how Ti isotopes can be fractionated differently in the two main magma series: calc-alkaline and tholeitic.

1.1. Petrologic Controls on Ti during Magmatic Differentiation. Tholeiitic series are found in plume, mid-ocean ridges, and arc settings, while calc-alkaline series are encountered almost exclusively in convergent arc-settings.\(^{15,32}\) Calc-alkaline magmas are noted for their higher water contents, higher oxygen fugacities \( (f_{\text{O}_2}) \), and lower Ti contents; which are byproducts of subduction.\(^{15,19,33}\) Calc-alkaline magmas typically also have higher initial SiO\(_2\) contents due to their production through water-induced flux melting of the mantle.\(^{34}\) The criteria for distinguishing between these series are mainly based on the behavior of Fe during differentiation. The divergence in Fe behavior is due to the sequence and rate of mineral crystallization,\(^{7}\) which also influences the behavior of Ti. However, unlike Fe whose behavior is influenced by the oxygen fugacity and crystallization of both mafic silicate and oxide minerals, Ti is predominantly affected by Fe–Ti oxides such as Ti-magnetite and ilmenite.

In tholeiitic series, the crystallization sequence is olivine, plagioclase feldspar, and clinoxyroxene (augite), with plagioclase crystallization dominating the mineral assemblage of crystallizing phases. Early on in the differentiation of tholeiitic series, the removal of high MgO/low FeO mafic minerals like olivine and pyroxene increases the total FeO content. At the same time, the removal of these SiO\(_2\)-poor mafic minerals is partially compensated by the removal of SiO\(_2\)-rich plagioclase, so that the SiO\(_2\) content of the melt remains more or less constant.\(^{14,35}\) The FeO content reaches a peak, and SiO\(_2\) remains approximately constant, prior to saturation and crystallization of spinels and Fe–Ti oxides. The FeO content then rapidly decreases, while the SiO\(_2\) content increases because the crystallizing phases are relatively FeO-rich and SiO\(_2\)-poor. At this point, the crystallization of plagioclase decreases and is less important in driving the chemical evolution of the magma. In contrast, the presence of water and higher \( f_{\text{O}_2} \) in the calc-alkaline series suppresses plagioclase crystallization and results in an early onset of spinel and oxide crystallization, which drives the SiO\(_2\) content to increase rapidly during the early stages of differentiation, while the total FeO content does not increase as dramatically as is observed in the tholeiitic series.\(^{14,15,17}\)

The difference in Fe behavior during differentiation controls the timing of spinel and Fe–Ti oxide saturation and crystallization, as well as the pace at which Ti is removed relative to the evolution of the melt with respect to SiO\(_2\). This behavior has important implications for the Ti isotopic composition and evolution of tholeiitic and calc-alkaline magmas, as the trajectory and evolution of Ti isotopic compositions during differentiation should be primarily driven by Ti isotopic fractionation between melt and Ti-bearing minerals, notably Fe–Ti oxides. Titanium isotopes therefore have the potential to inform us on the history of oxide crystallization and may be related to water content, \( f_{\text{O}_2} \), pressure, and initial geochemical composition of magmas during magmatic differentiation.

2. METHOD

2.1. Equilibrium Isotopic Fractionation Factors. To address the question of how and why Ti isotopes fractionate differently during differentiation of tholeiitic and calc-alkaline magmas, we calculated through an \textit{ab initio} density functional theory (DFT) approach the mean force constant \( (F \text{ in N/m}) \) of Ti bonds in various minerals from which equilibrium isotopic fractionation factors can be calculated as a function of temperature. We specifically focused on minerals relevant to magmatic systems and some exotic minerals in which Ti is present in a range of coordination environments. Wang et al.\(^{30}\) and Leitzke et al.\(^{31}\) also reported isotopic fractionation factors in a variety of Ti-bearing phases using DFT, and their results are compared with ours below.

The Ti isotopic composition is hereafter reported in \( \delta^{49}\text{Ti} \) notation, which is the permil deviation from the \( 49\text{Ti}/47\text{Ti} \) ratio of the Origins Laboratory Ti reference material (OL-Ti), which has a near-chondritic composition\(^{10}\)

\[
\delta^{49}\text{Ti}(\%e) = \left[ \frac{(49\text{Ti})_{\text{sample}}}{(47\text{Ti})_{\text{sample}}} \right]^{1/2} - 1 \times 1000
\]

(1)

Minerals modeled in this work include Ti\(^{4+}\)-bearing barium orthotitanate(IV coordination), potassium titanate(V),
fresnoite(V), anatase(VI), diopside(VI), geikielite(VI), karrooite(VI), titanite(VI), pseudobrookite(VI), and Ti$^{3+}$-bearing titanium oxide(VI). Additionally, Ti-magnetite(VI), ulvöspinel(VI), and ilmenite(VI) were also calculated but the structures were dynamically unstable, and the results cannot be trusted, so we do not report those results in the present contribution. We nevertheless describe briefly the unsuccessful attempts that we have made at solving this issue of dynamical instability to avoid replication of these attempts by future studies. Mineral structures were sourced from experimental data (described below in subsection Mineral Structures for DFT Calculation), reduced to primitive cells if possible, and their lattice parameters and atomic positions were relaxed until the residual forces on atoms and pressure were smaller than $10^{-4}$ Ry/au and 0.1 kbar.

A phonon calculation was then performed for each structure and partial phonon density of states (PDOS) for Ti (and all other elements) were calculated and averaged if more than one Ti atom was present in the unit cell (see Supporting Information, file S1). The average force constants for the Ti-bearing mineral phases were calculated using the formula$^{36}$

$$\langle F \rangle = \frac{M}{\hbar^2} \int_0^\infty g(E)E^2 \, dE$$  \hspace{1cm} (2)$$

where $F$ is the force constant of the Ti bonds in the mineral of interest in N/m, $M$ is isotope mass, $\hbar$ is the reduced Planck constant, $g(E)$ is the PDOS, and $E$ is the vibration energy. The
Table 1. Calculated (cal.) and Experimental (exp.) Crystal Lattice Parameters of Minerals Studied Here

<table>
<thead>
<tr>
<th>Mineral Phases (K2Ti2O5)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
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<td>98.93</td>
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<tr>
<td>Exp. 8.518</td>
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<td>5.366</td>
<td>90</td>
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<td>titanium oxide Ti2+3O3</td>
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</table>

2.2. Mineral Structures for DFT Calculations.

2.2.1. Ti4+ in Fourfold Coordination. In barium orthotitanate (Ba2Ti4O7), Ti4+ is tetrahedrally (fourfold) coordinated. The monoclinic cell used contains four times the structural formula (Z = 4, space group P21/n).41

2.2.2. Ti4+ in Fivefold Coordination. In potassium titanate (K2Ti5O8), Ti4+ is fivefold coordinated in a monoclinic cell with the coordination environment being a trigonal bipyramid (Z = 1, space group C12/m1).42

Titanium K-edge X-ray adsorption near edge structure spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) measurements showed that fivefold-coordinated Ti in silicate melt most closely resembles fresnoite, Ba2TiO(Si2O7), a mineral in which Ti is coordinated in a square base pyramid with a Ti–O bond at the apex (Z = 2, space group P4bmm).43

2.2.3. Ti3+ in Sixfold Coordination. The majority of minerals, including geikielite, karrooite, pseudobrookite, titanite, anatase, and atase and diopside have Ti in sixfold coordination. The motivation for modeling geikielite (MgTiO3) is the fact that DFT calculations of ilmenite (FeTiO3) yielded dynamically unstable structures as indicated by the presence of imaginary frequencies. For geikielite (MgTiO3, space group R3),51 we used the primitive rhombohedral cell (Z = 2). Karrooite (MgTiO3),45 and pseudobrookite (Fe3+3Ti4+O3) are both orthorhombic, space group Cmcm.46 Pseudobrookite displays an antiferromagnetic ordering. Titanite has a monoclinic cell, where Ti3+ occupies the octahedral sites (CaTiSiO5, space group R3)52), and the Boltzmann constant, and the Planck constant for the ratio 49Ti/47Ti, this equation becomes

\[ 100 \ln \beta_{49Ti/47Ti} \approx 3815 \frac{F}{T^2} \] (4)

Below, we apply the fractionation factors calculated by ab initio to MELTS models of magmatic differentiation of tholeiitic and calc-alkaline magmas to understand the driving factors responsible for the contrasting behavior of Ti isotopes between the two series. We are well aware that magma mixing and assimilation play significant roles in the petrogenesis of differentiated igneous rocks, notably calc-alkaline series53-58 but fractional crystallization remains the main driver59,60 and we will therefore focus on this end-member scenario.

2.2. Mineral Structures for DFT Calculations. We studied titanate, oxide, and silicate minerals where Ti3+ or Ti4+ is four-, five-, and sixfold coordinated with oxygen atoms (Figure 1). Several uncommon minerals were investigated as they host Ti in silicate melts.35

[1] Titanate, oxide, and silicate minerals where Ti3+ or Ti4+ is four-, therefore focus on this end-member scenario.

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2.2.4. Ti3+ in Sixfold Coordination. The last compound considered is titanium oxide (Ti2O3), where Ti3+ displays a sixfold coordination. We chose this last compound to investigate the role of high CN and low oxidation state on the force constant. This compound was modeled using the primitive rhombohedral cell (space group R3c, Z = 2).49

2.3. Ab initio Calculations. All ab initio computations were performed with Quantum ESPRESSO61 with plane-wave basis sets, Perdew, Burke and Ernzerhof (PBE) generalized gradient approximation (GGA) functionals,52 and norm-conserving pseudopotentials from ONCV library.59 The kinetic energy and charge-density cutoff were set at 85 and 340 Ry, respectively, for all systems. Monkhorst k-point and q-point grids34 were chosen to be 4 × 4 × 2, 2 × 2 × 2 for barium orthotitanate, 4 × 4 × 4, 3 × 3 × 3 for potassium titanate, 4 × 4 × 4, 2 × 2 × 2 for diopside, 3 × 3 × 3, 3 × 3 × 3 for geikielite, 4 × 4 × 2, 2 × 2 × 2 for karrooite, 3 × 3 × 3, 2 × 2 × 2 for titanite, 4 × 4 × 2, 2 × 2 × 2 for
for pseudobrookite, $4 \times 4 \times 4$, $3 \times 3 \times 3$ for titanium oxide, $2 \times 2 \times 2$, $2 \times 2 \times 3$ for fresnoite, $8 \times 8 \times 8$, and $2 \times 2 \times 2$ for anatase. Calculated (cal.) and experimental (exp.) crystal lattice parameters of each mineral are shown in Table 1.

2.4. Melt Coordination. The main driver behind the fractionation of Ti isotopes during magmatic differentiation is expected to be the difference in coordination between the Ti-bearing minerals and the silicate melt. The coordination environment of Ti in silicate melts is, however, not well constrained. Titanium XANES and EXAFS have been used to characterize the coordination of Ti in synthetic and natural materials, but for the most part, the glass and melt compositions studied are quite far from those that we are interested in for application to Ti high-temperature isotopic geochemistry.

Farges and Brown measured a series of glass samples that were either natural or synthetic with natural compositions. These samples were measured both below the glass transition and above the liquids. In all glasses, $[^{5}\text{Ti}]$ dominated but the more mafic samples contained 30–50% of $[^{6}\text{Ti}]$, while the more felsic samples contained 30–60% of $^{[4]\text{Ti}}$. Among the igneous rocks measured by Farges and Brown, the average coordination ranged from 5.4 in basalt to 4.5 in rhyolite. No drastic or systematic change in Ti coordination was seen when the glasses were melted. The volatile content (F, Cl, and H$_2$O) also seemed to affect the Ti coordination between the Ti isotope fractionation modeled here. To address the possibility that the coordination of Ti in a silicate melt changes under different SiO$_2$ concentrations as noted in Farges and Brown, we model the evolution of a tholeiitic and calc-alkaline melt under three different scenarios:

1. Ti in the melt is 100% fivefold coordinated.
2. Ti is 40% sixfold and 60% fivefold in mafic magmas (<52 wt % SiO$_2$), 100% fivefold in intermediate magmas (52–63 wt % SiO$_2$), and 45% fourfold and 55% fivefold in felsic (>63 wt % SiO$_2$) magmas.
3. We assume that Ti coordination (and force constant) is primarily driven by melt polymerization and parameterize it as a linear function of NBO/T.

Figure 2. (a) Non-bridging oxygen per silicon tetrahedron (NBO/T) of tholeiitic (red line) and calc-alkaline (blue line) magmas with respect to silica content from rhyolite-MELTS simulations. (b) NBO/T with respect to Ti coordination (basalt to rhyolite with an average coordination ranging from 4.7 to 5.5) in glass samples measured by Farges and Brown. Silica content of glasses are noted in the legend along with sample details.

Leitzke et al. studied the coordination and oxidation state of Ti in various synthetic minerals and glasses to interpret measurements of Ti oxidation state and isotopic fractionation in lunar rocks. They used lunar basalt starting composition, the glasses quenched after partial melting, and partial crystallization contained 42–51 wt % SiO$_2$ and Ti as 4+ and in fivefold coordination. Their data on the coordination of Ti in lunar basaltic magmas are, however, of limited use for interpreting Ti isotopic variations in terrestrial rocks as they focused on mafic compositions very rich in titanium (>7–22 wt % TiO$_2$) and devoid of alkali elements (K and Na).

Overall, it seems like Ti is predominantly in fivefold coordination with some contributions of sixfold coordination in more mafic magmas and fourfold coordination in more felsic magmas. According to Farges and Brown, Ti in fivefold coordination in silicate glasses and melts seems to form titanyl bonds which are also encountered in natural minerals fresnoite, innelile, and lamprophyllite, where Ti is in a square base pyramid. We use the fresnoite structure to emulate Ti in fivefold coordination in melts. We also calculated potassium titanate, as this mineral hosts Ti in a fivefold trigonal bipyramidal coordination, to provide a comparison with the fivefold square pyramid coordination. Farges and Brown did not detect any significant change in coordination below the glass transition and above the liquids but further work is needed to assess to what extent the bond stiffness of Ti in proxy minerals approximates that of Ti in the silicate melt, which may affect the Ti isotope fractionation modeled here. To address the possibility that the coordination of Ti in a silicate melt changes under different SiO$_2$ concentrations as noted in Farges and Brown, we model the evolution of a tholeiitic and calc-alkaline melt under three different scenarios:
2.5. MELTS Modeling. We used rhyolite-MELTS55,56 to simulate Ti isotopic fractionation during fractional crystallization. The starting compositions are primitive tholeiitic and calcalkaline compositions from refs 6 and 11. We tracked the compositions of the melt and minerals during fractional crystallization. For tholeiitic series simulations, crystallization starts at a liquidus temperature of 1215 °C and the simulation is run down to 845 °C in decrements of 5 °C, with the pressure set at 0.6 kbar.11 For calc-alkaline series simulations, the temperature decreases from 1120 to 760 °C and the pressure is set at 1 kbar.6 The initial oxygen fugacities of the tholeiitic and calc-alkaline melts were set at QFM −0.3 and +0.6, respectively. In both cases, the melts evolved with no oxygen fugacity buffer and at constant pressure. We explored the effect of buffering the oxygen fugacity but did not find a drastically different evolution for modeled Ti isotope composition for realistic buffer values. The MELTS calculations stopped at ~90 to 93% crystallization, at which point the SiO2 contents of the remaining melt had reached ~68 and 73 wt % for the tholeiitic and calc-alkaline series, respectively. Model outputs with associated isotopic mass balance calculations are provided in the main text as well as supplementary online materials.

The fractionation factors between the minerals and melt were calculated at each step using the modeled \( ab \) \( initio \) force constants for the melt (see Section 2.4 for the three coordination models considered for the melt), the mean force constants for the minerals, and the temperature (in Kelvin) at each step in the crystallization process. The fractionation between the two phases, melt and minerals, were calculated using the following equation

\[
\Delta^{49}\text{Ti}_{\text{melt-minerals}} = 1000 \ln \beta_{\text{melt}} - 1000 \ln \beta_{\text{mineral}} = 3815 \frac{(F)_{\text{melt}} - (F)_{\text{mineral}}}{T^2}
\]  

(5)

The isotopic composition of the residual melt at each step during the fractional crystallization process was calculated using the following relationship

\[
\delta^{49}\text{Ti}_{\text{melt},i+1} = \delta^{49}\text{Ti}_{\text{melt},i} + \Delta^{49}\text{Ti}_{\text{melt-minerals}} \left( \frac{f_{T_i}}{f_{T_{i+1}}} - 1 \right)
\]  

(6)

where \( \delta^{49}\text{Ti}_{\text{melt},i} \) and \( \delta^{49}\text{Ti}_{\text{melt},i+1} \) are the isotopic compositions of the melts at steps \( i \) and \( i + 1 \), \( \Delta^{49}\text{Ti}_{\text{melt-minerals}} \) is the equilibrium isotopic fractionation between melt and the minerals that have crystallized between \( i \) and \( i + 1 \), and \( f_{T_i} \) and \( f_{T_{i+1}} \) are the fractions of Ti remaining in the melt at steps \( i \) and \( i + 1 \). The isotopic composition of the instantaneous crystals that grew in equilibrium with the melt between steps \( i \) and \( i + 1 \) is simply

\[
\delta^{49}\text{Ti}_{\text{instantaneous minerals},i+1} = \delta^{49}\text{Ti}_{\text{melt},i} - \Delta^{49}\text{Ti}_{\text{melt-minerals},i} + 1
\]  

(7)

and the isotopic composition of the cumulative batch of minerals that have crystallized up to step \( i \) can be readily calculated by mass balance from the isotopic compositions of the melt and initial bulk \( \delta^{49}\text{Ti}_{0} \)

\[
\delta^{49}\text{Ti}_{\text{cumulative minerals},i} = \frac{\delta^{49}\text{Ti}_{0} - f_{T_{i+1}} \delta^{49}\text{Ti}_{\text{melt},i}}{1 - f_{T_{i+1}}}
\]  

(8)

We use the rhyolite-MELTS55,56 program to calculate \( f_{T_i} \) at each temperature decrement (and crystallization increment). Based on our estimates of the equilibrium fractionation factors of Ti between minerals and melts (\( \Delta^{49}\text{Ti}_{\text{melt-minerals}} \)) as a function of temperature, melt composition, and nature of the minerals that crystallize (Section 3.1), we can calculate the isotopic composition of the magma, as well as instantaneous and cumulative solids during fractional crystallization.

3. RESULTS AND DISCUSSION

3.1. Titanium-Bearing Mineral Force Constants and Isotopic Fractionation Factors. Because we are primarily interested in high-temperature applications, we focus on the first-order term in the polynomial expansion of the reduced partition function ratio (eq 3); the coefficients of that expansion are compiled in Table 2, which is proportional to the mean force constant of the Ti bonds calculated by taking the second moment of the phonon density of states (eq 4).36 We provide in the supplementary online materials the PDOS for Ti and other structural elements. Force constants were obtained for barium orthotitanate, fresnoite, potassium titanate, Ti-diopside, geikielite, karrooite, titanite, anatase, pseudobrookite, and Ti\(^{3+} \) titanium oxide, respectively (force constants listed in Table 2). The relationship between the force constants calculated in this study and the inverse of the cube of the bond length (the ionic bond model predicts a linear relationship between \( F \) and \( 1/r^3 \))37,58 together with reported literature values is shown in Figure 3. A correlation between the two variables and the coordination environment of Ti (with the exception of one outlier) is
observed. Greber et al. found a similar correlation from literature data, but our new force constant calculations shows that it extends to more minerals. The inter-mineral Ti isotope fractionation factors are plotted in Figure 4, and the Ti isotope $\beta$-fractionation factors and the fractionation factor between minerals and fivefold-coordinated fresnoite (a melt-proxy) are plotted as a function of temperature in Figure 5. We did not calculate the silicate melts directly due to the difficulty in modeling disordered structure, but as discussed in Section 2.4, previous studies have shown that Ti in silicate melts comprises a significant fraction of Ti in fivefold square pyramidal coordination as is encountered in fresnoite, which we take as a model mineral for this titanyl coordination. In mafic magmas, a significant fraction of Ti could be in sixfold coordination, while in felsic magmas, a significant fraction could be in fourfold coordination. There are however many complications as other parameters such as the nature and abundance of network modifiers (e.g., Na, K, and Ca) can affect Ti coordination, but their roles have not been elucidated. More work is needed to characterize Ti-coordination in silicate melts of geological relevance. The coordination of Ti in most natural Ti-bearing minerals is sixfold. Expectedly, we find that the strength of Ti bonds decreases with increasing CN from 4 to 6 (Figure 3a). Given that silicate melts have lower coordination than minerals, we expect minerals to have light Ti isotopic compositions relative to melts, consistent with the view that coordination is likely the main driver of Ti isotopic fractionation during magmatic differentiation.

Wang et al. also reported force constant determinations for Ti-bearing phases. Focusing on Ti$^{4+}$-bearing minerals, they reported calculations for several silicates (clinopyroxene, orthopyroxene, olivine, and pyrope) with Ti$^{4+}$ substituting for Si$^{4+}$ in fourfold coordination as well as Ti in oxides, namely geikielite, ilmenite, and rutile, where Ti is in sixfold
coordination. They further investigated how Ti dilution affected the force constant by using a supercell approach whereby only a fraction of the Si atoms was replaced by Ti. They found that dilution had little influence on the strength of the Ti bonds.

There is an overall good agreement between our calculations and the results of Wang et al., in that Ti coordination seems to have a strong control on the strength of the Ti bonds (Figure 3). In Figure 3, sixfold-coordinated Ti in Ti$_2$O$_3$ is represented using...
a different symbol as in this mineral, Ti is present as Ti$^{4+}$, whereas in all other minerals, Ti is present as Ti$^{3+}$, which is relevant to redox conditions encountered on Earth.

The average force constant of Ti bonds in our *ab initio* calculations for Ti$^{4+}$ in four-, five-, and sixfold coordination are 547, 462, and 327 N/m, respectively (Table 2). The average force constants of Ti bonds in Wang et al.$^{30}$ for Ti$^{4+}$ in four- and sixfold coordination are 390 and 378 N/m, respectively. For geikielite, Wang et al.$^{30}$ found a force constant of 399 N/m, which is slightly higher than the force constant in ilmenite of 332 N/m, that they also calculate. For comparison, we calculate a force constant for geikielite of 367 N/m. It is important to note that Wang et al.$^{30}$ and Leitzke et al.$^{31}$ use the LDA functional, whereas this study uses the GGA (PBE) functional, resulting in systematically longer bond lengths and lower calculated force constants in this study (by approximately 30 N/m). The different approach means that there will not be a unique fit in the data ($F$ = 5336/r$^2$ - 314, where $r$ is the average Ti-O bond length in Å, allows estimates on the force constants of Ti-bearing minerals that could not be modeled using DFT (Ti-magnetite and ulvospinel). The average bond lengths of these two minerals are 2.06 and 2.04 Å$^{65}$, respectively, corresponding to calculated force constants of 296 and 309 N/m. The relationship between Ti force constant and CN can be fit with a function ($F$ = -123 × CN + 1078 (note that sevenfold-coordinated Ti$^{4+}$ was not included in this fit of Ti$^{4+}$-bearing minerals).

Titanium isotopic compositions of mineral separates from different rocks crystallizing at various temperatures$^{59,68}$ allows for the comparison of our modeled Ti force constants with natural samples. In the Kneeling Nun Tuff that crystalized at $\sim$700 ± 30 °C, Mandl$^{68}$ reports $\Delta^{49}$Ti values between titanite–magnetite, ilmenite–magnetite, quartz-magnetite, and plagioclase–magnetite of +0.23, +0.10, +1.12, and +0.98% (all ±0.04% e), respectively. In the Kos magmatic suite from the Aegean arc, differences in the $\delta^{49}$Ti-measured compositions for quartz-magnetite (equilibrated at $\sim$700 °C), plagioclase–magnetite (equilibrated at $\sim$770 °C), and olivine–magnetite (equilibrated at $\sim$1150 °C) were +1.08, +0.77, and +0.43% e, respectively (all samples ±0.05% e).$^{30}$ In synthetic minerals and glasses produced at various $fO_2$ glasses equilibrated at 1260 °C (here reported at fO$_2$ = air), Rzezak et al.$^{69}$ reports $\Delta^{49}$Ti values between orthopyroxene-glass and armalcolite-glass of 0 and $-0.09%$ e (±0.01, 0.02, and 0.01% e for orthopyroxene, armalcolite, and glass, respectively). In Figure 4, the measured differences in $\delta^{49}$Ti between the mineral separates$^{59,68,69}$ are compared to those predicted by our DFT calculations with the assumption that the Ti force constant of Ba$_2$TiO$_4$ is a good analogue for olivine, plagioclase and quartz (in all phases, Ti is incorporated in fourfold coordination), and the melt for our predicted isotope fractionation is 40% [6] and 60% [S]. Although we did not model orthopyroxene and armalcolite here, we compare these measured compositions$^{69}$ to our predicted isotopic fractionations of clinopyroxene-melt and several Ti-rich oxides modeled here: pseudobrookite-melt, geikielite-melt, and karrroite-melt. The modeled and measured inter-mineral $\delta^{49}$Ti differences agree to a first order, with the largest difference being that Mandl$^{68}$ found a heavier Ti isotopic fractionation between titanite–magnetite than in ilmenite–magnetite, which is not predicted by this study. It is important to mention that isotopic analyses of natural samples do not always record equilibrium isotope fractionation; for example, samples may be not be co-genetic or may have experienced Ti diffusion. Estimating precise equilibrium temperatures is difficult, and the measured $\delta^{49}$Ti composition of minerals with low Ti concentrations could be additionally biased by mineral and melt inclusions.

As discussed in Section 2.4, we consider three scenarios for the coordination of Ti in silicate melt. For four-, five-, and sixfold coordinated Ti in silicate melt, we adopt the following force constants of Ti: (1) the fourfold-coordinated Ti is the average value of the only fourfold-coordinated mineral that we studied (Ba$_2$Ti$^{4+}$O$_4$; 547 N/m; Table 2) and the average of force constants calculated by Wang et al.$^{30}$ (592 N/m) and those calculated for minerals discussed by Leitzke et al.$^{31}$ for Ti$^{4+}$ in fourfold coordination (633 N/m; based on the relationship defined here between CN and force constant). (2) The fivefold-coordinated Ti is the value of fresnoite calculated here (Table 2, 468 N/m), which hosts Ti in a coordination that resembles that encountered in silicate glasses.$^{25}$ (3) The sixfold coordinated is the average value of sixfold-coordinated minerals investigated here (327 N/m; Ti-diopside; 383 N/m, geikielite; 367 N/m, karrroite; 335 N/m, titanite; 323 N/m, pseudobrookite; 274 N/m, anatase; 282 N/m), and the sixfold-coordinated values of Leitzke et al.$^{31}$ and Wang et al.$^{30}$ for clinopyroxene (426 N/m$^{30}$ and 354 N/m$^{-27}$), orthopyroxene (353 N/m$^{-20}$), pyrope (445 N/m$^{-20}$), geikielite (399 N/m$^{-20}$), ilmenite (332 N/m$^{-20}$), and rutile (314 N/m$^{-20}$). There are significant variations in the force constant of sixfold-coordinated Ti in minerals likely due to the different approaches (GGA vs LDA), but given that this coordination is a minor component of Ti in silicate melt, this uncertainty has little influence on the conclusions of this study.

For the three Ti-coordination models of silicate melt introduced in Section 2.4, we therefore use the following force constants:

1. $100% [S] = 468$ N/m.
2. $40% [6] + 60% [S] = 423$ N/m for <52 wt % SiO$_2$; $100% [S] = 468$ N/m for 52–63 wt % SiO$_2$, and 45% [4] + 55% [S] = 523 N/m for >63 wt % SiO$_2$.
3. $\langle F_{\text{melt}} \rangle = -60 \times NBO/T + 463$. To relate force constant to melt polymerization, we use the gross correlation between force constant and CN (Figure 3a; $\langle F_{\text{melt}} \rangle = -123.5 \times CN + 1078$) and use the relation of Ti coordination with CN in NBO/T in the data of Farges and Brown$^{57}$ (Figure 2b; CN = 0.485 × NBO/T + 5).

To test the validity of the Ti force constants adopted here for the melt, we compare our predictions with measured Ti isotopic fractionation in mineral-melt pairs from natural samples. Mineral separates from Kilauea Iki lava lake gave a fractionation of $\Delta^{49}$Ti$_{\text{melt-oxide}} = +0.39 \pm 0.06%$ e at 1000 °C.$^{11}$ Using the estimate of the coordination environment of Ti in basalt (BCR-2: 50% fivefold coordinated, 50% sixfold coordinated) from ref 25, the force constant of the melt should be ($F$ = 370 N/m). To achieve a +0.39% e $\delta^{49}$Ti isotopic fractionation at 1000 °C would require a force constant of Ti in minerals (in this case, a mixture of ilmenite and Ti-magnetite) of 204 N/m. This force constant is significantly lower than the *ab initio*-derived ($F$ value for Ti in sixfold-coordinated minerals of 327 N/m (this study) or the value of 332 N/m calculated for ilmenite by Wang et al.$^{30}$ The reason for this discrepancy is unclear but could be attributed to
differences in the coordination and force constant of Ti in silicate melts. For example, if we assume that Ti in the melt is in fivefold coordination and has a force constant of 468 N/m, then the force constant of the minerals required to explain the results of Johnson et al.11 becomes 302 N/m, which is more in line with our prediction for sixfold-coordinated minerals (327 N/m).

Alternatively, the force constant of ilmenite could be lower than the value of other sixfold-coordinated minerals, as it has among the lowest force constants (332 N/m) for all sixfold-coordinated minerals (range from 314−457 N/m) calculated by Wang et al.30

Measurements of the bulk mineralogical composition using scanning electron microscopy (SEM)−EDX of four samples from Kilauea Iki heavy mineral separates containing oxides indicate that the average abundance of Ti partitioned into ilmenite versus Ti-magnetite is 67.75 and 32.25%, respectively (see supplementary online material). The estimated amount of Ti in each mineral phase along with the ab initio-derived ⟨F⟩ value of ilmenite from Wang et al.30 allows us to calculate an ⟨F⟩ value of 238 N/m between Ti-magnetite and a fivefold-coordinated melt. For the model presented here, we use a range of different conditions to account for uncertainties. However, it is clear that more work is needed to quantify Ti isotopic fractionation in more mineral-melt pairs and to better constrain the coordination of Ti in geologically relevant melts.

3.2. MELTS Modeling: Ti Isotopic Fractionation during Magmatic Differentiation. We modeled the fractional crystallization and the corresponding Ti isotopic fractionation of tholeiitic and calc-alkaline basalts using rhyolite-MELTS55,56 and the equilibrium isotopic fractionation factors that we derived (Sections 2.5, 3.1, Figure 5). For specific details on the initial conditions, see Figure captions 6 and 7.

The Ti isotopic compositions of melts and minerals during magmatic differentiation were modeled using the abundances of the minerals crystallizing at each stage, the melt fraction, the corresponding Ti concentrations, and the Ti mean force constants derived from ab initio calculations and empirical relationships between the bond strength and interatomic distance (Section 3.1). For both the tholeiitic and calc-alkaline melts, the primary Ti-bearing mineral phases were solid solutions of clinopyroxene (CaTi0.5Mg0.5AlSiO6 and CaTi0.5Mg0.5Fe3+SiO6), spinel [Ti-magnetite: Fe2+(Fe3+,Ti)2O4 and ulvospinel: TiFe2+2O4], and rhombohedral oxide (primarily ilmenite: Fe 2+TiO3). The proportions of these Ti-bearing mineral phases were monitored throughout the course of the crystallization (Figure 7), and the force constants of the minerals were weighted based on the mineral proportions and Ti
contents. The Ti force constants adopted in the modeling for clinopyroxene, spinel, and rhombohedral oxide are as follows:

(i) Under reducing conditions (∼IW-1.7) and with large amounts of Ti, Leitzke et al.31 found based on XANES measurements of experimental run products that clinopyroxene consisted of a 50–50 mixture of four- and sixfold-coordinated Ti.4 In Ti-rich natural terrestrial diopside, Quartieri et al.71 found that Ti coordination ranged from mostly fourfold to a mixture of four- and sixfold sites. The coordination of Ti in clinopyroxene compositions more relevant to the magmatic differentiation series studied here is uncertain but as a first pass on this estimate, we will assume that it is a 50–50% mixture of 4 and 6. Wang et al.30 and Leitzke et al.31 calculated the force constant of Ti4+ in fourfold coordination substituting for Si and obtained values of $592$ and 363 N/m, respectively. For Ti in fourfold coordination in barium orthotitanite, Leitzke et al.31 calculated the force constant of Ti4+ in sixfold coordination substituting for Mg in clinopyroxene and obtained a value of 350 N/m. Our calculation for Ti in sixfold coordination in Ti-diopside gives a value of 383 N/m. Taking all fourfold (orthotitanate in Table 2, Si-substituted from Wang et al.30 and Leitzke et al.31) and sixfold values (Ti-diopside in Table 2, Mg-substituted from Leitzke et al.31), we obtain averages of 591 and 366 N/m, which corresponds to a clinopyroxene value of ∼478 N/m for a 50–50% mixture of 4 and sixfold coordination. Due to large uncertainties in Ti coordination in clinopyroxene, this value is uncertain but given that clinopyroxene plays a secondary role in the budget of Ti in tholeiitic and calc-alkaline series, this has little impact on the conclusions.

(ii) Ti-magnetite Fe3+−xTi4xo4 forms a solid solution between magnetite and ulvöspinel. For four oxygens, there are three cation sites: 1 tetrahedral A-site and 2 octahedral B-sites. In magnetite, the tetrahedral A-site is occupied by Fe3+, while the 2 B-sites are occupied by Fe3+ + Fe4+. Ti4+ substitution is thought to be achieved by replacement of Fe3+ in the B-site and conversion of Fe3+ to Fe4+ to respect charge balance. According to this view, Ti4+ is thought to be predominantly in sixfold coordination, which is supported by several observations.72−75 Hoare et al.12 recently argued for the presence of large amounts of Ti in fourfold coordination in Ti-magnetite based on data subsequently disputed in a study by Wechsler et al.76 As discussed in Section 2.4, we were unable to properly calculate the force constant of Ti in ulvöspinel and Ti-magnetite because the structures calculated by DFT were dynamically unstable and produced negative frequencies. For ulvöspinel, we used the primitive cell (space group $Fd\bar{3}m$) with an antiferromagnetic ordering. Optimized cell parameters show an agreement with experimental values76 similar as for other minerals, with a slight distortion of cell. Two negative frequencies out of the center of the Brillouin zone are obtained, even if the structural relaxation is constrained to the cubic cell. By neglecting these imaginary modes, we found a Ti force constant of 155 N/m. For Ti-magnetite, we also used the primitive cell (space group $Fd\bar{3}m$) and built a ferrimagnetic structure with the same charge ordering as in the theoretical work of Liu and Di Valentín77 for pure magnetite. By neglecting the imaginary frequency displayed out of the center of the Brillouin zone, we found a Ti force constant of 145 N/m. The DFT + $U$ (the on-site Coulomb term $U$) method is often used for improving the description of the electronic structure of Fe-bearing minerals like magnetite, but this improvement is often obtained at the expense of the structural properties. Obtaining the PDOS from the vibrational frequencies calculated in DFT + $U$ on a q-point grid requires large computational resources. Several attempts were performed here but results were not conclusive and seem very dependent on the pseudopotentials used. Therefore, to estimate the force constant of Ti in Ti-magnetite and ulvöspinel, we use the relationship between the inverse of the cube of the reported bond lengths and force constants of Ti-bearing minerals illustrated in Figure 3, which correspond to calculated force constants of 296 and 309 N/m for Ti-magnetite and ulvöspinel, respectively.

Oxygen fugacity will have an influence on the types and abundances of crystallizing minerals (e.g., in Rhyolite...
MELTS, the proportion of rhm oxide or ilmenite to spinel) as well as the partitioning of Fe$^{3+}$ versus Fe$^{2+}$ partitioned into various mineral phases. Because the force constant of spinel (and therefore the average of crystallizing minerals) could be affected by the spinel stoichiometry on the magnetite-ulvospinel solid solution, and in particular the proportion of Fe$^{3+}$, we express it as a linear function of the molar ratio $x = \frac{Fe^{3+}}{(Fe^{2+} + Fe^{3+})}$: $\langle F \rangle_{\text{spinel}} = \frac{3x}{2}\langle F \rangle_1 + \frac{1}{2}\left(1 - \frac{3x}{2}\right)\langle F \rangle_2$, where $\langle F \rangle_1$ and $\langle F \rangle_2$ are the estimated force constants that would correspond to the force constants of Ti-bonds in Ti-magnetite and ulvospinel, respectively. In the Rhyolite MELTS calculation, $x$ varies between 0.23 and 0.46 in the tholeiitic series and 0.3−0.54 in the calc-alkaline series, which is far from the pure end-member compositions.

(iii) Similar to Ti-magnetite and ulvospinel, DFT modeling of ilmenite is complicated by the fact that it contains Fe. Therefore, we have instead modeled geikielite (MgTiO$_3$), which is a rhombohedral titanate with the same crystal structure as ilmenite and contains Ti in sixfold coordination.

The two main uncertainties affecting the calculation of Ti isotopic fractionation during magmatic differentiation are the coordination of Ti in silicate melt (Section 2.4) and the force constant of Ti in the Ti-magnetite solid solution (Section 3.2). We set the force constants of ilmenite, clinopyroxene, and the Ti-magnetite solid solution to the values given in Section 3.2. In the melts, we consider three models for the coordination and force constant of Ti-bonds (Sections 2.4 and 3.2): (i) we assume that Ti is solely fivefold (Figure 8a), (ii) we assume that it changes from a mixture of six- and fivefold in more mafic magmas, pure fivefold in intermediate magmas, and a mixture of five- and fourfold in more felsic magmas (Figure 8b), and (iii) we assume that it changes with the degree of polymerization of the melt quantified using the NBO/T ratio (Figure 8c). The $\delta^{49}$Ti values of both compositions remain close to the chondritic value of $\sim 0\%e$ until the onset of Ti-bearing mineral crystallization (Figure 8). The Ti-bearing minerals such as clinopyroxene, ulvospinel, Ti-magnetite, and geikielite incorporate light Ti isotopes, driving the residual melt to heavier compositions. Our MELTS model correctly predicts that tholeiitic magmas should produce a steeper trend in the Ti isotope versus SiO$_2$ space compared to calc-alkaline magmas, although the trends do not match exactly the observed values in natural samples. The two first melt-coordination models (Figure 8a,b) highlighted above reproduce well tholeiitic series $\delta^{49}$Ti values, but we predict a steeper slope for calc-alkaline rocks than what is actually measured. The third melt-coordination scenario (Figure 8c) based on NBO/T is very successful in reproducing the observed trend of tholeiitic magmas and best reproduces the calc-alkaline trend observed in natural samples, although a large discrepancy remains for this magma series. The agreement between the data and model (Figure 8c) suggest that melt polymerization may have an important control on Ti isotopic composition, calling for further experimental validation. The reason for these models’ remaining discrepancies is unknown and further work is needed to explore how water content, $f_O$, pressure, temperature, and composition affect the coordination of Ti in calc-alkaline and tholeiitic magmas and crystallizing minerals. A possibility for the discrepancy between model predictions and measurements of natural samples could be due to the abundance and composition of Fe–Ti oxide crystallization during magmatic differentiation in the MELTS model, as various Fe-bearing minerals can have unique $\langle F \rangle$ (Table 2) which translate to variable Ti isotopic fractionation factors. Furthermore, in calc-alkaline magmatic systems, amphibole and biotite are common silicate phases that can also contain a substantial amount of Ti. Measurement of amphibole and biotite mineral separates indicate that they do not fractionate Ti isotopes as strongly as Fe–Ti oxides, but likely also have lighter $\delta^{49}$Ti compositions than the corresponding melt.

While the rhyolite-MELTS software predicts the evolution of the melt Ti concentration accurately during magmatic differentiation, it does not partition Ti into amphibole and biotite phases and thus likely overestimates the amount of crystallizing Fe–Ti oxides. The outcome of this would likely lead to a heavier modeled $\delta^{49}$Ti composition of the melt compared to reality. One other explanation for the disagreement between our modeled calc-alkaline magmas and natural samples is the possibility of assimilation or magma mixing as discussed in Greber et al.

To summarize, our work shows that Ti coordination has a major influence on Ti isotopic fractionation during magmatic differentiation and we can successfully reproduce the trend documented in tholeiitic rocks, but our model predicts a larger Ti isotopic fractionation in calc-alkaline rocks than what is measured. Once the controls on Ti isotopic fractionation are ascertained, this system can potentially be used to reconstruct the history of oxide crystallization of igneous rocks for which a full magmatic differentiation series is not available and possibly tease out the effects of assimilation and magma mixing.

It may also yield new insights into magma differentiation early in Earth’s history and compositions relevant to partial melting and differentiation in the Archean (e.g., rutile and TTGs).

4. CONCLUSIONS

The trends of titanium isotopic fractionation versus SiO$_2$ content differ significantly in calc-alkaline and tholeiitic magmatic series. These differences are attributable to variations in the nature and rate of removal of the Ti-bearing minerals that crystallize from the two magmas. In tholeiitic rocks, late onset of oxide crystallization drives the residual melt to higher TiO$_2$ concentrations, while at the same time, the SiO$_2$ remains nearly constant due to plagioclase crystallization. When Fe–Ti oxides start crystallizing, the $\delta^{49}$Ti value of the melt increases very
rapidly even though the SiO₂ is relatively low. In calc-alkaline rocks, early onset of oxide crystallization and delayed onset of plagioclase crystallization drives the δ⁴⁹Ti value to increase more modestly, while SiO₂ increases rapidly.

The Ti isotopic composition of tholeiitic and calc-alkaline magmas undergoing fractional crystallization was modeled using the rhyolite-MELTS software and ab initio-derived force constants that allow us to calculate melt-mineral fractionation factors. The majority of Ti in crystallizing phases is removed via sixfold-coordinated Ti-oxides, and the Ti remaining in the melt is modeled in different coordination environments. The force constants of the crystallizing minerals and the melt proxy presented in this study along with the timing and pace of Ti-bearing mineral crystallization predicted by MELTS modeling can provide insights into the observed δ⁴⁹Ti isotope compositions in tholeiitic versus calc-alkaline rocks. Future work should focus on constraining the differences in the coordination environment of Ti in melts with variable composition, water content, oxygen fugacity, and to a lesser degree pressure. Our results indicate that Ti isotopes, combined with other non-traditional stable isotope systematics such as Fe, can help (1) tease out the history of fractional crystallization and (2) ascribe a magma series origin, to magmas that otherwise lack geological context.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsearthspacechem.1c00172

PDOS for titanium and all other elements in all minerals investigated here (XLSX)

Stable titanium isotope fractionation calculated from rhyolite-MELTS model simulations and mineral-melt force constants (XLSX)

Chemical composition of ilmenite and Ti-magnetite from Kilauea Iki lava lake mineral separates measured by SEM–EDX and the abundance of these minerals relative to total Fe–Ti oxides (XLSX)

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