Redox-dependent Ti stable isotope fractionation on the Moon: implications for current lunar magma ocean models

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Received: 21 February 2022 / Accepted: 22 July 2022 / Published online: 4 August 2022
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Abstract
In terrestrial magmas titanium is predominantly tetravalent (Ti⁴⁺), in contrast, lunar magmas are more reduced (IW-1) and hence approximately 10% of their bulk Ti content is trivalent (Ti³⁺). Changes in oxidation state and coordination number are both important parameters that can serve to drive Ti stable isotope fractionation. As such, mineral–mineral and mineral-melt Ti stable isotope fractionation factors determined for terrestrial samples may not be appropriate for lunar samples that formed under more reducing conditions. To address this issue, several experiments were carried out in gas mixing furnaces over a range of \( f_O^2 \) (air to IW-1) to determine Ti stable isotope fractionation factors for minerals, such as ilmenite, clinopyroxene and rutile that are highly abundant on the Moon. Results show that the extent of Ti stable isotope fractionation significantly increases with decreasing \( f_O^2 \). For example, the isotopic difference between ilmenite and residual melt (\( \Delta ^{47}\text{Ti}_{\text{ilmenite-melt}} \)) is resolvably lower by \( \sim 0.44 \, \text{‰} \) from terrestrial-like FMQ-0.5 to lunar-like IW-1 at an intermediate precision of \( \pm 0.003 \, \text{‰} \) (95% c.i. OL–Ti). This confirms that fractionation factors determined for terrestrial conditions are indeed not applicable to lunar settings. Our new fractionation factors for ilmenite, clinopyroxene and silicate melt are mostly consistent with those previously determined by ab initio modelling based on density-functional theory. Using our new experimental data in conjunction with previously published high-precision HFSE data and Ti stable isotope data of lunar basalts, we modelled the solidification of the Lunar Magma Ocean (LMO). The model for LMO solidification included fractionation of Ti stable isotopes not only by Ti-oxides, but also by typical lunar silicate minerals as pyroxene or olivine. The resulting \( \delta ^{47}\text{Ti} \) for urKREEP and ilmenite-bearing cumulates are within error of previous estimates, but also indicate that ilmenite-bearing cumulates must have contained around 15% ilmenite.

Keywords Lunar magma ocean · Equilibrium stable isotope fractionation · Experimental petrology · MC–ICP–MS · Ti stable isotopes · Ilmenite · Rutile · Clinopyroxene
Introduction

The origin of the Moon is attributed to the accretion of ejected material from a giant impact event between the proto-Earth and one or more impactors (Canup 2004, 2012; Ćuk and Stewart 2012; Reufer et al. 2012; Rufu et al. 2017). As a result of the giant impact, material from the proto-Earth and the impactor(s) homogenised, as indicated by similarities in their O, Li, Si, Cr, Ti and Fe isotopic composition (Wiechert et al. 2001; Magna et al. 2006; Armitage et al. 2012; Bonnand et al. 2016; Millet et al. 2016; Sossi and Moynier 2017). In the aftermath of lunar cataclysm, the Moon was covered by a Lunar Magma Ocean (LMO), but its exact duration and extent are still being debated (Longhi and Pan 1988; Nemchin et al. 2009; Elkins-Tanton et al. 2011; Connelly and Bizzarro 2016; Barboni et al. 2017; Charlier et al. 2018; Thiemens et al. 2019).

The crystallization of the LMO has been investigated by modelling (Snyder et al. 1992; Longhi 2003; Elkins-Tanton et al. 2011; Johnson et al. 2021) and by complementary experimental approaches (Elardo et al. 2011; Lin et al. 2017; Charlier et al. 2018; Rapp and Draper 2018) assuming fractional crystallization (Elkins-Tanton et al. 2011; Charlier et al. 2018; Rapp and Draper 2018) or a combination of fractional and equilibrium crystallization (Snyder et al. 1992; Elardo et al. 2011; Lin et al. 2017; Johnson et al. 2021).

The complementarity seen in the REE patterns of lunar anorthositic crust and the LMO residuum supports the idea that the LMO was a global scale event (Warren and Taylor 2014; Gross and Joy 2016). Cumulate layers of the LMO destabilized as the denser Ilmenite-bearing cumulates (IBC) became gravitationally unstable due to its higher overall density (Hess and Parmentier 1995). This instability led to the overturn of the lunar mantle, which more closely resemble the Bulk Silicate Earth (BSE + 0.005 ± 0.005 ‰; Millet et al. 2016), whereas high-Ti basalts display higher δ49Ti values (+0.009 to +0.115 ‰; Millet et al. 2016; Kommescher et al. 2020). In addition, high-Ti basalts show clear evidence of High Field Strength Element (HFSE) fractionation. For example, overall low Zr/Nb (Shearer et al. 1996) and high Hf/W and Ta/W coupled with TiO2 enrichment (Neal and Taylor 1992; Münker 2010; Thiemens et al. 2019) suggest the presence of ilmenite, likely in the form of the ilmenite-bearing cumulates, in their mantle sources. This conclusion is supported by experimental work, which shows that ilmenite-melt equilibria can fractionate Ta/W and Hf/W (Klemme et al. 2006). In addition, Kommescher et al. (2020) noticed that ilmenite-bearing high- and low-Ti basalts are isotopically heavier in Ti than non-ilmenite bearing lunar basalts, which shows that Ti-oxides strongly affect Ti stable isotope fractionation.

Interestingly, at oxygen fugacities relevant to lunar magmatism – IW-1 (Wadhwa 2008), high-Ti basalts can incorporate up to 10% Ti3+ relative to their bulk Ti contents (Krawczynski et al. 2009; Borisov 2012; Leitzke et al. 2018; Simon and Sutton 2018). The presence of Ti3+ in lunar minerals was first indicated by the stoichiometry of armalcolite (Stanin and Taylor 1980). Changes in the oxidation state of Ti will result in differences in bonding energy and spatial coordination possibly resulting in redox dependent stable isotope fractionation as already seen for other redox-sensitive elements as V (Prytulak et al. 2017; Nielsen et al. 2014; Wu et al. 2016; Sossi et al. 2018) and Fe (Dauphas et al. 2009, 2014; Sossi et al. 2012). In comparison to these elements, data on redox-dependent Ti stable isotope fractionation are scarce, although ab initio modelling carried out by Wang et al. (2020) implies that the presence of Ti3+ could impact Ti stable isotope fractionation during magmatic processes. Fe–Ti-oxides, which incorporate Ti in VI-fold coordination are especially prone to fractionate Ti isotopes. Indeed, the ability of Ti-oxides to strongly fractionate Ti stable isotopes was observed for natural terrestrial (Deng et al. 2019; Hoare et al. 2020; Zhao et al. 2020) and lunar bulk samples (Millet et al. 2016; Kommescher et al. 2020). In addition, Ti stable isotope fractionation driven by the presence of Fe–Ti oxides has also been recently investigated in mineral separates (Johnson et al. 2019; Mandl 2019; He et al. 2020; Nie et al. 2021; Rzehak et al. 2021), as well as experimental studies (Rzehak et al. 2021). However, Ti stable isotope fractionation can occur not only driven by Fe–Ti oxides but also by silicate minerals as ab initio studies indicate (cf. Wang et al. 2020; Aarons et al. 2021). Pyroxenes and olivine from experimental high-Ti compositions at fO2 relevant to lunar magmatism can contain up to 25% trivalent Ti in VI-fold coordination, whereas the remaining Ti3+ was shown to be present in IV- or VI-fold coordination (Leitzke et al. 2018). Ti-oxides on the other hand were shown to incorporate up...
to 40% trivalent Ti in VI-fold coordination, whereas silicate glasses contained only tetravalent Ti on average in V-fold coordination (Leitzke et al. 2018). This observation was also made in a recent XANES study on Ti-rich glasses, where no trivalent Ti was found independently of $f_O_2$ (Tarrago et al. 2022). Although recent studies have highlighted the influence of redox state and coordination on Ti stable isotope fractionation (Hoare et al. 2020; Rzehak et al. 2021), it has been mostly omitted in models that seek to address the Ti isotope evolution during LMO crystallization (cf. Millet et al. 2016). Given that fractionation factors for orthopyroxene- and armalcolite-related equilibria have been shown to be redox-dependent (Rzehak et al. 2021), it is entirely possible that other mineral-melt and mineral–mineral equilibria are likewise affected. These data can then be used to refine LMO models and to identify magmatic processes that led to the formation of the different mare basalts.

To address Ti stable isotope fractionation relevant to lunar magmatism, several experiments were carried out in gas-mixing furnaces at different $f_O_2$, using synthetic compositions analogous to lunar high-Ti ilmenite-bearing and rutile-bearing basalts. The aim of these experiments was to investigate redox dependent changes in Ti stable isotope compositions of melt and minerals that are highly abundant in lunar compositions, i.e., clinopyroxene, ilmenite and rutile. In addition, we used our fractionation factors to model LMO solidification and processes that presumably led to the formation of today’s high- and low-Ti mare basalts, which we then compared to literature data of natural samples.

**Methods**

**Experimental approach**

The starting compositions of our experiments were made of dried high purity major element oxide reagents by Alfa Aesar. The starting composition yielding ilmenite (FT1–10) was mixed in the CaO–FeO–MgO–Al$_2$O$_3$–SiO$_2$–TiO$_2$ (CFMAS + TiO$_2$) system, whereas the one that yielded rutile (based on composition SM20 in Klemme et al. 2005) was mixed in the K$_2$O–Na$_2$O–FeO–TiO$_2$–CaO–MgO–Al$_2$O$_3$–SiO$_2$ (KNFT–CMAS) system. Starting materials were produced by grinding dried oxide powders together with acetone in an agate mortar, whereas CaCO$_3$ was decarbonated at 900 °C overnight prior to this step. Afterwards, the powders were dried, pressed into pellets, sintered at 900 °C and subsequently reground to promote homogenization of the starting materials. Starting compositions are shown in Supplementary Table 1.

The rutile-bearing experiment (SM-20) was performed using Pt wire in air. In contrast, the ilmenite-bearing experiments (FT1–10) were performed at different $f_O_2$ by mixing CO–CO$_2$ in different proportions (see Supplementary Table 1 for the gas mixes) using Re wire, since Re wire shows limited uptake of iron (Fonseca et al. 2007). All experiments were performed in 1-atm vertical tube gas mixing furnaces at the Universities of Cologne and Bochum (Germany) using the wire loop technique by Donaldson et al. (1979), while closely following the experimental protocol by Leitzke et al. (2016, 2017). Each sample powder was mixed with polyethylene glycol and water to produce a slurry, which was then placed onto a loop of the respective metal and placed inside the furnace at temperatures ~50–100 °C higher that the liquidus of the starting composition. After minimum 3 h to ensure complete melting and homogenization, samples were cooled down to their nominal target temperature using a cooling ramp of 2 °C/hour, where they remained another 72 h to ensure chemical equilibrium. The temperature was monitored using an external Type B thermocouple (Pt$_{70}$Rh$_{30}$–Pt$_{94}$Rh$_{6}$). This experimental protocol was designed to yield large enough crystals (>100 µm) to facilitate mineral separation (cf. Rzehak et al. 2021).

In each experimental run, two experiments with identical composition were performed simultaneously. After both experiments were quenched, one loop was mounted in epoxy, polished, and used for Secondary Electron Microscopy (SEM) analysis and Electron Probe Microanalysis (EPMA), whereas the other was gently crushed, and minerals and glasses were separated for Ti stable isotope analyses.

**SEM and EMPA measurements**

Backscattered electron images and element mapping were performed with a JEOL JSM-7200F scanning electron microscope with 20 kV, a working distance of 10 mm and a probe current of ~2 nA at the Center for Interface-Dominated High Performance Materials at the Ruhr-University Bochum. Element maps were acquired using the Oxford instruments Aztec software version 5.0. All element maps were obtained using a process time of 4, a number of 1024–2048 channels and a pixel dwell time of 100 µs for a duration of at least 20 min.

Major and minor element analyses were performed with a JEOL JXA-8530F electron microprobe at the University of Münster using natural minerals as standards (see Supplementary Table 3). The following standards were used for quantification: hypersthene (Si), rutile (Ti), diesthene (Al), fayalite (Fe), olivine (Mg), diopside (Ca), sandine (K) and jadeite (Na). The EPMA acceleration voltage was 15 kV and the beam current was 15 nA. The spot sizes were 1–5 µm depending on the grain size. Counting times were 15 s on the peak and 5 s on the background. Line profiles across different mineral phases in our experiments were performed with a Cameca SX Five FE at the University of Bochum using an
acceleration voltage of 20 kV and a beam current of 15 nA. Spot sizes were 1–3 µm, counting times were between 15 to 45 s on the peak and between 5 to 20 s on the background. The following standards were used: olivine (Mg, Si), diopside (Ca), rutile (Ti), fayalite (Fe) and spessartine (Al).

**Chemical purification of Ti stable isotopes**

Minerals were separated under reflected and transmitted light using a Zeiss stemi dv4 stereomicroscope with 32 times magnification. The glass fraction was always transparent and showed characteristic conchoidal fractures, clinopyroxenes were milky white or colourless depending on the fO2 (colourless at oxidizing conditions). Ilmenite was black and often showed a metallic lustre, whereas rutile was red–brown and easily distinguishable from the surrounding glass. To mitigate cross-contamination, only minerals and glass devoid of obvious inclusions were selected for use in the Ti separation chemistry.

The Ti separation procedure is described in detail in Rzehak et al. (2021). The aim of this protocol is to always keep Ti in solution and to avoid dry down steps that can lead to partial sample loss via precipitation. All mineral and glass fractions were weighed and digested in pre-cleaned Savillex® PFA beakers at 120 °C for 72 h using a 3:1 mixture of 14 M HNO3 and 24 M HF. Fractions from the rutile experiment and corresponding blanks were found to be more efficiently digested in Parr bombs at 120 °C for 48 h in a 3:1 mixture of 24 M HF and 14 M HNO3 (following Tusch et al. 2019). In addition to our handpicked phases, the procedural blank, the chemical reference material, and a glass reference material were also processed. The chemical reference material was either OL–Ti that was produced from a pure Ti metal rod and is commonly used as a reference standard for Ti stable isotope analyses (Millet and Dauphas 2014; Millet et al. 2016), or an in-house reference material Col–Ti that was produced in similar fashion (see Kommescher et al. 2020). The glass reference materials consisted of the bulk composition used for each experiment, which was fused until it was homogeneous. The bulk glass compositions were then used to perform mass balances based on the Ti concentration in each phase present in the experiments, their modal proportions, and their measured Ti isotope composition.

The chemical composition of fully digested sample aliquots was initially analysed using an iCap quadrupole ICP–MS at the University of Cologne. In addition to Ti contents, Cr and V that cause isobaric interferences with Ti isotopes were also monitored to check for possible contamination from the furnaces and reagents. However, their concentrations were always below detection limit, and any isobaric interferences were thus negligible. Sample aliquots that contained up to 30 µg Ti were mixed with a double spike in the ideal proportion of sample:spike 0.49:0.51 (Rudge et al. 2009; Millet and Dauphas 2014; Kommescher et al. 2020). For this purpose, we used a 47Ti–49Ti double spike with 410.9 ± 0.3 µg/g Ti (Kommescher et al. 2020) that was calibrated against OL–Ti. All of our samples are in the ideal range of 1 and 3 that ensures accurate Ti isotope measurements (Kommescher et al. 2020; see Supplementary Table 2). Afterwards, spiked samples were equilibrated overnight in closed Savillex® PFA beakers and evaporated at 75 °C on the hotplate. The dried samples were first refluxed in 14 M HNO3 > > 6 M HCl–0.06 M HF to dissolve secondary fluorides which show a tendency to incorporate Ti (Millet et al. 2016). Afterwards, samples were refluxed in 6 M HCl–0.06 M HF to dispose nitrate precipitates. Finally, samples were converted into 1 mL 1.75 M HCl–2 vol. % H2O2 and centrifuged for 10 min prior to column chemistry. The separation of Ti followed the procedure described by Rzehak et al. (2021). After evaporation, Ti cuts were treated with a 9:1 6 M HNO3–0.2 HF:30% H2O2 solution to destroy organic material derived by the resins. Finally, all samples were dissolved in 2 mL of the 0.3 M HNO3–0.014 M HF running solution and transferred into 5 mL ICP–MS vessels for MC–ICP–MS measurements. The mean relative yield from our method was ~90%. Procedural blanks were always around 10 ng and thus negligible.

**MC–ICP–MS measurements**

Analyses of Ti stable isotope compositions were performed on a Thermo Scientific Neptune Plus MC–ICP–MS at the University of Cologne (Germany) in high resolution mode to account for polyatomic interferences on 46Ti and 48Ti. Measurements were performed with an ESI APEX HF desolvating system and additional glassware fitted after the APEX HF for enhanced signal stability. Before each session, detector gain and instrument baseline were performed. A Ni sample cone and a Ni skimmer H-cone were used for all measurements. Typical resolving power was around 10,000, which was determined by 5–95% peak height (Weyer and Schwieeters 2003). Lens setting and gas flows were tuned daily to maximize resolving power and intensities. Each sample was measured 2–4 times in blocks of 60 cycles with an integration time of 8.4 s and bracketed by our reference material Col–Ti. Furthermore, before each set of samples, a block of standards was measured. Backgrounds for on-peak-zero corrections were measured before and after each standard-sample measurement block. Most analyses were measured in a 1 µg/mL Ti solution using a PFA nebulizer with an uptake rate of 125 µL/min. Signal intensities were 2 to 3 × 10−11 A for 49Ti, 48Ti, 47Ti using amplifiers having a 1011 Ω resistor in their feedback loop. Background levels in the pure 0.3 M HNO3–0.014 M HF running solution were between 1 to 4 × 10−14 and 10−15 A and washout times were around 5 min.
Data reduction was performed offline with a modified version of the algorithm by Compston and Oversby (1969), which allowed us to estimate the measurement precision using counting statistics (see Schoenberg et al. 2008; Kurzweil et al. 2018). The Ti stable isotope composition is expressed in the δ-notation relative to OL–Ti (Millet and Dauphas 2014):

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

(1)

For the sake of simplicity, henceforth δ^{49}Ti will be used in lieu of \(\delta(\text{^{49}Ti/^{47}Ti})\). Long-term reproducibility of OL–Ti is better than 0.033 ‰ (2 s.d.) after n = 138 measurements (95% c.i. = 0.003 ‰). Long-term reproducibility of Col–Ti is better than 0.048 ‰ (2 s.d.) after n = 558 measurements (95% c.i. = 0.002 ‰). Our long-term reproducibility of our glass reference material is better than 0.036 ‰ (2 s.d.) for FT1–10 after n = 6 measurements (95% c.i. = 0.019 ‰) and better than 0.014 ‰ (2 s.d.) for SM20 after n = 4 measurements (95% c.i. = 0.011 ‰). Measurements of Col–Ti, which ran through the complete separation procedure also yielded consistent results within uncertainties (2 s.d = 0.053 ‰) after n = 33 measurements (95% c.i. = 0.009 ‰). The 95% confidence interval includes the student t test. All spike:sample ratios from this study are shown in Supplementary Table 2.

Results

Experimental run products and attainment of chemical equilibrium

Most mineral phases in our run products had crystal lengths between 50 µm to several 100 µm. The silicate melt was always quenched to a homogeneous glass (Fig. 1). Overall, run products were homogeneous over the range of fO2 covered by experiments with respect to their mineral assemblages. Experiments carried out using the FT1–10 composition yielded ilmenite, clinopyroxene and glass, whereas the SM20 experiment contained rutile and silicate glass.

Grains of ilmenite and rutile, as well as clinopyroxene, were euhedral to subhedral in their crystal shape. Ilmenite shows a narrow range of variation in TiO2 contents from 53.2 to 55.9 wt.% across all experiments. Although some clinopyroxene grains show slight variations in their element contents, namely, in their Fe content, no variation of Ti could be observed in any crystal or glass phase from our experiments, neither by element mapping nor EPMA element profiles (Fig. 1 and Table 10 of the Supplementary), which is why we can assume equilibrium for Ti in our experimental samples.

Mass balance calculations of the Ti distribution in experimental run products

Mass balance calculations were performed for all our experiments except FT1–10 at IW-1, where only one loop was recovered, which was used for chemical Ti separation. The modal abundance of all phases was determined via image processing using ImageJ, and then recalculated to their mass fractions using the density of the respective mineral. The mass fraction of Ti contained by each phase was then determined using the mass fraction of each phase and its Ti content in wt.% as determined by EPMA. In the end, the fraction of each phase was multiplied by its Ti stable isotope composition and summed to determine the bulk Ti stable isotope composition of the experiment. This calculated composition was then compared with the measured bulk Ti stable isotope composition by MC–ICP–MS. Except for experiment FT1–10 at IW + 1, the bulk Ti isotope composition of each experiment calculated by mass balance, is within 95% c.i. of the respective glass standards (Table 5 of the Supplementary). The lack of reproducibility of experiment FT1–10 at IW + 1 is likely due to the contamination of ilmenite by either clinopyroxene or more likely glass during mineral separation. Nevertheless, for the bulk of the experiments, mass balance calculations, therefore, provide a valuable tool to verify the success of handpicking.
The Ti isotope composition of experimental run products

Results show that Ti-oxides have a lighter Ti stable isotope composition than corresponding clinopyroxenes and silicate melt (see Fig. 2a and Table 1). The $\delta^{49}$Ti of all phases shows variations with $f_{O_2}$, and isotopic differences ($\Delta^{49}$Ti$_{A-B} = \delta^{49}$Ti$_A - \delta^{49}$Ti$_B$) between ilmenite, clinopyroxene and silicate melt (FT1–10) become increasingly larger with decreasing $f_{O_2}$ (see Table 1) from FMQ–0.5 to IW-1. A similar relationship was observed for experiments yielding armalcolite, orthopyroxene and glass (Rzehak et al. 2021). The $\delta^{49}$Ti of ilmenite decreases from -0.010 ± 0.020 ‰ at FMQ-0.5 to -0.383 ± 0.093 ‰ at IW-1, whereas the $\delta^{49}$Ti of clinopyroxene ranges from a maximum of + 0.162 ± 0.029 ‰ at FMQ-0.5 to a minimum value of + 0.044 ± 0.005 ‰ at IW-1. The $\delta^{49}$Ti of glass increases from + 0.017 ± 0.016 ‰ to + 0.079 ± 0.012 ‰. For our rutile-bearing experiment in air, $\delta^{49}$Ti of rutile is at –0.025 ± 0.015 ‰, whereas the corresponding glass has a $\delta^{49}$Ti of + 0.161 ± 0.023 ‰.

Our results show that $\Delta^{49}$Ti$_{A-B}$ of equilibria associated with Ti-oxides become significantly larger with decreasing $f_{O_2}$ (Table 2) confirming the key role of Ti-oxides for Ti stable isotope fractionation (Fig. 2b). $\Delta^{49}$Ti$_{ilm-melt}$ (FT1–10) decreases from –0.026 ± 0.035 ‰ at FMQ-0.5 to –0.461 ± 0.093 ‰ at IW-1 and $\Delta^{49}$Ti$_{ilm-cpx}$ decreases from –0.172 ± 0.049 ‰ at FMQ-0.5 to –0.426 ± 0.093 ‰ at IW-1. In comparison, $\Delta^{49}$Ti$_{cpx-melt}$ (FT1–10) decreases from + 0.146 ± 0.033 ‰ at FMQ-0.5 to -0.035 ± 0.013 ‰ at IW-1. $\Delta^{49}$Ti$_{rut-melt}$ in air is –0.187 ± 0.027 ‰.

Discussion

Ti stable isotope composition of minerals

Terrestrial as well as lunar samples, show a wide range of $\delta^{49}$Ti, especially when they include Fe–Ti-oxides. In terrestrial systems, magmas that experience saturation in a Ti-bearing phase, i.e., Fe–Ti-oxides typically show wider

Table 1 $\delta^{49}$Ti isotope composition and 95% c.i. in ‰ of all synthetic phases from this study

| $f_{O_2}$ | Clinopyroxene (FT1–10) | Ilmenite (FT1–10) | Melt (FT1–10) |
|-----------|----------------------|------------------|---------------|
|           | $\delta^{49}$Ti      | 95% c.i.         | $\delta^{49}$Ti | 95% c.i. | $\delta^{49}$Ti | 95% c.i. |
| FMQ-0.5   | +0.162               | 0.029            | –0.010        | 0.020   | +0.017        | 0.016   |
| FMQ-1     | +0.177               | 0.011            | –0.036        | 0.031   | +0.053        | 0.014   |
| IW +1     | +0.125               | 0.018            | –0.007        | 0.013   | +0.065        | 0.019   |
| IW-1      | +0.044               | 0.005            | –0.383        | 0.093   | +0.079        | 0.012   |

Rutile (SM20) & Melt (SM20) & $\delta^{49}$Ti & 95% c.i. & $\delta^{49}$Ti & 95% c.i. 

Air & –0.025 & 0.015 & +0.161 & 0.023 

Experiments with FT1–10 composition were conducted at 1100 °C, whereas the SM20 experiment was performed at 1300 °C. For the amount of measurements $n$ refer to Supplementary Table 2.
variations in their $\delta^{49}\text{Ti}$ values compared to igneous samples, where no such saturation took place (Deng et al. 2018a, 2019; Zhao et al. 2020; Hoare et al. 2020). Moreover, the extent to which $\delta^{49}\text{Ti}$ varies as a function of magmatic differentiation appears to be tied to not only the onset, but also the timing of Ti-bearing oxide saturation (Deng et al. 2019; Hoare et al. 2020). Similar systematics have been observed for lunar rocks, as ilmenite-bearing high- and low-Ti basalts were shown to be systematically heavier than non-ilmenite bearing lunar basalts (Kommescher et al. 2020). Furthermore, the $\delta^{49}\text{Ti}$ of low-Ti basalts ($+0.01 \pm 0.047$ ‰; Millet et al. 2016; Kommescher et al. 2020) are similar to the BSE ($+0.005 \pm 0.005$ ‰; Millet et al. 2016) and chondritic values (Greber et al. 2017; Deng et al. 2018b), whereas high-Ti basalts show a wider range of $\delta^{49}\text{Ti}$ (between $+0.009$ and $+0.115$ ‰; Millet et al. 2016; Kommescher et al. 2020), which was specifically attributed to the fractional crystallization of Ti-oxides, as well as the partial melting of an ilmenite-bearing cumulates component (Kommescher et al. 2020).

Multiple studies have investigated the bulk Ti isotope compositions of terrestrial and lunar rocks. However, data for mineral–mineral or mineral-melt Ti stable isotope fractionation factors are currently scarce (Johnson et al. 2019; Mandal 2019; He et al. 2020; Greber et al. 2021; Rzehak et al. 2021; Hoare et al. 2022). Nevertheless, this information is crucial to understand and model the mechanisms of Ti stable isotope fractionation during magmatic processes that ultimately lead to the variations seen in the bulk Ti isotope compositions of magmatic rocks. Johnson et al. (2019) investigated terrestrial samples from the Kilauea Iki lava lake and showed that the Ti-oxides either displayed lighter or overlapping Ti stable isotope compositions than co-existing minerals and the bulk samples. Mandal (2019) investigated the Ti stable isotope composition of terrestrial Kneeling Nun Tuff (KNT) samples and also found that ilmenite and magnetite were isotopically lighter than corresponding silicates and the groundmass. A more recent study by He et al. (2020), who investigated mineral separates from the Qinghu monzonite, also yielded similar results. In their study, ilmenite and titanite were isotopically lighter than the whole rock, whereas hornblende, K-feldspar, plagioclase, and magnetite had higher $\delta^{49}\text{Ti}$ compared to the bulk rock. However, these results should be taken with caution, because magnetite was likely a late phase in the samples analysed by He et al. (2020) and thus not representative of an equilibrium mineral assemblage. Moreover, the feldspars in the He et al. study were very Ti-poor and likely vulnerable to contamination. This expectation was reinforced in a recent study by Greber et al. (2021) who found that magnetite had a lighter Ti stable isotope composition than the bulk rock, whereas olivine, quartz and plagioclase were heavier in $\delta^{49}\text{Ti}$. This was also shown in Hoare et al. (2022), who found that titanomagnetite displayed the lightest fractionation factor of all analysed Ti-oxides (rutile, ilmenite, magnetite) and attributed this to the Ti–O bond length in these minerals. Nevertheless, all studies on terrestrial rocks confirm the major role of Ti-oxides for Ti stable isotope fractionation, even if their geologic setting does not necessarily apply for lunar conditions due to their different redox regimes.

In addition to his work with terrestrial samples, Mandal (2019) determined the Ti stable isotope composition of different lunar mineral separates including ilmenite, pyroxene, plagioclase and olivine, finding that ilmenite is either isotopically lighter or within error of co-existing minerals and the bulk rock (e.g., sample 74,255 with $\delta^{49}\text{ilmenite} = +0.014$ ‰, $\delta^{49}\text{olivine} = -0.006$ ‰, $\delta^{49}\text{pyroxene} = +0.065$ ‰, $\delta^{49}\text{plagioclase} = +0.184$ ‰ and $\delta^{49}\text{bulk} = +0.041$ ‰, recalculated to OL–Ti). Likewise, our experimental Ti-oxides ilmenite and rutile are isotopically lighter than equilibrium silicate phases, namely, clinopyroxene and silicate melt, which is in agreement with previous findings (Millet et al. 2016; Johnson et al. 2019; Mandal 2019; He et al. 2020; Kommescher et al. 2020; Rzehak et al. 2021). Furthermore,
clinopyroxene from our study shows higher or overlapping $\delta^{49}\text{Ti}$ values compared to the co-existing silicate melt. This is in broad agreement with previous studies that determined the $\delta^{49}\text{Ti}$ content of mineral separates including silicates (Johnson et al. 2019; Mandl 2019; He et al. 2020; Rzehak et al. 2021) and confirms the key role of Ti-oxides for Ti isotope fractionation. However, silicate phases, especially olivine and pyroxene, are volumetrically more abundant than Ti-oxides, because they can make up to a 100% in certain stages of LMO solidification (cf. Table 7 of Supplementary) and may thus contain a significant amount of the bulk Ti of a sample. Therefore, their role in Ti isotope systematics cannot be neglected.

Interestingly, all mineral-melt and mineral–mineral equilibria from our study show a clear $fO_2$ dependent trend, whose sigmoidal shape is reminiscent of the $fO_2$ dependent partitioning of redox sensitive elements into several magmatic minerals, such as olivine, pyroxene or spinel determined by Mallmann and O’Neill (2007, 2009). The partition coefficients of Ti was shown to increase with decreasing $fO_2$ for orthopyroxene-melt, clinopyroxene-melt and olivine-melt equilibria, which was attributed to an increasing amount of trivalent Ti with decreasing $fO_2$ (Mallmann and O’Neill 2009). This behaviour is reflected by our results for $\Delta^{49}\text{Ti}_{\text{opx-melt}}$ (Rzehak et al. 2021), whereas $\Delta^{49}\text{Ti}_{\text{cpx-melt}}$ seems to behave differently, which is likely due to compositional differences that will be discussed in the following two sections. The sigmoidal shape of the redox-dependent curve depends on the stoichiometry of the redox reaction as a function of $fO_2$ that leads to a redox exchange of Ti and the equilibrium constant (see Supplementary document for more details). This redox-dependency was already observed for armalcolite- and orthopyroxene-bearing equilibria in our previous study (Rzehak et al. 2021) and can be mathematically described by a least-squares regression. Recent studies have addressed how the presence of $\text{Ti}^{3+}$ in more reduced phases, especially olivine and pyroxene, are volumetrically more abundant than Ti-oxides, because they can make up to a 100% in certain stages of LMO solidification (cf. Table 7 of Supplementary) and may thus contain a significant amount of the bulk Ti of a sample. Therefore, their role in Ti isotope systematics cannot be neglected.

Comparison with previously published reduced partition function values ($\beta$)

To compare our experimental data with the results of ab initio calculations, we first needed to calculate representative values for the reduced partition function (β) of our samples. Because $1000 \ln \beta = \Delta^{49}\text{Ti}_{\text{A-B}} \sim 1000 \ln \sigma_{\text{A-B}}$ (see Young et al. 2015 for more details), β, which is the reduced partition function, can be calculated for silicate melt from our experiments by subtracting our $\Delta^{49}\text{Ti}_{\text{arm-melt}}$ at IW-1 (Rzehak et al. 2021) from the β value for karrooite ($\text{MgTi}_2\text{O}_3$) reported by Leitzke et al. (2018). Karrooite is the iron-free endmember of the pseudobrookite group and is, therefore, comparable to our synthetic armalcolite which crystallized from an iron-free starting composition. With this estimate for β of silicate melt, it was possible to display the rest of our data set relative to the silicate melt line (Fig. 3a). We were then able to calculate the resulting β from our experimental data set for clinopyroxene, orthopyroxene and ilmenite, which we will compare to results from the literature in the following sections. To make more robust comparisons, all β values (including literature values) were recalculated to one temperature, namely, 1200 K (see Supplementary Table 6).

The $\beta_{\text{clinopyroxene}}$ of 1.12 ± 0.04 ‰ from our study is within the range of other clinopyroxene data from ab initio modelling (see Supplementary Table 6), which range from 0.92 to 1.74 ‰ (Leitzke et al. 2018; Wang et al. 2020; Aarons et al. 2021). The same applies for our $\beta_{\text{orthopyroxene}}$ of 1.39 ± 0.04 ‰, which overlaps with the range of 0.92 to 1.53 ‰ by other studies (Wang et al. 2020). Our calculated uncertainties are propagated from $\Delta^{49}\text{Ti}$. Leitzke et al. (2018) presented not only the β value for karrooite but also for endmembers of clinopyroxene, where Ti has different coordination numbers (four-/sixfold) and oxidation states ($\text{Ti}^{3+/4+}$; Fig. 3a). The lowest β values reported by Leitzke et al. (2018) were calculated for Ti in armalcolite and $\text{Ti}^{3+}$ on the octahedral Mg site of clinopyroxene, whereas their highest reported value can be associated with the substitution of $\text{Ti}^{4+}$ into the tetrahedral Si site of clinopyroxene. Our clinopyroxene line can be met with 21% $[\text{IV}]\text{Ti}^{4+}$ and 79% $[\text{VI}]\text{Ti}^{3+}$ or with 73% $[\text{VI}]\text{Ti}^{4+}$ and 27% $[\text{VI}]\text{Ti}^{3+}$. Our orthopyroxene line can be matched with 37% $[\text{IV}]\text{Ti}^{4+}$ and 63% $[\text{VI}]\text{Ti}^{3+}$ or with 55% $[\text{IV}]\text{Ti}^{4+}$ and 45% $[\text{VI}]\text{Ti}^{3+}$. However, if we compare these theoretical endmembers of our pyroxenes to XANES measurements by Leitzke et al. (2018) conducted with ortho- and clinopyroxenes of a composition similar to ours, our results are partially in contradiction to their measurements (Table 3).

Based on our estimates for β, the clinopyroxene in our experiments would appear to contain less $[\text{IV}]\text{Ti}^{4+}$ but more $[\text{VI}]\text{Ti}^{4+}$ and $[\text{VI}]\text{Ti}^{3+}$, which is what we would expect from XANES measurements of pyroxenes in natural high-Ti basalts that were shown to contain up to 60% $\text{Ti}^{3+}$ (Sung et al. 1974; Simon and Sutton 2018), because pyroxenes are expected to prefer $\text{Ti}^{3+}$ over $\text{Ti}^{4+}$ (Simon et al. 1991) due to its better fit in the octahedral site (Papike et al. 2005). For orthopyroxene we would expect the same behaviour as for clinopyroxene as indicated by ab initio fractionation factors derived by Wang et al. (2020). However, the range of experimental orthopyroxenes measured by XANES in Leitzke et al. (2018) seems to be consistent with a lower β for orthopyroxene, which could simply be due to the low
sample number of orthopyroxene \((n=2)\) crystals reported by Leitzke et al. (2018). Nevertheless, orthopyroxene from our samples shows a higher ß factor than clinopyroxenes, as well as a higher \(\Delta^{49}\text{Ti}\), which we will discuss more extensively in the next section.

Our estimated ß for ilmenite of \(0.70 \pm 0.10 \%\) is slightly lower than \(0.88 \%\) presented by Wang et al. (2020), but likely within error, since ab initio does not provide an error estimation. Furthermore, the oxidation state of Fe in our experiments can influence the amount and oxidation state of Ti within the ilmenite. Geikielite \((\text{MgTiO}_3)\) is not directly comparable to our Fe-rich ilmenites. Lower Fe contents

\[\text{Table 3} \quad \text{Comparison of calculated endmembers for our ß factors of pyroxene}\]

| Mineral            | \([\text{IV}]\text{Ti}^{4+}\) | \([\text{VI}]\text{Ti}^{4+}\) | \([\text{VI}]\text{Ti}^{3+}\) |
|--------------------|-----------------|-----------------|-----------------|
| Cpx (Leitzke et al. 2018) | 0.30–0.72       | 0.15–0.37       | 0.13–0.33       |
| Cpx (this study)    | 0.21            | 0.00            | 0.79            |
| Opx (Leitzke et al. 2018) | 0.30–0.35       | 0.33            | 0.32–0.37       |
| Opx (this study)    | 0.37            | 0.63            | 0.00            |

The range by Leitzke et al. (2018) was derived from experimental clinopyroxenes \((n=7)\) and orthopyroxenes \((n=2)\).
in geikielite could explain higher $\beta$ values (cf. Wang et al. 2020; Aarons et al. 2021).

Aarons et al. (2021) used fresnoite (Ba$_2$Ti(Si$_2$O$_7$)O) as a proxy for silicate melt due to the difficulty of performing ab initio modelling for silicate melt and to the fact that Ti is coordinated similarly (fivefold) in both phases. Using this approach Aarons et al. (2021) obtained a $\beta$ value of 1.23 %, whereas ilmenite from the Rzehak et al. (2021) study only have a maximum of 0.45 wt.% Al$_2$O$_3$ under the same conditions, whereas the orthopyroxene from the Rzehak et al. (2021) study only have a maximum of 0.45 wt.% Al$_2$O$_3$ under the same conditions. This is also indicated by its higher $\Delta^{49}$Ti$_{opx-melt}$ of +0.050 ± 0.025 % (Rzehak et al. 2021) compared to the lower $\Delta^{49}$Ti$_{cpx-melt}$ value -0.035 ± 0.013 % reported here for the same $f$O$_2$. This different behaviour, as well as the higher amount of [IV]Ti$^{4+}$ in orthopyroxene, could be related to the proportion of Al present in either pyroxene type, and differences in the interaction between Ti and Al in the M1 and T sites in each pyroxene type. Indeed, clinopyroxene in our experiments can contain up to 2.9 wt.% Al$_2$O$_3$ at IW + 1, whereas the orthopyroxene from the Rzehak et al. (2021) study only have a maximum of 0.45 wt.% Al$_2$O$_3$ under the same conditions. Other studies found that tetravalent fourfold coordinated Ti is occurring more often in minerals that were equilibrated at low pressures or high temperatures, and contain small amounts of tetrahedrally coordinated Al$^{3+}$, which typically enable a coupled substitution of Al$^{3+}$ and Ti$^{4+}$ in sixfold coordination into pyroxene (Sepp and Kunzmann 2001; Nazzareni et al. 2004). However, this possibility cannot be tested with our current data set, as it does not include experiments, where the proportion of Al$_2$O$_3$ has changed systematically at constant $f$O$_2$. Such an experimental data set would be desirable to isolate the singular effect that Al$_2$O$_3$ has on $\Delta^{49}$Ti$_{opx-melt}$ and $\Delta^{49}$Ti$_{cpx-melt}$. Nevertheless, it remains an interesting possibility and merits further study.

Overall, our $\Delta^{49}$Ti$_{cpx-melt}$ decreases from +0.146 ± 0.033 % at FMQ -0.5 to -0.035 ± 0.013 % at IW-1 at 1100 °C. Thus, our $\Delta^{49}$Ti$_{cpx-melt}$ are within the values expected from ab initio modelling that yield $\Delta^{49}$Ti$_{cpx-melt}$ between -0.234 to +0.251 % at the same temperature depending on the amount of Ti$^{3+}$ in cpx (Wang et al. 2020; Aarons et al. 2021).

The $\Delta^{49}$Ti$_{ilm-melt}$ calculated from our experiments, decreases from -0.461 ± 0.093 % at FMQ -0.5 to -0.461 ± 0.093 % at IW-1. This is lower than indicated from ab initio modelling. For example, the $\Delta^{49}$Ti$_{ilm-melt}$ by Wang et al. (2020) is -0.271 % at the same temperature (1100 °C, calculated with $f$$_{melt}$ by Aarons et al. 2021). However, if we recalculate the $\Delta^{49}$Ti$_{ilm-melt}$ of Wang et al. (2020) with our $f$$_{melt}$ of 1.31 %, a $\Delta^{49}$Ti$_{ilm-melt}$ of -0.332 % is obtained, which would be close to our estimated value especially considering that ab initio models provide no errors. Compared to the $\Delta^{49}$Ti$_{ilm-melt}$ of -0.188 % reported by Mandl (2019) for terrestrial samples from KNT, none of our $\Delta^{49}$Ti$_{ilm-melt}$ is in agreement. Mandl et al. (2019) obtained a $\Delta^{49}$Ti$_{ilm-melt}$ value of -0.368 % at an eruption temperature of 710 °C. Recalculated to the temperature of our experiments (1100 °C) the value of -0.188 %, is neither in agreement with our value for lunar conditions at IW-1 nor with our measured $\Delta^{49}$Ti$_{ilm-melt}$ of -0.026 ± 0.025 % at comparable terrestrial $f$O$_2$ (i.e., FMQ-0.5). The KNT samples characterized by Mandl (2019) are rhyolitic and more SiO$_2$-rich (Giles 1965) than our experimental compositions that are based on lunar basalts, and thus any $\Delta^{49}$Ti$_{ilm-melt}$ obtained from those samples might not be comparable to our experimental work.

Due to their compositional difference, our ilmenite-melt fractionation factors are not overlapping with fractionation factors for geikielite-melt from the literature. This is consistent with predictions from ab initio modelling by Wang et al. (2020). Geikielite represents an endmember of the ilmenite–geikielite solid solution and contains mostly Mg, whereas ilmenite contains a significant amount of Fe. Nevertheless, fractionation factors for geikielite are shown in Fig. 3b for the sake of completeness.

Our $\Delta^{49}$Ti$_{ilm-cpx}$ decreases from -0.172 ± 0.035 % at FMQ-0.5 to -0.426 ± 0.093 % at IW-1, where it should already contain a significant amount of trivalent Ti (up to 40%; Leitzke et al. 2018). This agrees well with calculated $\Delta^{49}$Ti$_{ilm-cpx}$ of -0.511 % (recalculated to 1100 °C, from Wang et al. 2020). Again, geikielite–clinopyroxene fractionation factors are shown in Fig. 3c. Although they are not necessarily comparable to our experimental Fe-bearing ilmenite, they overlap with our ilm-cpx fractionation factors (cf. Wang et al. 2020).

Overall, compared to $\Delta^{49}$Ti$_{armalcolite-melt}$ -0.200 ± 0.033 % presented by Rzehak et al. (2021), $\Delta^{49}$Ti$_{ilm-melt}$ of -0.461 ± 0.093 % from this study seems to show an elevated fractionation of Ti stable isotopes at comparable $f$O$_2$ (IW-1). The average reported valences of ilmenite and armalcolite at IW-1 are 3.65 ± 0.09 and 3.58 ± 0.13, respectively, and, therefore, within error of each other. Furthermore, Ti is in sixfold coordination in both minerals (Leitzke et al. 2018). The main difference between the armalcolites in the Rzehak et al. (2021) study and the ilmenite in this study is the fact that the latter is Fe-bearing, whereas the former is Fe-free (karrooite), which could be the reason for the difference in their $\Delta^{49}$Ti. This expectation is consistent with the conclusion by Wang et al. (2020) that $\Delta^{49}$Ti$_{ilm-melt}$ decreases with increasing Fe/(Fe + Mg) contents. Slightly
different bonding energies and force constants associated with the bonding environment of Ti in ilmenite may ultimately explain lower Δ49Ti\textsubscript{ilmenite-melt} at IW-1. Alternatively, the different nature of Ti second neighbours in the structures of ilmenite and armalcolite may also cause lower Δ49Ti\textsubscript{ilmenite-melt}, considering that similar interactions have been shown for Fe and Si isotopes in olivine by Rabin et al. (2021).

Rutile crystallization fractionates Ti isotopes even greater when compared to ilmenite under conditions, where Ti is exclusively tetravalent. This is exemplified by its Δ49Ti\textsubscript{rutile-melt} of −0.187 ± 0.027 ‰ (in air), compared to Δ49Ti\textsubscript{ilmenite-melt} of −0.026 ± 0.010 ‰, (FMQ-0.5). This can easily be explained by the force constant of Ti in rutile, which is much lower than for other minerals (Wang et al. 2020; Aaron et al. 2021) leading to lower Δ49Ti values. Our data are also within error of Δ49Ti\textsubscript{rutile-melt} of sample MDH15 from Hoare et al. (2022) that was originally an experimental sample by Klemme et al. (2005), derived by 1-atmosphere experiments at 1250 °C in air, which was subsequently processed by Hoare et al. (2022) to determine its Ti stable isotope composition. Due to its experimental conditions, this sample is comparable to our experimentally derived rutile. However, the Δ49Ti\textsubscript{rutile-melt} of sample Hd4 from the same study was obtained under more reduced conditions and is not within error of our experimental rutile, which is probably due to the fact that at more reduced conditions, more Ti\textsuperscript{3+} is incorporated into the rutile. Overall, our data meets expectation from the DFT modelling by Wang et al. (2020), with high-precision HFSE data by Thiemens et al. (2019). Following Thiemens et al. (2019), we have taken mineral/melt partition coefficients for olivine, pigeonite, plagioclase, orthopyroxene, clinopyroxene and armalcolite from van Westrenen et al. (2000), Fonseca et al. (2014) and Leitzke et al. (2016, 2017), whereas ilmenite/silicate partition coefficients consist of an average of all high-Ti experiments from Dygert et al. (2013; Table 4). Mineral modal abundances during LMO solidification were taken from different models by Snyder et al. (1992), Elkins-Tanton et al. (2011), Lin et al. (2017), Charlier et al. (2018) and Rapp and Draper (2018) and can be found in the Supplementary Table 7.

Implications for the behavior of Ti stable isotopes during lunar magmatism

Our data set of mineral-melt and mineral–mineral Δ49Ti has been used to model the Ti isotope composition and HFSE concentrations of the LMO and its cumulates during crystallization. High field strength elements can be used to trace Ti-oxide crystallization, since KREEP is enriched in incompatible elements, such as U and Th, whereas ilmenite favours the incorporation of Ti, Hf and Zr. The latter elements are thus expected to be fractionated by ilmenite-bearing cumulates (Münker 2010; Gross and Joy 2016). Moreover, since the petrogenesis of high- and low-Ti mare basalts is the result of partial melting of mixtures of LMO cumulates, our Ti isotope data can also be used to investigate these processes. However, as we had already published a prior model for the petrogenesis of high- and low-Ti basalts, we refer to the Supplementary document of this paper for an updated version of these models using our up-to-date experimentally determined isotope fractionation factors. For all our models, we combined our measured fractionation factors (Table 2), and the fractionation factor determined for olivine by Wang et al. (2020), with high-precision HFSE data by Thiemens et al. (2019). Following Thiemens et al. (2019), we have taken mineral/melt partition coefficients for olivine, pigeonite, plagioclase, orthopyroxene, clinopyroxene and armalcolite from van Westrenen et al. (2000), Fonseca et al. (2014) and Leitzke et al. (2016, 2017), whereas ilmenite/silicate partition coefficients consist of an average of all high-Ti experiments from Dygert et al. (2013; Table 4). Mineral modal abundances during LMO solidification were taken from different models by Snyder et al. (1992), Elkins-Tanton et al. (2011), Lin et al. (2017), Charlier et al. (2018) and Rapp and Draper (2018) and can be found in the Supplementary Table 7.

In all lunar magma ocean crystallization models, solidification begins with olivine and is followed or coupled with the crystallization of orthopyroxene, where these relatively dense minerals sink to the bottom of the LMO and form cumulates. This is followed by the crystallization of plagioclase and clinopyroxene, where flotation of the former led to the formation of the lunar anorthositic crust as plagioclase was buoyant in the LMO (Walker and Hays 1977). Towards the end of LMO solidification, ilmenite becomes a liquidus phase together with pigeonite (Snyder et al. 1992; Elkins-Tanton et al. 2011; Lin et al. 2017; Charlier et al. 2018; Rapp and Draper 2018; Johnson et al. 2021).

### Table 4

| Mineral-melt pair         | DTi | DHf | DTa | DZr | DW | DU | Reference |
|---------------------------|-----|-----|-----|-----|----|----|-----------|
| Olivine-melt              | 0.008795 | 0.000390 | 0.000054 | 0.000330 | 0.005000 | 0.000013 | 2         |
| Clinopyroxene-melt        | 0.189038 | 0.024000 | 0.000990 | 0.010000 | 0.047000 | 0.001300 | 2, 3      |
| Orthopyroxene-melt        | 0.058760 | 0.005000 | 0.000760 | 0.001600 | 0.005900 | 0.000510 | 3         |
| Ilmenite-melt             | 4.700843 | 1.000000 | 1.360000 | 1.010000 | 0.963609 | 0.003227 | 3         |
| Plagioclase-melt          | 0.021735 | 0.000220 | 0.000250 | 0.000360 | 0.000590 | 0.000420 | 2, 3, 4    |
| Pigeonite-melt            | 0.071000 | 0.005000 | 0.000760 | 0.001600 | 0.005900 | 0.000500 | 3, 5       |
| Armalcolite-melt          | 5.600000 | 1.000000 | 1.360000 | 1.010000 | 0.963609 | 0.003227 | 3         |

(1: Dygert et al. 2013, 2: Fonseca et al. 2014, 3: Leitzke et al. 2016, 4: Leitzke et al. 2017, 5: van Westrenen et al. 2000)
and perhaps along with other oxides, such as magnesioferrite (MgFe\textsubscript{3}Ti\textsuperscript{2+}O\textsubscript{4}), ulvöspinel (Fe\textsuperscript{2+}\textsubscript{2}Ti\textsuperscript{4+}O\textsubscript{4}) or chromite (FeCr\textsubscript{2}O\textsubscript{4}) forming oxide-rich cumulates (Elkins-Tanton et al. 2011). These ilmenite-bearing cumulates represent a late stage of LMO solidification (usually > 90 Percent of Solidification PCS; Snyder et al. 1992; Elkins-Tanton et al. 2011; Lin et al. 2017; Charlier et al. 2018; Rapp and Draper 2018) and are expected to have an isotopically lighter Ti stable isotope composition due to the presence of ilmenite, which preferentially incorporates light Ti isotopes (cf. Millet et al. 2016). The co-genetic urKREEP (potassium-, rare earth element- and phosphorous-rich silicate liquid), however, which represents the last degree of LMO solidification (Warren and Wasson 1979) is isotopically heavier, as shown by positive δ\textsuperscript{49}Ti values of natural lunar KREEP-rich basalts, which display δ\textsuperscript{49}Ti values between +0.117 ± 0.027 and +0.330 ± 0.034 ‰ (Greber et al. 2017; Kommescher et al. 2020), far in excess to the average mare basalt (~0.01 to +0.03 ‰; Millet et al. 2016).

The presumed co-genetic relationship between urKREEP and ilmenite-bearing cumulates, and their disparate Ti isotope compositions, allow us to test the petrogenic processes associated with these ancient lunar reservoirs by modelling the solidification of the LMO in tandem with our experimental results. To model LMO solidification and how the Ti isotope composition of the LMO changes throughout this process, we used an initial LMO composition with 3180 µg/g Ti (recalculated from Lin et al. 2017). In contrast to previous studies, we incorporated our measured silicate-melt equilibrium isotope fractionation factors, coupled with ab initio olivine data from Wang et al. (2020), into our modelling, whereas previously only a bulk fractionation factor for Ti-oxides was considered (cf. Millet et al. 2016; Kommescher et al. 2020). All fractionation factors were adapted to the modal abundances of each step of LMO solidification. The ilmenite-bearing cumulates are best represented by the last 10% of solid, whereas the urKREEP is represented by the last percent of liquid. As the IBC were denser than the last 10% of solid, whereas the urKREEP is represented by the last ten percent of LMO solidification as it is important to notice that in the various petrological models shown, the onset of Ti-oxide crystallization takes place at different PCS of LMO crystallization, as, e.g., the model by Elkins-Tanton et al. (2011), where Ti-oxide crystallization starts at 87 PCS. Furthermore, the increments of mineral stabilities slightly differ between the different models as can best be seen in the close-up of Fig. 4, where δ\textsuperscript{49}Ti calculated using the Rapp and Draper (2018) LMO crystallization model (black line) increases slightly earlier when compared to the δ\textsuperscript{49}Ti calculated from other models.

All scenarios are compared to the modelling results for δ\textsuperscript{49}Ti\textsubscript{urKREEP} and δ\textsuperscript{49}Ti\textsubscript{IBC} by Millet et al. (2016) and Kommescher et al. (2020). Kommescher et al. (2020) obtained a δ\textsuperscript{49}Ti\textsubscript{urKREEP} of +0.26 ± 0.10 ‰ (98 PCS), +0.29 ± 0.07 ‰ (99 PCS) and +0.31 ± 0.05 ‰ (99.2 PCS) and δ\textsuperscript{49}Ti\textsubscript{IBC} of -0.010 ± 0.013 ‰ (98 PCS), -0.0075 ± 0.0062 ‰ (99 PCS) and -0.0060 ± 0.0034 ‰ (99.2 PCS), whereas Millet et al. (2016) modeled a δ\textsuperscript{49}Ti\textsubscript{urKREEP} of +0.288 ‰, which will subsequently be used as a comparison for values at 99 PCS.

In scenario a (Fig. 4a), where only ilmenite is considered to fractionate Ti isotopes using the equilibrium isotope fractionation factor estimate from Millet et al. (2016) as done previously by Kommescher et al. (2020), the δ\textsuperscript{49}Ti\textsubscript{urKREEP} of both models by Millet et al. (2016) and by Kommescher et al. (2020) is perfectly reproduced, which is not surprising as we basically recalculated their model with the mineral abundance of the different petrological models. Scenario a results in a mean δ\textsuperscript{49}Ti\textsubscript{urKREEP} of +0.286 ± 0.032 ‰ (99 PCS) and +0.329 ± 0.036 ‰ (99.5 PCS) and δ\textsuperscript{49}Ti\textsubscript{IBC} of -0.100 ± 0.001 ‰ (99 PCS) and -0.101 ± 0.001 ‰ (99.5 PCS). At 98 PCS not all petrological models contain ilmenite, which is the reason why for scenario a (and b) we did not calculate a mean value for ilmenite-bearing cumulates and urKREEP at this step. The great fit of scenario a results from the relatively high fractionation factor of ~ −0.103 ‰ (~1220 °C) from Millet et al. (2016) that was derived empirically by modelling the evolution of a primitive basaltic melt and was also used by Kommescher et al. (2020) to model LMO solidification. Millet et al. (2016) determined a bulk oxide-melt equilibrium fractionation factor from their terrestrial rocks, which results in a good estimate for urKREEP for all LMO models, although the basalt used for their model strongly differs from a typical lunar basalt.

However, assuming Ti-oxides are solely responsible for Ti stable isotope fractionation does not result in an overlap with any urKREEP estimates when we use our experimentally
determined fractionation factor for ilmenite-melt (Fig. 4b) as this results in $\delta^{49}\text{Ti}_{\text{urKREEP}}$ of $+1.282 \pm 0.142$ ‰ (99 PCS) and $+1.476 \pm 0.163$ ‰ (99.5 PCS) and in $\delta^{49}\text{Ti}_{\text{IBC}}$ of $-0.446 \pm 0.004$ ‰ (99 PCS) and $-0.451 \pm 0.003$ ‰ (99.5 PCS). The reason for these high values is our fractionation factor for ilmenite of $-0.38$ ‰ that is way higher than the fractionation factor derived empirically at a comparable temperature ($\sim 1220$ °C) by Millet et al. (2016). Since our fractionation factors for ilmenite are overlapping with literature values from mineral separates and ab initio modelling, our fractionation factor for ilmenite seems reasonable. However, data from these studies indicate Ti stable isotope fractionation by all Ti-bearing minerals, which is why the assumption that only Ti-oxides fractionate Ti stable isotopes seems to be incorrect.

Therefore, for scenario c (Fig. 4c), we assumed that Ti isotopes are fractionated by all minerals, and equilibrium fractionation factors for clinopyroxene, orthopyroxene, ilmenite and armalcolite and olivine were used. This scenario fails to fully reproduce modelled $\delta^{49}\text{Ti}$ values for urKREEP from Kommescher et al. (2020) and Millet et al. (2016) no matter which modal abundances we use. Our mean modelled $\delta^{49}\text{Ti}$ for urKREEP are $+0.046 \pm 0.070$ ‰ (98 PCS), $+0.150 \pm 0.051$ ‰ (99 PCS) and $+0.173 \pm 0.058$ ‰ (99.5 PCS) and are, therefore, significantly lower compared to $\delta^{49}\text{Ti}_{\text{urKREEP}}$ by Millet et al. (2016) and Kommescher at al. (2020). Our mean $\delta^{49}\text{Ti}_{\text{IBC}}$ are $-0.022 \pm 0.027$ ‰ (98 PCS), $-0.052 \pm 0.017$ ‰ (99 PCS) and $-0.053 \pm 0.017$ ‰ (99.5 PCS) and, therefore, within error of $\delta^{49}\text{Ti}_{\text{IBC}}$ by Kommescher et al. (2020). However, the discrepancy between our modelled urKREEP values is unrelated to our positive fractionation factor for orthopyroxene since exchanging it with one determined for clinopyroxene also fails to reproduce the $\delta^{49}\text{Ti}$ of urKREEP. Nevertheless, small improvements can be observed for LMO crystallization models, where orthopyroxene is highly abundant (Elkins-Tanton et al. 2011; Lin et al. 2017).

To meet the estimates for urKREEP, we increased the ilmenite contents of ilmenite-bearing cumulates from an average of 10% (5–14% depending on the LMO model) to 15% at 99 PCS in scenario d at the expense of plagioclase (Fig. 4d), while still assuming that all other mineral phases contribute to the fractionation of Ti isotopes during LMO crystallization. This is not an unreasonable assumption as Hess and Parmentier (1995) argued that the ilmenite-bearing cumulates could contain $\sim 15\%$ ilmenite and $\sim 85\%$ pyroxene ± plagioclase. The slight increase of ilmenite in the ilmenite-bearing cumulates provides a good fit for urKREEP for all lunar models used in this study leading to a mean $\delta^{49}\text{Ti}_{\text{urKREEP}}$ of $+0.075 \pm 0.065$ ‰ (98 PCS), $+0.283 \pm 0.031$ ‰ (99 PCS) and $+0.326 \pm 0.036$ ‰ (99.5 PCS) and to $\delta^{49}\text{Ti}_{\text{IBC}}$ of $-0.039 \pm 0.023$ ‰ (98 PCS), $-0.079 \pm 0.008$ ‰ (99 PCS) and $-0.079 \pm 0.008$ ‰ (99.5 PCS). For individual results from each LMO model, the reader can refer to Fig. 4c.
to Table 9 of the Supplementary. In Table 5, we provide an overview of all mean modelled values from scenario a to d.

Since experimental as well as modelled Δ^{49}Ti values (Wang et al. 2020; Aarons et al. 2021) are available now, we consider it important to model Ti isotope fractionation during LMO solidification by including fractionation factors for all minerals that can incorporate Ti into their mineral structure. Therefore, we approve scenario d as the most reliable model for LMO solidification. Importantly, this scenario requires a slightly higher ilmenite content of ~15% in IBC to reproduce estimates of δ^{49}Ti of urKREEP.

In addition to δ^{49}Ti, we modelled the concentrations of several trace elements as Hf, Zr, Ti, Ta, U and W in the LMO using scenario d (Fig. 4d). As KREEP is enriched in incompatible elements such as U and Th and ilmenite-bearing cumulates are enriched in Ti, Hf and Zr, these elements can be used to trace Ti-oxide crystallization (Münker 2010; Gross and Joy 2016). Our starting composition contained 17.1 µg/g Zr (Synder et al. 1992), 0.51 µg/g Hf (Snyder et al. 1992), 0.08 µg/g Ta (recalculated from Nb/Ta by Münker 2010 and Nb by Snyder et al. 1992), 0.0205 µg/g W (Münker 2010) and 0.06 µg/g U (Wänke et al. 1977). Using available partition coefficients for HFSE (Table 4), the abundance of HFSE in KREEP after ilmenite-bearing cumulates formation can be modelled and compared to former estimates for urKREEP (Warren 1989; Table 6).

An even better indicator for Ti-oxide crystallization than trace element concentrations are HFSE ratios, since Ti, Hf and Zr are much more compatible in ilmenite than U. Therefore, it is most convenient to consider the last percent (96 to 99.9 PCS) of LMO solidification when ilmenite is present. Most models reach predictions from Warren (1989) at 99 PCS (Fig. 6a–c). Overall, scenario b with slightly increased ilmenite contents in ilmenite-bearing cumulates not only reproduces U/Hf, U/Zr and U/Ti from Warren (1989), but also the estimates for δ^{49}Ti of urKREEP of 0.26–0.31 ‰ (Millet et al. 2016; Kommescher et al. 2020). A special case, however, is Hf/W, where our modelled values and even natural KREEP-rich samples result in a higher Hf/W than the range of 8.7–16.7 given by Warren (1989). This could indicate that their W estimate is too low (Fig. 6d). However, fractional crystallization of the ilmenite-bearing cumulates increases δ^{49}Ti and decreases the Hf/W of the modelled

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**Table 5** Overview of modelled values for urKREEP and ilmenite-bearing cumulates from Lunar Magma Ocean solidification at 98 percent of solidification (PCS), 99 PCS and 99.5 PCS

| Scenario/a | δ^{49}TiurKREEP | δ^{49}TiIBC | δ^{49}TiurKREEP | δ^{49}TiIBC | δ^{49}TiurKREEP | δ^{49}TiIBC |
|------------|-----------------|------------|-----------------|------------|-----------------|------------|
| Millet et al. (2016) | +0.26±0.10 ‰ | +0.288%e | +0.010 ±0.013 ‰ | +0.29±0.07 ‰ | +0.0075±0.0062%e | +0.31±0.05 ‰ |
| Kommescher et al. (2020) | +0.286±0.032 ‰ | +0.329±0.036 ‰ | +0.100±0.001 ‰ | +0.446±0.004 ‰ | +0.451±0.003 ‰ | +0.326±0.036 ‰ |
| Scenario a | +0.046±0.070 ‰ | +0.283±0.031 ‰ | +0.022±0.027 ‰ | +0.283±0.031 ‰ | +0.079±0.008 ‰ | +0.326±0.036 ‰ |
| Scenario b | +0.075±0.065 ‰ | +0.283±0.031 ‰ | +0.039±0.023 ‰ | +0.283±0.031 ‰ | +0.079±0.008 ‰ | +0.326±0.036 ‰ |
| Scenario c | +0.286±0.142 ‰ | +1.476±0.163 ‰ | +0.52±0.017 ‰ | +0.52±0.017 ‰ | +0.52±0.017 ‰ | +0.52±0.017 ‰ |
| Scenario d | +1.282±0.142 ‰ | +1.476±0.163 ‰ | +0.52±0.017 ‰ | +0.52±0.017 ‰ | +0.52±0.017 ‰ | +0.52±0.017 ‰ |

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**Table 6** Comparison of our modelled HFSE concentrations for urKREEP at 99 PCS with modal abundances from Lin et al. (2017) and the values proposed by Warren (1989) in µg/g

| Element | HFSE of urKREEP at 99 PCS in µg/g (best fit) | Warren (1989) in µg/g |
|---------|-----------------------------------------------|-----------------------|
| Ti      | 12,272                                         | 12,000                |
| Ta      | 4.2                                            | 5                     |
| Hf      | 38                                             | 38                    |
| Zr      | 1382                                           | 1400                  |
| U       | 6.0                                            | 6.1                   |
| W       | 1.9                                            | 3                     |

The modal abundances by Lin et al. (2017) provided the best fit; however, all modelled HFSE concentrations can be found in Supplementary Table 9.
liquid starting roughly at a ratio of ~25 before the onset of ilmenite crystallization. This overlaps with the value that is proposed for the BSE by König et al. (2011) and is consistent with the assumption that Earth and Moon initially had the same Hf/W ratio before core formation as pointed out by Thiemens et al. (2019).

With the new constraints we provide on lunar mineral–mineral and mineral-melt Ti isotope fractionation factors, we find that most modelled δ\(^{49}\)Ti and HFSE values overlap with estimates of urKREEP by Warren (1989), Millet et al. (2016) and Kommescher et al. (2020). This finding not only validates the modal abundances from all LMO models that were used in this study (Snyder et al. 1992; Elkins-Tanton et al. 2011; Lin et al. 2017; Charlier et al. 2018; Rapp and Draper 2018) but also shows that Ti isotope fractionation is controlled by minerals other than Ti-oxides.

**Concluding remarks**

Ti stable isotope fractionation factors for clinopyroxene-melt, rutile-melt, ilmenite-melt and ilmenite–clinopyroxene equilibria were determined from an experimental data set obtained at different fO\(_2\) from more oxidized to more reducing lunar conditions (IW-1). Δ\(^{49}\)Ti\(_{A→B}\) shows increasing fractionation with decreasing fO\(_2\) (down to IW-1), which appears to be correlated with the increasing abundance of Ti\(^{3+}\) within the minerals (see Leitzke et al. 2018). Furthermore, this redox-dependent fractionation
of Ti stable isotopes is reminiscent of the crystal/silicate melt partitioning of Ti reported by Mallmann and O’Neill (2007, 2009), which has previously been observed for another armalcolite-bearing data set by Rzehak et al. (2021). Moreover, these newly determined fractionation factors were combined with mineral-melt partition coefficients by van Westrenen et al. (2000), Dygert et al. (2013), Fonseca et al. (2014) and Leitzke et al. (2016, 2017), high-precision HFSE data by Thiemens et al. (2019) and with $\delta^{49}$Ti data of natural high- and low-Ti basalts by Millet et al. (2016), Mandl (2019) and Kommescher et al. (2020) to improve existing LMO models. We observed that by including Ti stable isotope fractionation through silicates and by increasing the ilmenite content of the ilmenite-bearing cumulates to 15%, our modelled $\delta^{49}$Ti value by Millet et al. (2016; purple star) is always displayed at the mean HSFE ratio proposed by Warren (1989). The green area represents the silicate Moon as described in Thiemens et al. (2019). Straight lines represent 96–99 PCS, whereas dotted lines represent 99–99.9 PCS. The white arrow indicates increasing solidification of the LMO. Most models reach the estimates for urKREEP by Warren (1989) at 99 PCS model of the LMO considering that not only experimental (Rzehak et al. 2021) but also ab initio studies (Wang et al. 2020; Aarons et al. 2021) indicate that also silicates can fractionate Ti stable isotopes—a fact that was omitted in previous studies (Millet et al. 2016; Kommescher et al. 2020) due to the lack of suitable $\Delta^{49}$Ti values at that time.

**Supplementary Information** The online version contains supplementary material available at https://doi.org/10.1007/s00410-022-01947-0.

**Acknowledgements** The authors are grateful to Frank Wombacher and Carsten Münker for access to their Isotope Geochemistry lab at the University of Cologne. Furthermore, we want to thank the ZGH Bochum as well as Jasper Berndt and Stephan Klemme from the University of Münster for generously providing their SEM and EPMA. We would like to express our continued thanks to Marc-Alban Millet and Nicolas Greber for sharing the OL–Ti reference material. We also thank Zhengbin Deng for discussions that helped advance our paper. We are grateful for the comments of two anonymous reviewers and the editing by Hans.
Kepler that helped shaping our paper greatly. LJAR, SK, LH and FK are thankful for funding by the Deutsche Forschungsgemeinschaft (LJAR and SK DFG grant 698/6-1, LH DFG grant 698/14-1, FK DFG grant KU 3788/1-1). ROCF is grateful for funding of a Heisenberg Professorship by the Deutsche Forschungsgemeinschaft (DFG grant FO 698/13-1).

**Authors contributions** ROCF, PS and FPL conceptualized the project. LJAR, ROCF and FPL designed the experimental protocol. LJAR, SK and FK created the analytical protocol. LJAR did analysis and investigation of all samples, as well as the interpretation of the results and the writing of the manuscript. All authors contributed to the discussion and reviewing of the manuscript. All authors read and approved the final manuscript.

**Funding** Open Access funding enabled and organized by Projekt DEAL. LR and SK were funded through the DFG grant FO 698/6–1. LH was funded through the DFG grant FO 698/14–1. ROCF is grateful for funding of a Heisenberg Professorship by the Deutsche Forschungsgemeinschaft (DFG grant KU 3788/1–1) as part of the priority program 1833 “Building a Habitable Earth”.

**Availability of data and materials** All authors made sure that all data and materials comply with field standards.

**Conflicts of interest** The authors declare that they have no conflict of interest.

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