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Experimentally determined Si isotope fractionation between zircon and quartz

Dustin Trail[1], Paul S. Savage[2] and Frédéric Moynier[3,4]

[1]Department of Earth & Environmental Sciences, University of Rochester, Rochester, NY 14627, USA.

[2]School of Earth and Environmental Sciences, University of St Andrews, Irvine Building, Scotland, UK, KY16 9AL

[3]Université de Paris, Institut de physique du globe de Paris, CNRS, F-75005 Paris, France

[4]Institut Universitaire de France, Paris, France

Corresponding author: Dustin Trail (dtrail@ur.rochester.edu)

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Abstract. The silicon isotope composition of detrital quartz and zircon have the potential to inform us about secular changes to the silica cycle and weathering reactions on Earth. However, inferring source melt Si isotope composition from out-of-context minerals is hampered by the fact that, to-date, there is limited Si isotope equilibrium fractionation data for minerals. Here, we report experimental data to constrain Si isotope equilibrium fractionation between zircon and quartz, using two fundamentally different strategies, but with the same experimental design. First, zircon and quartz were hydrothermally synthesized from $Zr(OH)_4$ and SiO_2 at 1.5 GPa and temperatures of 725, 800, and 900 °C. The second experimental strategy utilized the three-isotope method; the starting materials consisted of natural zircon and isotopically-labelled SiO_2. Three sets of hydrothermal time-series experiments were conducted at the same pressure and temperatures as the direct synthesis experiments. For all experiments, quartz and zircon were separated and $^{30}Si/^{28}Si$ and $^{29}Si/^{28}Si$ ratios were measured by solution multi-collector inductively coupled plasma mass spectrometry. The three-isotope method, which provides the best indicator of equilibrium fractionations, yields the following relationship:

$$\Delta^{30}Si(qtz\text{-}zrc) = (0.53 \pm 0.14) \times 10^6/T^2$$

where $\Delta^{30}Si$(qtz-zrc) is the relative difference in $^{30}Si/^{28}Si$ between quartz and zircon in permil, T is temperature in K, and the error is 2 s.e. This relationship can be used to calculate the fractionation between zircon and other phases, and to estimate the Si isotope composition of the melt from which a zircon crystallized. The results may be used to assess equilibrium-disequilibrium isotope fractionations between quartz and zircon and co-existing phases in igneous rocks. These data can also be applied to out-of-context zircon (and quartz) to estimate the isotope composition of the host rock. Zircons crystallizing from a melt derived from purely igneous sources – i.e., without the involvement of "weathered" material – are expected to display a $\delta^{30}Si_{NBS\text{-}28}$ (permil deviation of the $^{30}Si/^{28}Si$ from the NBS-28 standard) range from -0.7 to -0.35‰. Deviations from this range indicate assimilation of non-igneous (i.e., sedimentary) material in the melt source.

1. Introduction

The processes of silicate weathering and assimilation of sedimentary material into crustal melts have been explored in detail through measurements of oxygen isotope ratios in whole rock for over 50 years (Taylor, 1968; Taylor and Sheppard, 1986). This is because oxygen isotope ratios of supracrustal and aqueously-altered rocks are fractionated away from the canonical mantle value (O'Neil and Chappell, 1977; Harmon and Hoefs, 1995). Anatexis of such altered material during the formation of melt thus yields different bulk-rock $^{18}O/^{16}O$ ratios when compared to primitive mantle-derived magmas. In most cases, supracrustal contamination yields igneous rocks enriched in ^{18}O compared to the upper mantle, because weathering results in relatively large enrichment in the heavy isotopes of the weathered rocks (Savin and Epstein, 1970). Trends to $^{18}O/^{16}O$ values lower than mantle may occur by assimilation of high-temperature, hydrothermally-altered material caused by a change in the fractionation direction vs. temperature during chemical weathering (e.g. Wenner and Taylor, 1973; Chacko et al., 2001), or by assimilation of material altered by meteoric water (e.g., Bindeman et al., 2007).

Using oxygen isotopes as a proxy for supracrustal contamination in igneous systems at the mineral-scale requires knowledge of the direction and magnitude of O isotope fractionation among phases. Experimentally-, empirically, and theoretically-derived mineral-mineral oxygen isotope fractionations (Keiffer, 1982; Mathews et al., 1983; Chiba et al., 1989; Chacko et al., 2001; Trail et al., 2009) have resulted in a clearer understanding of the relationship between crustal weathering, recycling, and the isotopic composition recorded in individual igneous phases. One phase that has offered many important insights is zircon, which is generally unaffected by chemical weathering (e.g., Valley et al., 1994; 2003; Grimes et al., 2013; Loewen and Bindeman, 2015, 2016) and can be dated by U-Pb geochronology (Harrison et al., 2017). For instance, some zircons older than 4.0 Ga have oxygen isotope compositions that are enriched in ^{18}O relative to mantle zircon (Valley et al., 1998; Cavosie et al., 2009), providing evidence for low-temperature fluid alteration of their protoliths and suggesting that significant volumes of liquid water were interacting with the crust as early as 4.2 to 4.3 Ga (Mojzsis et al., 2001; Cavosie et al., 2005).

Other isotope tracers, such as $^{7}Li/^{6}Li$ and $^{26}Mg/^{24}Mg$, have been used with success to study silicate weathering (e.g. Teng et al., 2010, Wimpenny et al., 2011) though perhaps no other isotope system is more important than Si due its pervasive abundance in the lithosphere and weathered products. Silicon isotopes, like oxygen isotopes, fractionate away from igneous compositions during weathering in many low-temperature water-rock interactions, particularly during desilicification and neoformation of clay minerals (Opfergelt et al., 2012; Savage et al., 2013). There is also evidence that a supracrustal Si isotope signature can be transferred to a melt; depletions in the light isotopes of Si were detected in several peraluminous leucogranites (Poitrasson and Zambardi, 2015). Savage et al. (2012) also identified measurable differences in the Si isotopic composition of igneous rocks from the Lachlan Fold Belt, Australia, which revealed new information about the source materials of these (S)edimentary- and (I)gneous- type granitoids. Specifically, Ordovician sediments near these granitoids are often interpreted to represent the supracrustal end-member for the S-type rocks (e.g., Keay et al., 1997), yet Si isotope compositions strongly suggest that these sediments were not the only source of material (Savage et al., 2012); pre-Ordovician metasedimentary crust may have also contributed to the isotopic character of the LFB granitoids (Chappell et al., 1988).

Studies have also coupled Si and O isotope ratios to infer that Si from marine hydrothermal origin and a minor fraction from continental weathering contributed to the chemistry of banded iron formations, as early as 3.8 Ga (Heck et al., 2011). More recently, new insights into the terrestrial silica cycle and weathering reactions prior to 3.8 Ga have been gleaned from coupled Si and O isotope measurements of Archean and Hadean detrital zircons (Trail et al., 2018). These data provide evidence for the presence (and subsequent melting) of fluid-altered, crustal assemblages such as serpentinites and possibly authigenic silica on the Hadean Earth.

As with O isotopes, the direction and magnitude of Si isotope high temperature fractionations among co-existing igneous phases needs to be well constrained so that the bulk-rock Si isotope composition can be confidently inferred, particularly when *ex-situ* mineral phases are analyzed. This will allow for any signature of supracrustal material in the melt source to be better elucidated via this isotope system. The importance of this is amplified because Si isotope fractionations produced during weathering or low temperature hydrothermal processes are typically smaller in magnitude than O isotopes. The Si isotope composition of clays, for example, are typically confined to -0.5 to -3 ‰ (relative difference when compared to the mantle frame of reference; Opfergelt et al., 2012), though Bayon et al. (2018) showed that a small fraction of clays can in be isotopically unfractionated relative to average (unweathered) felsic crustal composition. In comparison, clay mineral $^{18}O/^{16}O$ ratios with differences of +10 ‰ compared to the mantle frame of reference are common (Savin and Epstein, 1970; Chacko et al., 2001).

Variations in $\delta^{30}Si$ between natural igneous mineral assemblages have been measured in previous studies (Savage et al. 2011, 2012), where $\delta^{30}Si$ is defined as the permil difference of the $^{30}Si/^{28}Si$ ratio of the sample relative to the same ratio in NBS-28 silica sand, as follows:

$$\delta^{30}Si = \left[\frac{^{30}Si/^{28}Si_{sample}}{^{30}Si/^{28}Si_{NBS-28}} - 1\right] \times 1000 \ (1).$$

Silicon isotope mineral-mineral fractionations at igneous temperatures are typically range from 0.05 – 0.50 ‰ (Savage et al., 2012; and Trail et al., 2018), though density functional theory (DFT) calculations predict quartz-clinopyroxene (i.e., diopside and clinoenstatite) fractionations that approach or exceed 0.5 ‰ (1000 K; Méheut et al., 2009; Qin et al., 2016). The direction and magnitude of fractionation is thought to be controlled by the relative degree of polymerization of the minerals. Restated, phases with higher proportions of Si-O-Si bonds tend to prefer the heavier Si isotopes (e.g., Méheut et al., 2009; Savage et al., 2011); i.e., orthosilicates (e.g., olivine) are almost always isotopically lighter than tectosilicates (e.g., feldspar).

Due to the orthosilicate structure of zircon, it is predicted that zircon should be isotopically light, particularly if crystallizing from a high silica melt where most liquidus phases are tectosilicates (Qin et al., 2016). Quartz, on the other hand, should be enriched in the heavy isotopes of Si. This was confirmed by Trail et al. (2018), who measured zircon-quartz fractionation values for an aliquot of zircon and quartz from the I-type Jindabyne tonalite, from the Lachlan Fold Belt (LFB), Australia (Trail et al., 2017). A fractionation of $\delta^{30}Si(qtz) – \delta^{30}Si(zrc) = \Delta^{30}Si(qtz\text{-}zrc) = 0.47\pm0.06$ ‰ (T_{cryst} ~750 °C) was measured via multi-collector inductively-coupled-plasma mass-spectrometry (MC-ICP-MS). These measurements also agree with DFT calculations for analogous mineral pairs. That is, quartz-pyrope fractionations (pyrope being an orthosilicate) are equal to 0.48 ‰ at 750 °C (Méheut and Schauble, 2014).

However, there are some important caveats for the above generalizations. Firstly, implicit in constraining a fractionation from natural samples is the assumption that zircon and quartz crystallized contemporaneously and in equilibrium, which may or may not be the case. Secondly, it is not clear to what extent the predicted polymerization-related fractionation rule holds when other network-modifying cations, such as Al, OH^-, B are present in high abundances in the melt and crystallizing phases. The control of relative polymerization on Si isotope fractionation is clearly not a consistent phenomenon, as both empirical measurements and first principle DFT calculations imply that olivine is isotopically heavier than coexisting clinoenstatite, despite having more "non-bridging" oxygens (Méheut et al., 2009; Savage et al., 2011). Moreover, measured fractionations between quartz and biotite/phlogopite (Ding et al. 1996; Georg, 2006) are lighter than would be expected by a applying the simple polymerization rule for the three corner-sharing structure of trioctahedral phyllosilicates (Méheut and Schauble, 2014). Zircon also exhibits unique properties among the silicate minerals whose fractionations were calculated by DTF (Qin et al., 2016). That is, its calculated $^{30}Si/^{28}Si$ reduced partition function ratio vs. Si-O polyhedron volume is well outside the trend identified for other silicates, which is due to a large distortion in the zircon silica tetrahedron (Qin et al., 2016). Thirdly, even I-type granitoids are known to contain inherited zircons (e.g., Kemp et al., 2005), which means that the natural quartz-zircon fractionation noted above could be affected by a mixture of multiple zircon populations. Finally, stable isotope fractionation is a temperature-dependent process. Constraining the sensitivity of $\Delta^{30}Si$(qtz-zrc) to crystallization temperature is critical to accurately infer whole-rock/melt compositions from out-of-context minerals.

Thus, there is a need to approach the topic of igneous Si isotope fractionation between zircon and whole-rock/coexisting minerals in a systematic and controlled fashion. While several studies have conducted calculations to constrain Si isotope fractionations among coexisting minerals and fluids (Méheut et al., 2007, 2009; Méheut and Schauble, 2014; Huang et al., 2014; Qin et al., 2016), we aware of no experimental Si isotope fractionation data for igneous minerals. We present high temperature Si isotope fractionation experiments between zircon and quartz by direct synthesis, and through application of the three-isotope method (e.g. Matsuhisa et al., 1978; Shahar et al., 2008; Macris et al., 2013), to place inferences made from zircon Si isotope measurements in a more complete context. We show that the direction of experimentally determined Si isotope quartz-zircon fractionations agrees with natural and theoretical data (Qin et al., 2016; Trail et al., 2018), though some differences in the magnitude are observed. When experimentally determined quartz-zircon fractionations are combined with measurements collected on natural samples, we also show that the Si isotopic difference between zircon and whole rock can be confidently estimated in simplified scenarios.

2. Methods

2.1 Experimental strategy and design

High temperature Si isotope fractionations – in this case quartz and zircon – are typically described by the following relationship:

$$\delta^{30}Si(qtz) - \delta^{30}Si(zrc) = \Delta^{30}Si(qtz - zrc) \cong 10^3 \times \ln\left(\alpha_{qtz-zrc}\right) = \frac{A \times 10^6}{T^2} \quad (2)$$

where T is in K, and $\alpha_{qtz\text{-}zrc}$ is the fractionation factor defined by the $^{30}Si/^{28}Si$ value in quartz divided by the equivalent ratio in zircon, and A is a constant parameter. This relationship is typically assumed to be a valid description of high temperature (≥500 °C) isotope fractionations (Bottinga and Javoy, 1973). While polynomial expressions such as $10^3\ln(\alpha_{mineral1-mineral2}) = Ax - Bx^2 + Cx^3$ – where $x=10^6/T^2$ – are frequently used for theoretical calibrations (e.g., Qin et al., 2016), such functions are rarely used for high temperature experimental or naturally-calibrated fractionation studies because the obtained fractionations are typically not precise enough to resolve the *B*- and *C*-values. For the data presented here, we utilize equation (2) which implies an assumed linearity for $\Delta^{30}Si(qtz\text{-}zrc)$ vs. $1/T^2$, that $\alpha_{qtz\text{-}zrc}$ is close to 1, and that *A* can be solved for by knowing T and the Si isotope compositions of quartz and zircon. We conducted a series of fluid-saturated experiments in a piston cylinder device to characterize the *A*-value using two different experimental designs.

2.1.1 Direct synthesis experiments

We performed direct synthesis experiments of zircon and quartz with starting materials consisting of $Zr(OH)_4$, SiO_2, and a 10 mM $CaCl_2$ solution. The SiO_2 consisted of 325 mesh fused ~amorphous powder from Alfa Aesar with a stated purity of 99.8%. The $Zr(OH)_4$ was made by first dissolving 99.9% pure $ZrCl_4$ from Sigma Aldrich in distilled water under a fume hood; a $Zr(OH)_4$ gel was precipitated by adding NH_4OH to this solution (Montel et al., 1989; Trail et al., 2011). The gel was carefully rinsed, left to sit at room temperature until dry, and then ground. A 10 mM $CaCl_2$ solution was made by dissolving $CaCl_2 \cdot 2H_2O$ (99% purity, Alfa Aesar) and trace $DyCl_3$ (99.99% purity; Sigma Aldrich) in distilled water.

The SiO_2 and $Zr(OH)_4$ were weighed out for each individual experiment in 2:1 abundances by mole, for a total mass of ~70 mg. This material was coarsely mixed by hand in the weighing paper with a spatula before loading it into a 4.8 mm diameter capsule machined from an Ag rod with an outer diameter of 7.3 mm. Approximately 60 μL of 10 mM $CaCl_2$ solution was added with a micro-syringe. The capsule was then surrounded by components of the solid media pressure cell (**Figure 1**), loaded into a pressure vessel with a ¾" tungsten-carbide core, and then end-loaded. The Ag capsule was pressure-sealed to a 2 mm thick Ag lid by applying pressure to the sample piston with a hand pump.

Experiments were heated to 900, 800, or 725 °C with a ramp rate of ~300° per minute. Specifically, they were ramped at 300 °C per minute to 25° below the set point, and then at 100° per minute for the final 25°. The temperature was monitored using calibrated 25%WRe–3%WRe thermocouple wire. The temperature choices result in approximately equivalent spacings when T (in K) is expressed as $10^6/T^2$. The pressure was kept fixed at 1.5 GPa using a 20 cm Heise gauge and experiment durations were 48, ~94, or 140 h for 900, 800, and 725 °C experiments, respectively. Experiments were quenched by cutting power to the transformer. Prior to opening the capsules, they were gently cleaned with a file and a lathe to remove Mg-oxide pressure media and a small amount of the exterior wall the Ag capsule. All capsules exhibited evidence for fluid-under-pressure, and expelled liquid once the water-tight seal was breached. In preparation for MC-ICP-MS measurements, quartz crystals (50 – 300 μm) were extracted from the capsules with tweezers, sonicated in ethanol, and then inspected for inclusions by reflected light, transmitted light, and backscattered electron imaging. Zircon crystal picking was prohibitive due to size (~<5 μm), so aliquots were treated in dilute HF acid overnight to remove residual silica quench or quartz. Hydrofluoric acid cleaning of non-metamict zircon effectively separates zircon from other silicate material (e.g., Watson et al. 2006; Trail et al. 2009) and zircon crystal surfaces are not altered by acid treatment (Cherniak and Watson, 2010).

To prevent entry of foreign material, HF treatment was carried out in a teflon container that was loosely-capped, but the cap was not tightened based on the expectation that volatile SiF_4, formed by reaction of the acid with quartz+quench, would be preferentially lost. After treatment, the HF was carefully poured out of the container and discarded, with the last drop wicked away with a kimwipe®. The remaining material was rinsed several times in ethanol and dried. A small amount of pre- and post-treated "zircon fraction" was cast into epoxy, polished with an automated polisher with a slurry of 1 μm $Al_2O_3+H_2O$, and then finished with colloidal silica. Cathodoluminesence (CL) and secondary electron (SE) images were collected for the samples.

2.1.2 Three-isotope exchange method

Our second set of experiments implemented the three-isotope exchange method (e.g. Matsuhisa et al., 1978; Shahar et al., 2008), though were otherwise identical to the design presented in Figure 1. The method involves doping one of the equilibrating phases – quartz in this case – in the denominator isotope (^{28}Si). Quartz will thus plot below the terrestrial mass isotope fractionation line (TMFL). The bulk composition of the quartz and undoped zircon mixture will define a secondary mass fractionation line (SMFL; **Figure 2**). As these two phases are brought to equilibrium by recrystallization at high temperature, each will progressively approach the SMFL. The loci of the SMFL in isotope space is therefore constrained by the slope of the SMFL and the isotopic composition of the system (i.e., quartz+zircon). Here we assume a slope (γ) of 0.5178 for the SMFL based on equilibrium isotope fractionation theory:

$$\gamma = \frac{\frac{1}{m_{29}} - \frac{1}{m_{28}}}{\frac{1}{m_{30}} - \frac{1}{m_{28}}} \quad (3)$$

where m_{28} is the mass of ^{28}Si, etcetera (Young et al., 2002). A series of isothermal experiments conducted for progressively longer durations should produce an array of points for each phase that trends toward the equilibrium fractionation value, defined by the intercept with the SMFL.

We prepared SiO_2 for our experiments by mixing reagent-grade SiO_2 with ^{28}Si-enriched SiO_2 from Isoflex USA ®, with a stated purity of 99.4% $^{28}SiO_2$. First, an initial mixture containing about 1.1 wt% of isotopically-labeled SiO_2 was mixed with the same Alfa Aesar material as the previous section. This was ground in a ceramic Al_2O_3-based mortar and pestle (Diamonite ®) for approximately 1 hour. A small chip of the Diamonite® mortar was removed, mounted in epoxy, polished, and analyzed by energy dispersive spectroscopy confirming that it is Al_2O_3-based, with a binding agent containing Ca, Mg, Si, and Cr.

The ^{28}Si-enriched mixture yielded $\delta^{29}Si_{NBS-28}$ and $\delta^{30}Si_{NBS-28}$ values of ~–10.7 ‰. In these experiments, it is important not to "overspike" with $^{28}SiO_2$, so that the amount of extrapolation to the SMFL is reasonable (Shahar et al., 2017). "Underspiking" may result in changes to the equilibrating phases during the experiment that are too small to detect with the MC-ICP-MS precision. Early attempts to conduct experiments with the above spiked mixture were unsuccessful because the extrapolation to the SMFL was too large. Thus, we produced a second SiO_2 mixture in which the $\delta^{30}Si$ ~–10.7 ‰ material was diluted further by adding additional Alfa Aesar SiO_2 (TMFL) material. This resulted in a mixture consisting of about 0.29 wt% of isotopically-labelled $^{28}SiO_2$. Approximately 2 grams of SiO_2 was thoroughly mixed in a Diamonite ® mortar and pestle for approximately 1 hour.

The zircon starting material was a ~5 gram crystal from the Mud Tank carbonatite (Currie et al., 1992). The crystal was inspected optically and was found to be free of visible inclusions, though it did contain infrequent and small (1-5 μm) secondary opaques, likely Fe-oxides, along fractures in the crystal. It was crushed and ground under ethanol for approximately 1 hour. The resulting material was sieved to a size fraction smaller than 70 μm, and then ground again. As later verified by SEM, this produced angular fragments of zircon which were expected to have relatively high reactivity during the experiments. That is, the surfaces of crystal shards are likely to have lower activation energy barriers causing them to more rapidly undergo dissolution – and thus recrystallization – than primary crystal facets.

Silver capsules, of the same design described above, were loaded with equimolar amounts of Si for each phase, resulting in a total weight of approximately 130 mg for each experiment. For experiments performed at 900 and 800 ºC, we added 4 wt. % of the same 10 mM $CaCl_2$ fluid to the capsule, which also contained trace $DyCl_3$. Like the direct synthesis experiments, the $CaCl_2$ was added because it has been shown to enhance re/crystallization of zircon (e.g., Geisler et al. 2001). Based on the expectation that higher fluid contents would result in faster equilibration, we added additional fluid (8 wt. % total) to our lowest temperature series (725 ºC). Dysprosium was included because it is a known cathodoluminescence emitter in zircon and was thus used to evaluate the extent of recrystallization in trace element poor Mud Tank zircon in the experimental products. Time series experiments ranged from 20 to 150 h for 900 ºC, from 20 to 500 h for 800 ºC, and from 20 to 1099 h for 725ºC. At least 15 mg and 45 mg of cleaned quartz and zircon, respectively, were recovered from each experiment and processed as for the direct synthesis experiments for MC-ICP-MS measurements.

2.2 MC-ICP-MS measurement

Starting materials, experimental products, and external standards were processed through the same HF-free dissolution and purification procedure before Si isotope analysis. This method is based closely on that described in detail in Georg et al. (2006) with specific modifications and further details noted in Savage and Moynier (2013). The use of HF for sample dissolution is avoided with use of an alkali flux digestion method. Each sample was weighed into a silver crucible (made of 99.99% pure Ag sheet) along with enough NaOH flux (semiconductor grade, 99.99% pure, Sigma Aldrich) such that the mass ratio of sample to flux was ~1:20. The crucible was then placed in a muffle furnace, heated to 720°C, for approximately 15 minutes. The crucible was removed from the furnace, left to cool for 30 seconds, and submerged in ~ 20ml of Milli-Q ® water (18.2 MΩ·cm) in a PTFE container. The resultant fusion cake is water-soluble and is readily removable from the crucible: this was performed by submitting the crucible-containing PTFE container to ultrasonication and gentle heating, then pipetting the dissolved cake into a pre-cleaned polypropylene bottle. The transferred fusion material is diluted further with Milli-Q ® water and then acidified to 1% HNO_3 v/v with thermally distilled nitric acid (~15.7 M) – the amount of HNO_3 added is calculated based on the mass of NaOH used in each fusion. The degree of dilution (i.e., how much water is added to the final solution) is estimated, based on the initial amount of sample dissolved, to allow for a final solution concentration of between 10 and 20 ppm Si. The Si concentration in each solution is determined photometrically using the "Heteropoly-Blue" method (with Hach-Lange ® Ultra-low range Si reagents) and fusion yield estimated based on the weighed amount of sample and the measured ppm of Si. The calculated fusion yields were all between 95 and 99% Si recovery.

The Si from the samples and standards were purified using a one-step column procedure utilizing 1.8ml of BioRad AG50 X-12 (200-400 mesh) cation exchange resin loaded into BioRad "Poly-Prep" columns, again following methods detailed in Georg et al. (2006) and Savage and Moynier (2013). Silicon in neutral to acidic media does not adhere to the resin, and elutes straight through, whereas other cations are held on to the resin and are quantitatively removed from the matrix. All other anions, if present, are at too low concentrations relative to Si to affect isotopic measurement (c.f. Georg et al 2006). Total procedural blanks are on the order of 0.1 µg Si, which typically represents ~0.35% of total Si and are therefore negligible.

Over the course of this study, Si isotope measurements were made on two Neptune Plus Multi-Collector Inductively Coupled Plasma Mass spectrometers (MC-ICP-MS); one at the Institut de Physique du Globe de Paris (IPGP), the second in the St Andrews Isotope Geochemistry (STAiG) laboratories. Running conditions for both instruments are as described in Trail et al. (2018) and more general details are provided in Savage and Moynier (2013). Both instruments were operated in 'medium' resolution mode to avoid polyatomic interferences (in particular the large $^{14}N^{16}O^{+}$ interference that would otherwise overwhelm the $^{30}Si^{+}$ signal). Samples were introduced to the instrument using a 75 µl min^{-1} ESI PFA microflow nebulizer via the Thermo Scientific "SIS" spray chamber.

Samples were analyzed at a concentration of 2 ppm Si, which gave ~16V on the ^{28}Si beam (using a 10^{11} Ω resistor) in medium resolution mode. Ratios were measured in static mode, and each measurement consisted of 25 cycles of ~3 s integrations with a 3 s idle time. Sample δ^{29}Si (i.e., $[(^{29}Si/^{28}Si_{sample})/(^{29}Si/^{28}Si_{NBS\text{-}28}) -1]\times1000$) and δ^{30}Si values were calculated using the standard-sample bracketing method (relative to NIST RM 8546 silica sand, historically called NBS-28). Aliquots of the USGS geostandard BHVO-2 and the Si standard 'Diatomite' were routinely ran alongside the unknown samples to monitor accuracy. These analyses are given in Table 1. Our analyses match the 'accepted' reference values for these standards exactly (Reynolds et al., 2007; Savage et al., 2014). Standards "BHVO-2 STAiG old" and "Diatomite STAiG" are aliquots taken from the same sample dissolutions as those for the relevant IPGP measurements; comparison of these data show that there is no systematic instrumental offset between the two measurement locations. Additionally, "BHVO-2 STAiG new" is a repeat dissolution of BHVO-2 performed at St Andrews; the lack of offset between this datum and previous BHVO-2 measurements shows that Si isotope analysis at St Andrews produces accurate data with comparable precision.

3 Results

3.1 Images and description of experimental products

Electron microscopy shows that the zircon crystals produced by direct synthesis are relatively euhedral and approximately 1 to 5 µm (**Figure 3a**). Quartz crystals from the same experiments (not shown) were approximately 50 to 300 µm. With respect to the three-isotope exchange method, the crushed Mud Tank zircon shards used in experiments show clear evidence for recrystallization, analogous to observations made by Ayers et al. (2018) for their zircon-fluid partitioning experiments. An example secondary electron image of the starting material reveals numerous angular fragments (Fig. 3b) that exhibit evidence for dissolution as the experiment duration is increased (Fig. 3c,d).

"Zircon fractions", extracted directly from the capsule after hand cleaning, showed occasional quartz (Fig. 3c). After treatment of this material in cold HF acid, no evidence for quartz remained. In post-treated zircon fractions, we did not see evidence for quenched SiO_2 in epoxy grain mount either. If HF treatment removes the quartz, it is reasonable to expect that the quench material, with smaller size (<<50 µm) and larger surface area to volume ratios, are also likely removed. These results, including the observations made after the HF cleaning procedure, agree with past studies (Trail et al., 2009). Quartz crystals are mostly free of inclusions, though they do contain rare occurrences of sub- to micron-sized zircons (Fig. 3e). We estimate that all mineral aliquots separated for isotope analyses were >95% pure.

Evidence for zircon recrystallization is also present through inspection of CL images. While the starting material shows only modest luminescence (Fig. 3f), the experimental products show evidence of recrystallization near the rims of the crystals (Fig. 3g-i). This is caused by substitution of CL-active Dy, added as a trace impurity in the starting fluid, into the zircon lattice.

3.2 Silicon isotope data

Silicon isotope ratios (^{30}Si/^{28}Si and ^{29}Si/^{28}Si) are reported relative to NBS-28 quartz sand. Table 1 provides external standard data, and Tables 2 and 3 contains the analyses of the direct synthesis and 3-isotope experimental run products, respectively. Analytical errors for individual phases represent the 2 standard deviations (2 s.d.) of 4 to 5 analyses of a purified sample aliquot (Tables 2 and 3).

The long-term external reproducibility of the MC-ICP-MS measurements can be assessed using external standard data; each Si isotope analytical session includes measurement of an aliquot of BHVO-2 (and often Diatomite) which was processed through chemistry at the same time as the other samples being analyzed. The long-term reproducibility can be therefore quantified by calculating the 2 × standard deviation of the $\delta^{30}Si_{NBS-28}$ and $\delta^{29}Si_{NBS-28}$ BHVO-2 (and Diatomite) values generated in each measurement session. As each standard measurement also represents a separate chemical separation procedure, this reproducibility also takes into account the variations in the Si isotope separation method. For the IPGP instrument, over a period of 5 months, the external precision on BHVO-2 was $\delta^{30}Si_{NBS-28}$ ± 0.04‰ and $\delta^{29}Si_{NBS-28}$ ± 0.03‰ (2 s.d.). For the St Andrews instrument, over a period of 9 months, the external precision on both BHVO-2 and Diatomite was $\delta^{30}Si_{NBS-28}$ ± 0.03‰ and $\delta^{29}Si_{NBS-28}$ ± 0.03‰ (2 s.d.).

These long term external reproducibilities are comparable to, and are mostly lower than, the 2 s.d. values calculated for each individual sample measurement, based on the 4 or 5 analyses of the same purified sample aliquot (Tables 2 and 3). For simplicity, we could choose to apply the external precision to all data. However, this does not tell the whole story, as instrumental running conditions can be variable, and will differ between each measurement session, meaning that "short-term" precision on sample measurements will also differ. Because samples are often measured only once, and all samples presented in this study were not measured during the same session, we prefer to utilize the individual analytical errors (as 2 s.d.) in the subsequent discussion and error propagation.

3.2.1 Direct synthesis

Direct synthesis experiments yield Δ^{30}Si(qtz-zrc) values of 0.27 ± 0.07, 0.29 ± 0.09 and 0.21 ± 0.08 ‰ for respective temperatures of 725, 800, and 900 ºC (Table 2). The Δ^{30}Si(qtz-zrc) errors are calculated via ($\sqrt{[(err_{qtz})^2 + (err_{zrc})^2]}$), using 2 s.d. errors for quartz and zircon. The measured $\delta^{30}Si_{NBS-28}$ value of the starting material is -0.14 ± 0.05 ‰. In all three cases, this is less than 0.1 ‰ from calculated mass balance values of the experiments. Considering the average error associated with this estimate (±0.08 ‰), the average Si isotopic composition for quartz and zircon supports Si isotope mass balance for the direct synthesis experiments.

3.2.2 Three-isotope method.

The δ^{29}Si and δ^{30}Si values for starting materials and experimental products are reported in Table 3. The starting material for 900 and 800 °C experiments consisted of quartz pre-synthesized in a piston cylinder device, whereas the starting material for the 725 °C experiments used mechanically mixed SiO_2 powder without pre-synthesis. The δ^{30}Si(ave) column is calculated by taking the average δ^{30}Si(qtz) and δ^{30}Si(zrc) for each experiment, and assuming a 1:1 quartz to zircon ratio, by mole. This reveals that the experimental charges exhibit very good agreement with the average isotopic composition of the starting material, which indicates the experiments approximate a closed system with respect to Si (**Figure 4**). When compared to the starting materials, Si isotopic compositions of quartz and zircon show progressive exchange for longer experiment durations. A simple percent exchanged calculation, which compares the amount of isotope exchange between the initial and the experimental product with the difference between the initial composition and intercept, ranges between 15 and 36%.

After Figure 2, the starting compositions and the measured phases for each isotope exchange experiment were plotted on a δ^{29}Si vs. δ^{30}Si plot. A line was fitted to the data using a York regression in the Origin 2016 ® software package. This line was extrapolated to intercept the SMFL. In all cases, our three sets of experiments show quartz and zircon approaching the SMFL. Intercepts and the errors were solved for each zircon and quartz pair. These intercepts constrain the Δ^{30}Si(qtz-zrc) at each of the three experiment temperatures.

These intercepts are also constrained by mass balance of the system (Figure 4). To take this into consideration, our final calculated fractionations involved a Monte Carlo simulation of possible Δ^{30}Si(qtz-zrc) equilibrium values constrained by the SMFL intercept, the 95% confidence intervals associated with the SMFL intercept, and the mass balance of the system. Inputs for δ^{30}Si(qtz) and δ^{30}Si(zrc) were randomly generated by assuming the probability of distribution was defined by the 95% confidence intervals of the intersection to the SMFL. The next criterion requires that selected δ^{30}Si(qtz) and δ^{30}Si(zrc) values satisfy mass balance of the system, where tolerances for this criterion are provided on Figure 4. We randomly selected 10,000 δ^{30}Si(qtz) and δ^{30}Si(zrc) SMFL intercept values that satisfy mass balance, and the average of these results was used to predict the fractionation. In general, the errors associated with the York fits for zircon were smaller and quartz. While the error on the fit may be larger if quartz is considered independently, the error becomes smaller when the mass balance constraint is utilized. The standard deviation of the successful Monte Carlo sampling was used to calculate the error (see the Electronic Annex for additional details). Our calculated Δ^{30}Si(qtz-zrc) fractionations for 900, 800, and 725 °C are 0.40 ± 0.46, 0.51 ± 0.18, and 0.50 ± 0.29 ‰ (2 s.d.), respectively (**Figure 5**).

4 Discussion

4.1 Si isotope quartz-zircon fractionation calibration

For each experiment, the orthosilicate zircon preferentially incorporates the lighter isotopes of Si relative to quartz, as predicted by first principles equilibrium isotope theory and previous – but limited – natural sample measurements (Méheut et al., 2009; Savage et al., 2012; Qin et al., 2016; Trail et al., 2018). However, there is systematic shift between the fractionation factors determined via the direct synthesis and three-isotope exchange methods. The average difference between the larger Δ^{30}Si(qtz-zrc) fractionations calculated for the three-isotope exchange method, compared to the direct synthesis experiments for the three temperatures, is 0.18 ‰. This difference is smaller than the average Δ^{30}Si(qtz-zrc) three-isotope method errors (±0.31 ‰, 2 s.d.). The error calculated for the direct synthesis is 0.08 ‰ (2 s.d.), which only takes into consideration the reproducibility of the measurements. The larger errors associated with the three-isotope method are because they represent the uncertainty of the measurements *and* the extrapolation of phases – that exchanged at most ~40% of their Si during the experiment – to the SMFL. Although the direct synthesis and three-isotope methods yield Δ^{30}Si(qtz-zrc) values that are similar when error is considered, this sort of magnitude in Si isotope space is on the same order as the isotopic difference between basaltic and rhyolitic magmas (Savage et al., 2011), and is therefore worth commenting upon. Here we explore potential reasons that may be affecting the resultant isotope fractionations predicted using both methods.

First, there are limited experimental studies in which Si isotope fractionations between phases have been characterized by different techniques for comparison. There are, however, experimental data for Si isotope fractionations between molten silicate and metal, which used methods similar to the direct synthesis and three-isotope methods employed here (Shahar et al. 2009; 2011; Hin et al. 2014). While silicate-metal systems are not directly analogous to our experiments, they are of interest here because the different techniques utilized in these studies yielded different Δ^{30}Si(silicate-metal) vs. $1/T^2$ calibrations. For experiments conducted using the three-isotope scheme, the silicate material was doped with ^{28}Si to trace the exchange of Si between the metal and silicate. Experiments were performed at 1 GPa or 7 GPa, and from 1800 to 2200 ºC (Shahar et al., 2009; 2011). On the other hand, Hin et al. (2014) experimentally calibrated the Si isotope fractionation between metal and silicate liquids using undoped materials, though with other deviations from the general design of Shahar et al. (2009; 2011). For instance, Hin et al. (2014) used modest to moderately different starting compositions. The main differences were that they added a combined total of ~2.5 wt% Na_2O and K_2O to their silicate mixture, and used a Fe-Si metal which contained ~1 wt% Mo and 10 wt% Sn for most of the experiments. That said, the absence of Sn from two of their experiments did not lead to an appreciable change in their Δ^{30}Si(silicate-metal) vs. $1/T^2$ relationship. Hin et al. (2014) also used a centrifuging piston cylinder for most of their experiments, though for a single experiment conducted in a standard piston cylinder, the Δ^{30}Si(silicate-metal) vs. $1/T^2$ relationship was not appreciably different. With these differences and comparisons noted, Hin et al. (2014) reported smaller Δ^{30}Si(silicate-metal) fractionations than those of Shahar et al. (2011), once temperature is considered. As a specific example, Hin et al. (2014) predicts Δ^{30}Si(silicate-metal) = -1.08±0.01‰ at 1750 ºC, whereas the three-isotope calibration of Shahar et al. (2011) yields Δ^{30}Si(silicate-metal) = -1.82±0.10‰ at the same temperature. The explanation for this difference suggested by Hin et al. (2014) is that some Si was lost to the capsule thus compromising the simple application of the three-isotope method presented in Figure 2. In our experiments, we can rule out loss of Si to the capsule wall as Si-oxide is insoluble in Ag. The fluid medium does result in dissolved silica during the experiment, which leads to a loss of silica from the SiO_2-zircon system. This effect appears to be negligible as it pertains to the isotopic composition of the system, an inference based on the attainment of isotope mass balance for each experiment (i.e. Figure 4). Hence, this is unlikely to be the explanation for the systematic offsets.

A second possibility is that, in the isotope exchange setup implemented here, the degree of reaction of one of the starting materials with the fluid component could have been larger than for the other phase. The direct synthesis method does not require dissolution of pre-existing zircon which can be temporally prohibitive due to the refractory nature and slow dissolution kinetics of zircon. This would essentially mean that calculation of the SMFL based on an equimolar mixture is incorrect. However, this effect does not seem to be pronounced in our experiments because the average composition of the experimental products agree with the starting composition, and the calculated percent exchanged for zircon and quartz pairs in individual experiments are in broad agreement (**Figure 6**).

A third possibility – fractionation of isotopes by diffusion – is not considered a viable explanation for the differences observed either. While such effects may be possible in experiments in which metal is a phase of interest (Lazar et al., 2012), the diffusion of cations in most mineral oxides are not fast enough in most scenarios. The images presented in Figure 3 show that recrystallization during the experiments occurs at the micron-scale for zircon. The scale is perhaps tens of microns for quartz if the zircon inclusions identified within the quartz crystals are used as a marker (Figure 3e). These distances are significantly longer than length scales for self-diffusion of Si in quartz and zircon. The characteristic diffusive length scale ($[4D\cdot t]^{1/2}$, D = diffusivity and t = time) for Si in quartz is only ~1 nm for a temperature of 900 ºC and a duration of 10^4 years using the Arrhenius relationship of Béjina and Jaoul (1996). The same temperature and time yield a similar length scale for self-diffusion of Si in zircon (Cherniak, 2008). While these calculations were conducted by extrapolating diffusivities collected from ~1600 to 1300 ºC down to 900 ºC, the resulting characteristic diffusive length scales strongly suggest kinetic effects related to self-diffusion of Si are not important, when compared to recrystallization. The slow diffusivities of Si in quartz and zircon also mean that time series experiments are not likely to fully remove any kinetic-based isotope fractionations due to crystal growth.

A fourth possibility to consider is the crystallization of the phases of interest during heating of the direct synthesis experiments. Non-equilibrium fractionations were invoked by Clayton et al. (1972) to explain the discrepancy between quartz-fluid oxygen isotope fractionation synthesis and exchange experiments whose heating times range between 20 and 40 minutes for temperatures of 250 to 500 ºC. No evidence for disequilibrium was reported for experiments conducted at 750 ºC for experiments of a similar design (Clayton et al., 1972). Our experiments were heated at a rate of ~300º/min, to lessen the severity of this effect, however we return to the issue of early phase nucleation in light of the differences in isotope fractionations measured between the two techniques. To supplement our understanding of the heating step, we conducted a 'zero time' experiment. This was heated at 300º/min to 900 ºC and then immediately quenched. All other aspects of the experiment were identical to the direct synthesis procedure presented in section 2.1.1. The heat-treated product was extracted from the capsule, and an X-ray diffraction (XRD) pattern was collected with no other sample preparation. For comparison, an XRD pattern was also collected for the starting material. This revealed a starting material that is almost exclusively amorphous – with a minor fraction of tridymite detected – whereas the heat-treated product contains evidence for abundant quartz and zircon (Electronic Annex). Element transport of O during the heating process is unlikely to be restricted, that of Si is likely is highly restricted, with crystallization occurring without full chemical communication of the entire capsule. While speculative, this scenario may result in an underestimate of Si isotope fractionation factor, with both phases having compositions closer to the bulk experimental composition.

The presence of nucleated zircon and quartz during heating, coupled with the low expected transport of silica, is reason to consider the direct synthesis fractionations with caution. We therefore consider the fractionations derived from the three-isotope method experiments to the be the best reflection of equilibrium fractionations. These Δ^{30}Si(qtz-zrc) data are plotted against $1/T^2$ (in K) and fitted by regressing through the origin. This latter constraint is common among stable isotope fractionation studies, whether used for theoretical results, experimental data, or empirical studies (e.g. Qin et al., 2016; Shahar et al. 2009; Valley et al., 2003), which significantly reduces the error on the slope in almost all cases. We assume that this constraint is applicable here for our data, and in doing so, an *A*-value of 0.53 ± 0.14 is obtained using only the three-isotope fractionations (equation 2).

4.2 Comparison of Si isotope quartz-zircon fractionations

While we view this *A*-value estimation as capturing the pertinent features of our data, this it is not as robust as *A*-values reported for other isotope systems (e.g., Shahar et al., 2008), due to the slower approach to equilibrium of silicate phases. We use this section to provide a simple comparison of other available constraints and predicted Δ^{30}Si(qtz-zrc) fractionations. The latter are provided at 700 ºC, a typical temperature for zircon crystallization in terrestrial magmas (e.g., Watson and Harrison, 1983; Watson et al., 2006; Boehnke et al., 2013). Using an *A*-value of 0.53 presented in the previous section yields a δ^{30}Si(qtz) value 0.56 ‰ higher than co-existing zircon at 700 ºC. If only data from the direct synthesis experiments are used, this would yield Δ^{30}Si(qtz-zrc) = 0.32‰. Trail et al. (2018) reported Si isotope measurements for an aliquot of zircon (~10^3 grains) and quartz from the Lachlan Fold Belt Jindabyne tonalite. The zircons from this tonalite have an average crystallization temperature of 755 ºC (Trail et al., 2017). Assuming this temperature represents crystallization T of the mineral pair, and that Δ^{30}Si(qtz-zrc) tends toward zero when temperature tends toward infinity, an *A*-value of 0.50 can be calculated (and a Δ^{30}Si(qtz-zrc) = 0.53 ‰ at 700 ºC). While the direction of the predicted fraction is the same for both experimental methods, these natural data are in best agreement with the *A*-value calculated with three-isotope method experiments. Finally, Qin et al. (2016) reported calculations, based on density functional theory, to quantify the fractionation factors for a wide range of silicates. This study predicts a Δ^{30}Si(qtz-zrc) fractionation of 0.39 ‰ at 700 ºC, which is in closest agreement with the direct synthesis only work presented here. A summary of these fractionations is provided in **Figure 8** and Table 4.

4.3 Inferring whole rock Si isotope composition from out-of-context zircon and quartz

A goal of this work is to better constrain the Si isotope composition of an igneous rock via analysis of zircon or quartz, as both minerals are common in the detrital record. Here, we provide a relatively robust parametrization to allow for this, albeit within a simplified model. The first requirement is to explore how the δ^{30}Si(qtz) and δ^{30}Si(zrc) values relate to the whole rock (WR). In general, the present observations of natural samples show that the quartz Si isotope composition is a broad proxy for WR δ^{30}Si. Felsic WR and mineral separate data reported by Savage et al. (2012) show that quartz is generally isotopically heavier than whole rock, but with only a small (+0.05‰) enrichment in the heavier Si isotopes. This is perhaps not surprising, especially in granites, where quartz has high modal abundances. For example, for a $\delta^{30}\mathrm{Si}_{\mathrm{NBS\text{-}28}}$(zrc) = -0.55 ‰, we predict a $\delta^{30}\mathrm{Si}_{\mathrm{NBS\text{-}28}}$(qtz) of -0.05 ‰, for a crystallization temperature of ~700 ºC. This would give an approximate $\delta^{30}\mathrm{Si}_{\mathrm{NBS\text{-}28}}$(WR) of -0.10‰.

However, the nature of the Δ^{30}Si(WR-zrc) relationship is less predictable as host-rock composition (and mineralogy) change. In other words, there is no simple isotope relationship between the WR and mineral because this relationship is a function of WR mineralogy and composition. Nevertheless, broad predictions can be made within our current framework of understanding. As mentioned, it appears that the relative polymerization degrees of the various mineral and melt phases exert a strong control on the relative Si isotope fractionation between these phases. High-SiO_2 melts are both highly polymerized and typically precipitate framework silicates such as quartz, feldspars, and feldspathoids which tend to prefer the heavier isotopes of Si. Zircon (an orthosilicate) crystallizing in this system should therefore strongly favor the lighter isotopes of Si. The largest Δ^{30}Si(WR-zrc) should therefore be associated with zircons formed from high-SiO_2 melts, because these systems also crystallize at the lowest temperatures. It is also likely that in evolved but silica-undersaturated systems, where feldspathoids dominate, the difference in polymerization degree between these minerals and zircon – if saturated – should still mean that our Δ^{30}Si(qtz-zrc) calibration will provide a broad estimate of whole-rock Si isotope composition.

It is less clear how Δ^{30}Si(WR-zrc) will scale with significantly lower bulk SiO_2 concentration, but we predict that this magnitude will be smaller for zircons crystallizing from more primitive melts. This could be particularly important for kimberlitic zircons; although their petrogenesis is debated, they are often found intergrown with mafic phases such as Fe-rich olivine, Cr-rich diopsides, and Fe-Ti oxides (Spetsius et al., 2002; Page et al., 2007). The difference in polymerization degree between these phases is minimal, and hence this factor should not exert such a strong control on the Si isotope composition of zircons in this system.

In fact, (limited) measurements and calculations do imply that Δ^{30}Si(WR-zrc) positively correlates with the SiO_2 content of the WR (Qin et al. 2016; Trail et al., 2018). For instance, Trail et al. (2018) reported a Δ^{30}Si(WR-zircon) value of 0.37 ‰ for a tonalite (~65 wt% SiO_2), which broadly agrees with calculations by Qin et al. (2016) who estimated a Δ^{30}Si(WR-zrc) fractionation for an intermediate felsic rock of ~0.3 ‰ at 750 °C. Moreover, the Duluth Gabbro "mantle" zircons analyzed by Trail et al. (2018) have $\delta^{30}Si_{NBS\text{-}28} \approx -0.36$‰, which is only subtly lighter than the current estimate for bulk silicate Earth (-0.29 ± 0.07‰, Savage et al., 2014). The effect that decreasing the SiO_2 content of the system is predicted to have on Δ^{30}Si(WR-zrc) is illustrated in **Figure 9**, where the "mafic" value for *A* (see equation 2) is estimated from the offset of Duluth Gabbro zircons from Si isotope composition of the mantle (δ^{30}Si(BSE) = -0.29 ‰; Savage et al., 2014) and a formation temperature of 800 °C. It is shown schematically that Δ^{30}Si(WR-zrc) should decrease as SiO_2 of the system decreases; however it should not be assumed that Δ^{30}Si(WR-zrc) and SiO_2 content will vary linearly. This schematic predicts that, when estimating δ^{30}Si(WR) from an out-of-context zircon, one might over- or underestimate the whole rock composition by around 0.25 ‰, which is on the order of the precision of a typical ion microprobe Si isotope measurement.

Constraining the sensitivity of Δ^{30}Si(WR-zrc) to whole-rock SiO_2 is potentially important for better bulk-rock Si isotope composition from Archean-age and older zircons, where the bulk composition of the continental crust is a subject of debate (e.g. Harrison et al., 2017; Greber et al. 2017; Caro et al., 2017; Cawood and Hawkesworth, 2019; Deng et al., 2019). Nevertheless, zircons crystallizing from a melt derived from purely igneous sources – i.e., without the involvement of "weathered" material – are expected to display a $\delta^{30}Si_{NBS\text{-}28}$ range from -0.70 to -0.35‰ (if we base the higher bound on the Duluth Gabbro sample). This inference applies to rocks with ~50-78 wt.%, SiO_2. Deviations from this $\delta^{30}Si_{NBS\text{-}28}$(zircon) range should indicate the presence of "non-igneous" material in the melt source.

4.4 Δ^{30}Si(qtz-zrc) and Δ^{18}O(qtz-zrc) as geothermometers?

Our experiments and natural measurements predict resolvable Si isotope inter-mineral fractionations between zircon and quartz in igneous systems, larger than most other mineral-

mineral pairs (Savage et al., 2011, 2012; Trail et al., 2018). This opens the possibility that Δ^{30}Si(qtz-zrc) values could be used as a geothermometer in rocks where quartz and zircon are in equilibrium. In this regard, a key source of comparison is the widely used Ti-in-zircon geothermometer and the Ti-in-quartz geothermobarometer (Watson and Harrison, 2005; Ferry and Watson, 2007; Thomas et al., 2010). This method requires measurement of the Ti content in the phase-of-interest, which is a simple measurement by *in-situ* techniques. The calibrations are precise (~±20 °C) though there may be uncertainties in the titania activity during zircon and quartz saturation, which could propagate additional uncertainties into the final calculated temperature. Watson and Harrison (2005) estimate a *ca.* 50° increase in the calculated zircon crystallization temperature for titania activities that change from 1 to 0.5. The titania activity term does not simply cancel out if both phases are considered together because the Ti concentration in quartz is pressure-dependent too (Thomas et al., 2010).

However, Δ^{30}Si(qtz-zrc) or Δ^{18}O(qtz-zrc) fractionations can only provide crude inferences about the crystallization temperature, if reasonably pure aliquots of zircon and quartz are obtainable. Such a measurement is also significantly more complex analytically. A measured Δ^{30}Si(qtz-zrc) of 0.56 ‰ with a precision of 0.06 ‰ would result in a temperature estimate of ~700±150 °C (2 s.d.). A similar calculation for Δ^{18}O(qtz-zrc) = 2.46 ‰ with a precision of 0.2 ‰ yields ~700±130 °C when the O isotope $A_{qtz\text{-}zrc}$ of 2.33 ± 0.24 is applied (Trail et al., 2009). Thus, the current calibrations do not make useful geothermometers, given that errors are so large as to make any such T-based calculation to be of limited value. Considering the isotope systems together, however, may help evaluate whether the two phases crystallized in equilibrium (**Figure 10**). The slope of Δ^{18}O(qtz-zrc) vs. Δ^{30}Si(qtz-zrc) fractionation vs. T is 4.4, reflecting the ratio of the *A*-values. Coupled measurements of Si and O isotopes in zircon and quartz that are well resolved from a slope of 4.4±1.5 (2 s.d) are likely to have crystallized out of equilibrium.

While these igneous T estimates are very crude by most modern techniques, there are systems where such strategies could be of value. Recently, Ackerson et al. (2018) measured Ti contents in quartz from the Tuolumne Intrusive Suite, located in the central Sierra Nevada, California. Coupled with independent pressure estimates, the low Ti contents were interpreted to reflect crystallization temperatures from ~475 to 560 ºC. This was not predicted to be an isolated occurrence; for instance, perhaps 75% of the quartz in this suite could have crystallized 100 to 200 ºC below the wet granite solidus (Ackerson et al., 2018). The use of coupled Δ^{18}O(qtz-zrc) and Δ^{30}Si(qtz-zrc) to probe temperature is potentially appealing because the low predicted temperatures will result in larger fractionations. In the case of the former, if the same precisions for Δ^{18}O(qtz-zrc) and Δ^{30}Si(qtz-zrc) specified above are applied, the error on both temperature estimates is ~100 ºC (2 s.d.) at 500 ºC, which may be sufficient to explore the low temperature histories of granites or metamorphic systems in certain situations. At low temperatures, such isotope fractionations may be advantageous over the well-established Ti-in-zircon thermometry because the predicted Ti concentration in the presence of rutile and quartz is only ~0.2 ppm Ti at 500 ºC, which makes this a more challenging measurement than typical igneous zircons.

5. Outlook

Since Si and O are abundant in the lithosphere and exhibit isotope fractionations at low temperatures, it is logical to consider both systems when probing the nature of water rock interactions and crustal weathering. This advantage, for example, was used to explore weathering and precipitation processes in Archean greenstone belts. Abraham et al. (2011) measured bulk rock

δ^{30}Si and δ^{18}O values of silicified basalts and bedded cherts from the Barberton Greenstone belt. This belt exhibits variable degrees of silica alteration, which is evidence for active silica cycle, including mobilization and precipitation on the Archean Earth. Authigenic, seawater-derived silica tends to have positive δ^{30}Si relative to igneous rocks because of the enrichment of heavier isotopes in riverine silica, which is the major Si flux to the oceans (Frings et al., 2016). This study discovered enrichments in ^{18}O and ^{30}Si correlated with increasing silicification, implying that seawater was the dominant source of this silica.

Coupled Si-O isotope investigations have also been performed on the mineral scale, with *in-situ* ion microprobe measurement of authigenic silica such as chert. In cases where chert or quartz forms via hydrothermal precipitation, either in a marine or continental setting, the O and Si isotope signatures in silica can reflect the degree of fractionation from hydrothermal fluids. The trajectory and magnitude of δ^{18}O and δ^{30}Si in these silica precipitates is a strong function of the hydrothermal environment and the fluid to rock ratio (Kleine et al., 2018), in addition to Si isotope equilibrium fractionations (Pollington et al., 2016). Deviations in silica δ^{30}Si from mantle values in Archean banded iron formations were interpreted to be the product of marine hydrothermal activity, with a minor fraction of input from continental weathering (Heck et al., 2011). Other possibilities include input from continent-derived freshwaters (~10 %) and very minor (<0.1 %) high-T hydrothermal activity (Delvigne et al., 2012).

While the geologic record is not always permissive of direct interrogation of sedimentary material to trace low temperature surficial processes, burial and assimilation of this material into crustal melts means that such chemical information may be inherited in igneous rocks. Whole rock (WR) measurements are obvious targets, though in some cases, mineral-scale measurements are the only possibility. With the goal of extracting useful and interpretable isotope information from single minerals in igneous systems, high temperature (igneous) isotope fractionations must be characterized. Our report of Δ^{30}Si(qtz-zrc), to our knowledge, is the first experimental study to characterize Si isotope fractionation between igneous silicate minerals. In this case, the pertinent question bears not just on the isotopic composition of the mineral in question, but whether this information can be used to provide clues about the composition of the melt from which the mineral crystallized, and furthermore, about the material involved in the formation of the melt (Trail et al., 2018). Our results enable, to first order, separation of contamination by low temperature weathering products into magmas, and the subsequent high-temperature fractionation that exists between silicate phases. These experimental data help establish Si isotopes as an emerging geochemical tool that could be used in combination with O isotopes to address key issues about the character and evolution of crust-atmosphere-hydrosphere interactions that span the breadth of Earth history. Detrital quartz and zircon are two clear cases where mineral-scale observations – and corresponding predictions about the composition of the host rock – will be of value. The most obvious application to target is zircon because it can be dated by U-Pb geochronology, though by sediment volume, quartz makes up a vastly larger fraction of sedimentary material and thus may be a valuable source of information.

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Figure Captions

Figure 1 Schematic of the experimental configuration, formed of NaCl cells surrounding borosilicate glass and a graphite furnace, which was used for all experiments. Silver capsules were machined with an outer diameter of 7.3 mm and inner diameter of 4.8 mm. Capsules were 8 mm in length with a 2 mm lid. During cold pressurization, the Ag lid seals the capsule shut without requiring heating of the metal by welding (Trail et al., 2009; Thomas et al., 2010). This also results in a systematic and well-defined geometry for each experiment. The pressure media – i.e., MgO – is embedded in the exterior of the capsule during the dwell time at temperature, which means that comparing weight of capsules before and after the experiment cannot be used to assess weight loss. Additional details related to creation of a water-tight seal using the pressure-sealing technique is located elsewhere (e.g., Ayers and Watson, 1991; Ayers et al., 1992; Ayers and Watson 1993a,b).

Figure 2. Schematic diagram for the three-isotope exchange method used for some experiments conducted in this study. The SiO_2 was doped off the terrestrial mass fractionation line to target δ^{29}Si and δ^{30}Si values of ~-3 ‰ (all δ^{x}Si relative to NBS-28), whereas terrestrial mantle zircon was used for the starting material (δ^{29}Si = -0.17‰, δ^{30}Si = -0.34‰; Trail et al. 2018). Longer experiment durations led to increased isotopic exchange between the two reservoirs. The intersection of the experimental data with the secondary mass fractionation line (SMFL) is used to calculate the equilibrium fractionation. Note that in our experiments the SMFL intercept is also constrained by the mass balance.

Figure 3. Representative SEM and CL images of the starting materials and experimental products. **(a)** SE image of zircon from a direct synthesis experiment (725 °C) showing ~3 μm zircons. **(b)** Secondary electron (SE) image of crushed and ground Mud Tank zircon used as the starting material for the three-isotope method experiments. This material is representative of the size and appearance of zircons fragments added to experiments. **(c)** SE image of quartz and zircon from the "zircon fraction" for the 800 °C, 500 h experiment before HF treatment. Note the lack of angular grain fragments which is evidence that the zircon starting material underwent micron-scale recrystallization during the experiment. **(d)** SE image of zircons from an 800 °C experiment held for 500 hours, after HF treatment overnight. **(e)** Backscattered electron image of quartz grains (900 °C, 150 h) showing small micron-sized zircon inclusions circled in the image. **(f)** Cathodoluminescence image of untreated Mud Tank zircon. **(g-i)** CL image showing the changes in zircon luminescent characteristics after 20, 150, and 500 h (respectively) at 800 °C. The CL features near the rims of heat-treated zircons are interpreted to represent incorporation of Dy due to recrystallization of zircon.

Figure 4 Average Si isotope compositions of three-isotope method experiments plotted against experiment duration. The initial composition (open symbol) is plotted at t = 0. The δ^{30}Si averages and 2 s.d. values for each temperature series are included. These average values, which are used to constrain the isotopic composition of the system and to calculate the fractionation values, agree well with the initial composition.

Figure 5. Three-isotope plots for the three different temperatures explored in this study (isotope ratios are reported relative to NBS-28). Si isotope fractionation between zircon and quartz are calculated by extrapolation to the secondary mass fractionation line (SMFL) and constrained by mass balance. The dashed lines represent 95% confidence intervals.

Figure 6. The % exchanged of zircon plotted against % exchanged quartz for individual experiments for three-isotope exchange experiments. The % exchanged is calculated by subtracting isotope composition of the starting material from the experimental product and then dividing by the total length of the isotope line whose endpoints are defined by the starting material and the extrapolated intersection of the data with the SMFL.

Figure 7. Results of experiments showing Si isotope fractionation between quartz and zircon for the three different temperatures for both experimental methods (error bars are 2 s.d.). The fit to the three-isotope data yields an *A*-value of 0.53±0.14 (2 s.e.). Direct synthesis experiments are not included in the fit (see text for details).

Figure 8. A comparison of quartz-zircon Si isotope fractionations lines using the different *A*-values in Table 3. The experiment lines are derived independently from three-isotope the direct synthesis methods. The direct synthesis method is in closest agreement with the calculations of Qin et al. (2016), whereas the natural data presented in Trail et al. (2018) yield the best agreement with the three-isotope method.

Figure 9. Schematic showing the predicted relationship between Δ^{30}Si(WR-zrc) as the SiO_2 composition of the system decreases, because of the reduction in polymerization between crystallizing zircon and other phases. The red curve represents Δ^{30}Si(qtz-zrc) calibration defined by this work ($A = 0.53$). The Δ^{30}Si(WR-zrc) value, with $SiO_2 \approx 65$ wt. %, is calculated from δ^{30}Si(zrc) and δ^{30}Si(WR) values reported in Trail et al. (2018) for a tonalite. The mafic, or "$SiO_2 \approx 50$ wt.%", curve is estimated from the offset of Duluth Gabbro zircons from Si isotope composition of the mantle (δ^{30}Si(BSE) = -0.29 ‰; Savage et al., 2014) and an estimated formation temperature of ~800 °C, assuming Δ^{30}Si(WR-zrc) $\rightarrow 0$ as $T \rightarrow \infty$. Note that the two WR examples, while illustrative of the overall qualitative trend we wish to highlight, do not capture the complexities of fractional crystallization and zircon saturation in intermediate and mafic systems (Watson and Harrison, 1983; Boehnke et al., 2013).

Figure 10. Silicon-oxygen isotope fractionation concordia diagram for the zircon-quartz system. An *A*-value of 0.53±0.14 is used to describe Si isotope fractionation and 2.33±0.24 is used for O isotopes (Trail et al. 2009), the latter of which is in broad agreement with the empirical calibration reported by Valley et al. (2003). The dashed lines propagate *A*-value errors. The slope of the line is 4.4±1.5.