LETTER

Isotopic signature of core-derived SiO_2

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ABSTRACT

We apply an experimentally based thermodynamic model of Si+O saturation for the core to determine the saturation level of these elements under the conditions when the core formed. The model limits the bulk Si content of the core to between 0.4 and 3.1 wt% depending on the pressure, temperature, and oxygen content of the metal when it segregated from silicate. With knowledge of the core's Si content, the measured ^{30}Si content of the silicate Earth, and the experimentally determined metal-silicate fractionation factor, we can calculate the core's δ^{30}Si, which is between –0.92 to –1.36‰. SiO_2 cycled through the core and then released into the mantle might be trapped in inclusions in diamond formed in the lower mantle. These would be characterized by significantly lighter δ^{30}Si values of -1.12 ± 0.13‰ (1σ), compared to bulk silicate earth values of –0.29‰ and a potentially key indicator of mass transfer from the core to the mantle.

Keywords: Si, core, SiO_2, core-mantle interaction

INTRODUCTION

The Earth formed through a relatively rapid process during which approximately chondritic materials aggregated as a discrete body from the protoplanetary disk and differentiated into a metallic core and a silicate crust and mantle (Wood et al. 2006). During the melting arising from the accretion process (from impact energy, heat production from short-lived radionuclides, gravitational potential energy release from differentiation), either a planetary-scale magma ocean or spatially restricted magma lakes arose, imparting a relatively low-pressure differentiation signal [compared to the pressures of either the core-mantle boundary (CMB) or the planet's center] on the moderately siderophile elements (Li and Agee 1996; Wade and Wood 2005; Siebert et al. 2011, 2013; Fischer et al. 2015).

Concurrent with siderophile element partitioning, some major elements also entered the metal destined for the core: Si, O, and Mg are potential candidates (O'Neill et al. 1998; O'Rourke and Stevenson 2016; Badro et al. 2016; Hirose et al. 2017). In particular, some Si is believed to reside in the core because the Mg/Si and Al/Si ratios in the bulk silicate Earth are higher than chondritic values (Palme and O'Neill 2003). Based on high-pressure experiments at CMB conditions, Hirose et al. (2017) developed a model for SiO_2 saturation in core metal that allows the amount of Si+O potentially ingested by the core during accretion to be assessed. The Si+O is subsequently expelled back into the mantle as SiO_2 as the core cools. Escape of SiO_2 from the core is virtually certain due to its low density relative to silicate at the CMB (Hirose et al. 2017). This cycling through the core imprints core-derived Si with the metal-silicate stable isotope fractionation prevailing at the conditions of differentiation (Georg et al. 2007; Shahar et al. 2011) rather than bulk silicate Earth values and potentially provides a way to identify SiO_2 previously hosted by the core. The core's estimated Si content is based on a new, experimentally based set of constraints not previously exploited, to our knowledge, for making a metal-silicate isotope balance. We explore core-hosted SiO_2 isotopic signatures here; the physical mechanism for expelling SiO_2 from the core is described separately (Helffrich et al. 2018).

METHODS

We use Hirose et al.'s (2017) Si+O solubility model to determine joint Si+O solubility at various pressure (P) and temperature (T) conditions during the course of core formation and cooling. The conditions of core formation are set using a single-stage core formation model to approximate the range of pressures and temperatures encountered during accretion. The conditions are set as fractions of the CMB pressure, leading to a P range of 30–55 GPa [see Rubie et al. (2011) for one reckoning of the range]. From P, the associated T is obtained from two different equations for the peridotite liquidus and solidus, $T(P)$ (Wade and Wood 2005; Fiquet et al. 2010), respectively. Figure 1 shows a suite of saturation curves at various core formation pressures, calculated by evaluating the joint Si-O saturation expressions at the P and corresponding T on a grid and contouring (Hirose et al. 2017).

The method we use to estimate Earth's core's Si content is new, and based on joint Si+O solubilities in core metal, the constitution of the Earth's core, and the high-pressure behavior of the eutectic compositions of Fe-Si and Fe-FeO. In particular, Hirose et al. (2017) note that the Earth's inner core requires that it crystallize essentially pure Fe, which restricts the core liquid composition to the intersection of the SiO_2 saturation contour and the compositional triangle bounded by SiO_2, the Fe-Si eutectic, and the Fe-FeO eutectic (Fig. 1). The Fe-FeO eutectic moves to higher O content with increasing pressure (Komabayashi 2014; Morard et al. 2017), but the asymptotic behavior of the SiO_2 solubility contours with increasing O do not strongly affect the lower bound for Si. In contrast, Fe-Si's eutectic moves Fe-ward at high pressure (Fischer et al. 2013; Ozawa et al. 2016). At the pressure of the Earth's CMB, Fischer et al. (2013) placed the eutectic at 5–12 wt% Si, and various estimates of the maximum core Si content by Hin et al. (2014) and Dauphas et al. (2015) placed it at 6–8 and 0–9 wt%, respectively. However, the study by Ozawa et al. (2016) of the eutectic dependence on pressure narrowed the bound considerably to 1.5 wt%, which we use to define the Fe-Si eutectic in the O-free system. Figure 1 depicts the bounds constraining core Si.

A Si isotope balance of the Earth (subscript BE) may be written in terms of its

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partitioning between the core's metal (subscript C) and the mantle and lithosphere's silicate (subscript BSE)

$$\delta^{30}\mathrm{Si}_{BE} = f_c \delta^{30}\mathrm{Si}_c + \left(1 - f_c\right)\delta^{30}\mathrm{Si}_{BSE} \tag{1}$$

f_c is the mass fraction of Si in the core to the Si in the entire Earth. We use a pyrolitic model for the silicate Earth (McDonough and Sun 1995) to obtain its Si content (21 wt%) and the Si+O solubility model to determine the core Si content. To account for the silicate-metal partitioning during core formation, we use Shahar et al.'s (2011) temperature-dependent fractionation factor $\Delta^{30}\mathrm{Si}(T) = -7.45(\pm 0.41)\times 10^6/T^2$. Hence,

$$\delta^{30}\mathrm{Si}_c = \Delta^{30}\mathrm{Si}(T) + \delta^{30}\mathrm{Si}_{BSE} \tag{2}$$

$\delta^{30}\mathrm{Si}_{BSE}$ is –0.29 ± 0.02‰ (Fitoussi et al. 2009), and the *P-T* conditions of core formation sets the fractionation factor and f_c from the Si+O saturation model. From Equations 1 and 2 and these values, $\delta^{30}\mathrm{Si}_{BSE}$ may be calculated.

We use a single-stage core formation model, but more elaborate methods that track the evolution of the mantle's ^{30}Si content through the accretion process are also possible (Zambardi et al. 2013; Hin et al. 2014). We know experimentally that Si partitioning between metal and silicate is not pressure dependent (Fischer et al. 2015; Hirose et al. 2017) so the core's Si content is fairly constant during accretion (Tuff et al. 2011), yielding little difference between multi-stage core formation models and single-stage. Hin et al. (2014) showed that the difference between $\delta^{30}\mathrm{Si}_{BE}$ and $\delta^{30}\mathrm{Si}_{BSE}$ during their accretion histories is never more than 0.3‰. The signal that we predict is 3–4 times larger than this, justifying, post hoc, the use of the single-stage model for obtaining $\delta^{30}\mathrm{Si}_c$.

Xu et al. (2017) investigated Si diffusion in stishovite and provided an expression for the pressure- and temperature-dependent Si diffusion coefficient. Using lower mantle pressure and temperature range of 20 GPa, 2000 K to 135 GPa, 4000 K [see, e.g., Helffrich (2017)], leads to Si diffusion times over 1 mm distances of at least 300 Myr to 620 Gyr (due, in part, to the diffusion coefficient's strong pressure dependence). Assuming that $CaCl_2$-structure SiO_2, the SiO_2 polymorph stable at higher pressures than stishovite, behaves similarly, Si isotopic disequilibrium may be maintained over the times required for detection in diamond inclusions.

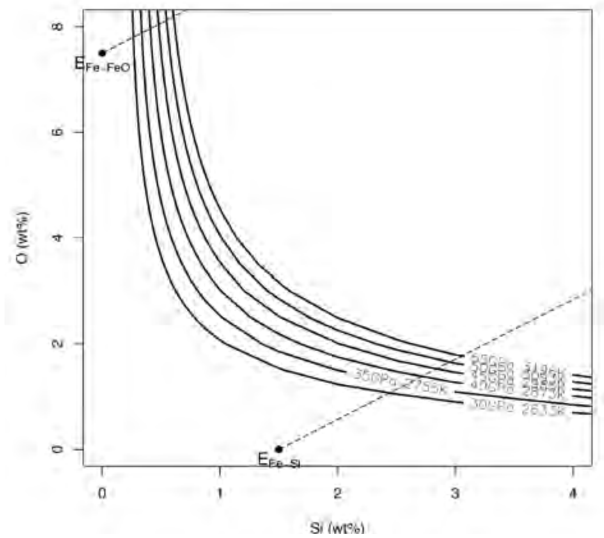

Figure 1. Saturation of Si and O in metallic iron at a range of pressures corresponding to core formation. Labels on each saturation line are *P* and *T* of formation; *T*(*P*) from Fiquet et al. (2010). The Si uptake depends on the O content, and hence yields a range for the mass of Si carried to the core in metal. Quasi-diagonal lines show the SiO_2 loss trend; for inner core properties like Earth's, feasible Si+O contents must be more O-rich than the Fe-Si eutectic (lower line) and less O-rich than the Fe-FeO eutectic (upper line). This limits core Si content to be 0.4–3.1 wt%.

Results

Limits on the uptake of Si by the core may be obtained from Figure 1. The present properties of the Earth's core (Hirose et al. 2017), the shape of the saturation contours, and the positions of the Fe-FeO eutectic ($E_{\text{Fe-FeO}}$) and the Fe-Si eutectic ($E_{\text{Fe-Si}}$) control the core's Si content. While the asymptotic nature of the relation at low Si renders the estimate insensitive to $E_{\text{Fe-FeO}}$, $E_{\text{Fe-Si}}$, and the slope of the SiO_2 loss line define the upper limit of Si saturation. The intersection of the SiO_2 loss line with the saturation contours therefore provides the 3.1 wt% upper bound that we use. These limits set core Si content to be 0.4–3.1 wt%. In turn, the limits place f_c in the range $0.91\% \leq f_c \leq 6.62\%$. By Equation 1, the core mass fractions lead to a δ^{30}Si fractionation range of $-0.37 \leq \delta^{30}\mathrm{Si}_{BE} \leq -0.30$‰. Alternative coefficients for $\Delta(T)$ (Hin et al. 2014; Ziegler et al. 2010) lead to $-0.33 \leq \delta^{30}\mathrm{Si}_{BE} \leq -0.29$‰. When compared with the values for bulk silicate Earth –0.29 ± 0.02, we find that the ranges largely overlap. This has implications for the Earth's source materials and formation conditions (Zambardi et al. 2013; Hin et al. 2014; Dauphas et al. 2015), but we do not discuss them here.

Discussion

Figure 2 shows the ^{30}Si fractionation predicted by the Si+O saturation model. The uncertainties include the effective pressure of segregation, alternative temperatures of segregation, and the range of permissible O content of the core, which also affects Si saturation. It is assumed in these calculations that there is no pressure-dependent silicon isotope fractionation (Shahar et al. 2016) at the temperatures associated with core formation.

Depending on the pressure and the solidus temperature model chosen, the Si isotope composition of the core is –1.12 ± 0.13‰ (1σ), significantly different from the BSE value of –0.29 ± 0.02‰ (2σ) and all of the chondritic meteorite classes (Fig. 2), except at the highest differentiation pressure using the Hin et al. (2014) coefficient. Diamonds are known to trap SiO_2, including those thought to come from the lower mantle (Stachel et al. 2000; Kaminsky 2012). Some SiO_2 inclusions are likely to be due to deep subduction of eclogite (Walter et al. 2011) and would have values close to bulk silicate Earth. The signature of a core source for SiO_2 would be an absence of aluminous phases and a light δ^{30}Si content of the SiO_2.

The values we report here represent lower bounds on the anticipated δ^{30}Si of core-hosted SiO_2 because we are also neglecting any fractionation of ^{30}Si during SiO_2 crystallization in the core itself, which will shift δ^{30}Si to less negative values. At the end of accretion, the core is likely to be hotter than the mantle and will cool rapidly (Lebrun et al. 2013). The SiO_2 crystallization required to run the Earth's dynamo corresponds to a cooling rate of 50–100 K/Gyr (Hirose et al. 2017), which is significantly lower than ~1000 K/Gyr rates expected in early Earth conditions. Hence the bulk of SiO_2 crystallized from the core will have separated under correspondingly higher temperatures than that of the present-day CMB. Independent of the $\Delta^{30}\mathrm{Si}(T)$ metal-silicate fractionation factor used, the shift will be within the 1σ uncertainty depicted in Figure 2 if crystallization initially occurred at 7000–8000 K. Firmer predictions of

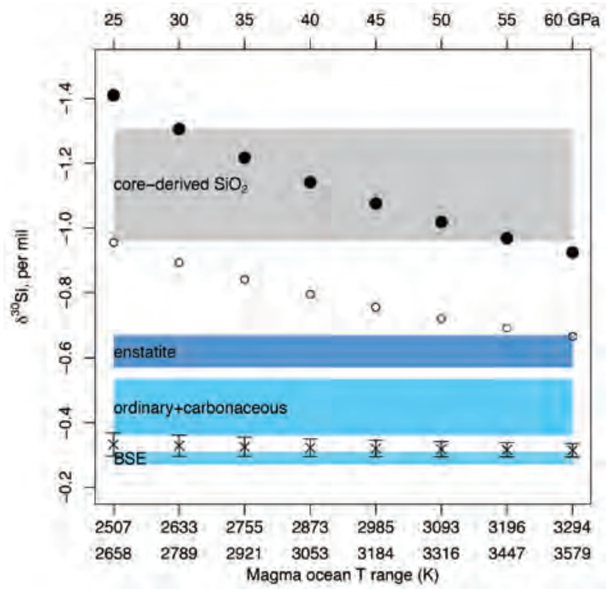

FIGURE 2. Bulk Earth (cross) and core-hosted SiO_2 (filled circle, open circle) ^{30}Si fractionation calculated using Si+O saturation at various temperatures corresponding to core formation compared to chondrites. Error bars on each $\delta^{30}Si_{BE}$ point correspond to variation due to metal-silicate separation temperature (at pressure given on top scale), O composition of core, and alternative $\Delta^{30}Si(T)$ coefficients. Colored bands show reported range of δ^{30}Si of various chondrite classes (Armytage et al. 2011; Fitoussi et al. 2009; Fitoussi and Bourdon 2012). Within the uncertainty of the formation conditions, $\delta^{30}Si_{BE}$ is similar to BSE. Core-hosted SiO_2 calculated using different fractionation factors (filled circle = Shahar et al. (2011); open circle = Hin et al. (2014); gray band is $\pm 1\sigma$ of filled circles points) is under most conditions lighter than chondritic meteorites and BSE, making it a useful diagnostic of core-mantle mass transfer.

uncertainty from this source require more detailed models of early Earth evolution focused on the end-stages of accretion and evolution past the magma ocean era.

IMPLICATIONS

The Si+O saturation model developed by Hirose et al. (2017) provides a way to estimate the core's bulk Si content and to estimate the core and bulk earth ^{30}Si fractionation. We find that the core's δ^{30}Si is between –0.92 and –1.36‰, depending on the conditions of core formation. The bulk Earth δ^{30}Si is $-0.37 \leq \delta^{30}Si_{BE} \leq -0.30$‰, which overlaps bulk silicate Earth and is marginally heavier than the ordinary and carbonaceous chondrite groups. We also predict that any SiO_2 that originated in the core and was later trapped as an inclusion in diamond should have significantly lighter δ^{30}Si of around -1.12 ± 0.13‰.

We also described a way to calculate the core's Si content using joint solubility constraints for Si and O in metal that may prove useful to draw up budgets for other stable isotope systems.

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