THE NON-CHONDRITIC SILICON ISOTOPE COMPOSITION OF THE BULK SILICATE EARTH.

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Introduction: It has long been proposed that the Earth's core must contain significant quantities of light elements, such as H, C, Si, S and K [1]. The super-chondritic Mg/Si of the terrestrial mantle has been used to argue that Si in particular is an important component in the core [2-4]. Recent estimates indicate that the core might contain as much as 5-7wt% Si, which compares with 21wt% Si in the primitive mantle [5, 6]. Based on isotope analyses of Si in different meteoritic, lunar and terrestrial samples, Georg *et al.* [7] found that the Si isotope compositions of the Earth and Moon are heavier than chondrites and hence concluded that this was a consequence of silicon isotope fractionation during core formation.

Their average δ^{30}Si value for chondrites is δ^{30}Si −0.58±0.05‰ (±1SD) and for Bulk Silicate Earth (BSE) it is δ^{30}Si −0.38±0.06‰, which corresponds to a fractionation on the order of ~1.7‰ assuming the core contains 5 wt% Si. This fractionation is in agreement with theoretical predictions and also experimental studies [8]. However, a second study by Fitoussi *et al.* [9] claims to have found barely resolvable differences between carbonaceous chondrites and terrestrial samples. On the basis of their models of magma ocean conditions, they conclude that Si isotopes per se do not provide evidence for or against Si in the Earth's core.

To try and resolve the contrast in these two datasets we have analysed a number of chondrites and terrestrial samples such as basalts and peridotites. In addition we have analysed an aliquot of a meteoritic sample published in [7].

Method: The method for measuring Si isotopes using multi-collector ICP-MS is similar to that outlined in [7]. The chemistry is a two stage process with a fusion step followed by cation-exchange chromatography. After the fusion step, which involves an alkaline flux to dissolve the sample, the resultant "fusion-cake" is made up into a weakly acidic solution with either HNO_3 or HCl. The aliquot from [7] that was measured in our new study had only been processed through this first fusion stage. Therefore both the "new" samples and the "old" sample were processed through the same cation-exchange chemistry simultaneously to facilitate a direct comparison.

The Si isotopic compositions were determined using Nu Plasma HR MC-ICP-MS at high resolution using the sample-standard bracketing technique against NBS-28. The external reproducibility of chemically processed pure Si standards (IRMM018, Diatomite) and rock samples is shown to be <0.20‰ (2SD) for δ^{30}Si. Six chondrites from different groups (CI, CK, CO, CM, CV, H5) were analysed in this study and also repeated dissolutions of Allende (CV3). The terrestrial samples included basalts and MORB glasses. About 10-20mg of the meteorite were used though larger samples (~60-100mg) were ground first in a boron-carbide mortar and pestle in an effort to homogenise the samples.

Results: The average δ^{30}Si of the chondrites and the terrestrial samples are plotted in Fig. 1 along with the values from [7] normalised to BSE. It is clear from the diagram that the difference (Δ^{30}Si) between the terrestrial and chondrite averages is still measureable though not as marked as in [7]. The value found in this study is Δ^{30}Si = 0.13 in comparison to $\Delta^{30}Si_{Georg}$ = 0.2.

There is also a difference in the absolute δ^{30}Si values between the previous work [7] and this study. Our chondritic and terrestrial values are both slightly heavier, being -0.45±0.06‰ (1SD) and -0.32±0.05‰ respectively, but agree within 2 SD with previously published values of [7]. Unfortunately there are no values for Si isotopic compositions given by Fitoussi *et al.* [9], so no quantitative comparison can be made to assess any discrepancy.

The aliquot of Allende solution from [7] had a δ^{30}Si value of -0.50±0.04‰ (2s.e.) when measured in this study. This is slightly heavier than the previously published value of -0.58±0.03‰ but is still in the range of the external reproducibility. The different fresh splits of Allende processed in this study show a range in δ^{30}Si from -0.43 to -0.36‰ with a mean of -0.40±0.03‰ (1SD). The overall δ^{30}Si Allende mean including the aliquot from [7] is -0.41±0.05‰ (1SD). The various Allende solutions were made up with different acids, but our tests show that this does not generate a systematic difference in the measured isotopic composition. The ordinary chondrite sample (Allegan, H5) had a δ^{30}Si = -0.49±0.03‰, which places it within the range of the carbonaceous chondrites.

Discussion: The new data acquired in this study confirm the conclusion from [7] that there is a measurable difference between chondrites and terrestrial samples. However, absolute values of both are slightly heavier and the difference appears to be smaller than that previously published [7]. The procedural repeats of Allende with some slight differences in processing (e.g. filtering of solution, different acids and amount of sample) showed no effect that is able to produce a systematic bias as seen between the two datasets for meteorites. In analyzing bulk chondrites there is always the question as to how well homogenized the sample is, especially with small volumes of material. In this study it is less of an issue as in many cases the meteorite samples come from the same homogenized powder as [7].

There are a number of processes acting in the early Solar System that could give rise to the variations seen in silicon isotope ratios between chondrites and terrestrial samples. One explanation for the isotope effects of Fe and Si is partial loss caused by evaporation and condensation during the giant impact, which formed the Moon. The Earth is enriched in highly refractory elements [11], which is sometimes considered to be caused by losses during impact erosion. However, this explanation is hard to reconcile with Mg and Li isotope data which show no difference between mantle-derived silicates from the Earth, Moon, Mars or Vesta [12-14], despite similar half-mass condensation temperatures [15] for Li, Mg, Si and Fe.

Shahar *et al.* [8] found Si isotope fractionation during high P/T metal-silicate partitioning experiments (1GPa, 1800ºC) as high as 2‰ (δ^{30}Si). Their data, although not necessarily representative of P/T conditions prevailing at the core-mantle boundary, show that Si isotopes are fractionated with the magnitude and direction sufficient to explain the isotopic difference between BSE and chondrites.

Conclusions: Albeit with slight differences in absolute δ-values, these new Si isotope results support the conclusion of Georg *et al.* [7] that there is a resolvable difference in δ^{30}Si values between chondrites and BSE. The question as to why the absolute δ-values appear to be slightly different has to be addressed in further inter-laboratory exercises. However, it needs to be stressed that even pure Si standards cannot be reproduced to better than 0.2‰ when comparing different laboratories, and the relatively small differences in absolute δ-values for meteorites and terrestrial samples found between this study and [7] are <0.15‰.

Considering the experimental Si isotope data for metal-silicate partitioning experiments, fractionation of Si isotopes during core formation appears to be the likeliest cause for observed differences between chondrites and BSE, making Si a strong contender for being one of the light elements in the Earth's core.

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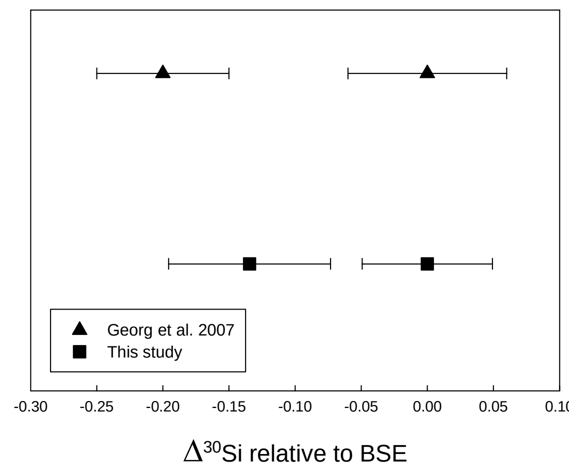

Fig. 1. Plot of average δ^{30}Si values for meteorites and terrestrial samples normalised to BSE of this study, in comparison to previously published results from [7]. The plotted error bars are 1 SD similar to [7].