

SILICON ISOTOPE FRACTIONATION BETWEEN METAL AND SILICATE AT HIGH PRESSURE AND HIGH TEMPERATURE – IMPLICATIONS FOR EARTH’S CORE. J. Kempl¹, D. J. Frost², P. Z. Vroon¹, P. M. Kowalski³ and W. van Westrenen¹, ¹VU University Amsterdam, Faculty of Earth and Life Sciences, De Boelelaan 1085, 1081 HV Amsterdam, the Netherlands, w.van.westrenen@vu.nl), ²Bayerisches Geoinstitut, University of Bayreuth, Germany, ³Forschungszentrum Jülich, Institute of Energy and Climate Research (IEK-6), Jülich, Germany.

Introduction and Aim: Constraints on the conditions prevailing during metallic core formation in both small and larger planetary bodies are traditionally obtained by combining observed concentrations of minor and trace elements in silicate materials with experimental data on metal-silicate partitioning of these elements [1-3]. These studies all rely on the availability of a substantial set of hundreds of experimental metal-silicate partitioning data obtained over several decades (e.g., the recent compilation by Righter [1]). Due to the advent of multi-collector (MC) ICP-MS techniques it has become possible in recent years to approach the question of core formation using stable isotope partitioning between metal and silicate, with the behavior of Si isotopes of particular interest [4-6]. Here, we report results of an experimental high-pressure, high-temperature study into the fractionation of Si isotopes between metal and silicate.

Background: Silicon is composed of three stable isotopes: ²⁸Si, ²⁹Si and ³⁰Si. Variations in silicon isotopic composition are expressed using the delta notation relative to reference material NIST RM 8546, with $\delta^{30}\text{Si} = \left(\frac{{}^{30}\text{Si}/{}^{28}\text{Si}_{\text{sample}}}{{}^{30}\text{Si}/{}^{28}\text{Si}_{\text{standard}}} \right) \times 1000$ (unit: per mil). The average $\delta^{30}\text{Si}$ isotopic signature of samples from the Bulk Silicate Earth (BSE) and lunar samples is approximately -0.29 ‰ (± 0.1 ‰, 2 S.D), slightly higher than the average $\delta^{30}\text{Si}$ for primitive meteorites, -0.48 ‰ (± 0.2 ‰, 2 S.D) [7-9]. The resulting difference in Si isotopic composition $\Delta^{30}\text{Si}_{\text{BSE-Chondrites}} = \delta^{30}\text{Si}_{\text{BSE}} - \delta^{30}\text{Si}_{\text{Chondrites}} = 0.19 \text{ ‰}$ (± 0.1, 2 S.D.) has been explained by equilibrium metal-silicate Si isotope fractionation during core formation at high temperatures and high pressures, driven by the different chemical bonding environment of Si in silicate mantle rocks and in metallic liquid.

Translation of these results into corresponding core Si concentrations requires knowledge of Si equilibrium isotope fractionation factors between silicate and iron-rich metal at high-temperature and high-pressure conditions. To date, these have mostly been derived from theoretical calculations, suggesting that the Si concentration in the outer Earth’s core could comprise between 2.5 wt% and 16.8 wt% Si - a range that is even larger than estimates on the Si content of the core derived from Si elemental partitioning data (1-11 wt%) [10]. To expand the currently available experimental

data set on Si isotopic fractionation between metal and silicate [4,5] we performed high-pressure experiments.

Methods: Experiments were performed in the Bayerisches Geoinstitut 1000 and 1200 ton multi-anvil devices. Time series were performed to assess the kinetics and extent of Si isotope fractionation at 9 GPa and ~2150 °C in MgO capsules. Phases in the run products were chemically analysed by electron microprobe at VU University Amsterdam. Samples were micro drilled and metal and silicate were separated by hand picking. Sample aliquots were chemically digested, purified and diluted for Si isotope analyses on a Thermo-Finnigan MC-ICPMS at VU University Amsterdam using established techniques [11].

Results: Run products consist of quenched silicate melt and a sphere of quenched Si-bearing metal alloy (Figures 1a and 1b).

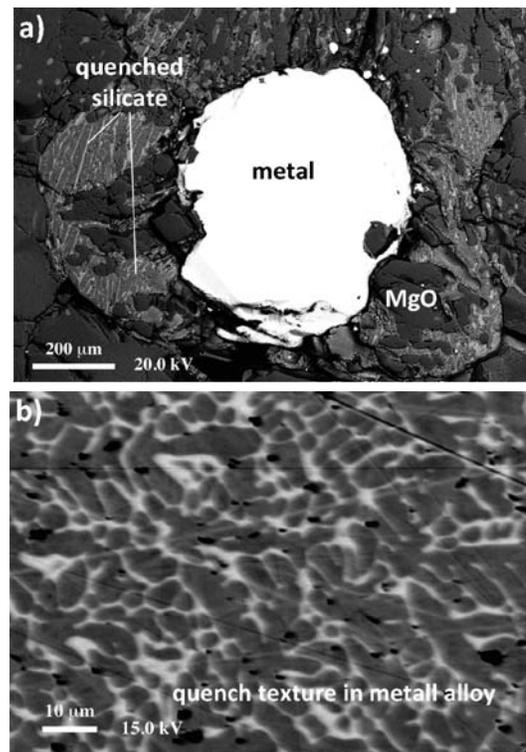


Figure 1: Typical run product of high-pressure multi-anvil experiments at 9 GPa and 2100 °C after 30 minutes. Quench textures in silicate (a) and metal (b) indicate that both phases were molten.

Based on electron microprobe analyses of Fe and FeO concentrations in metal and MgO capsule, respectively, we calculate oxygen fugacities of our experiments to be ranging between -4 and -6 log units below the iron-wüstite (IW) buffer. Our time series results show that Si isotopic equilibrium is reached after 30 minutes at our pressure and temperature conditions, resulting in a Si concentration of 8.8 wt% in the metal phase. At equilibrium, we find $\delta^{30}\text{Si}_{\text{metal}} = -0.77\text{‰}$ for the metal, and 0.19‰ for the silicate. As expected, the silicate is concentrating the heavier isotopic fraction due to stronger chemical bonding, whereas the metal is enriched in the lighter Si isotope fraction.

Our data can be combined with literature data [4,5] if all measurements are corrected to a common temperature. To do this, we assume that Si isotope fractionation between metal and silicate shows an inverse dependence on T^2 . Our data can be combined with literature data spanning the range 1-9 GPa and 1800-2150°C [4,5]. Temperature-corrected data show a negative pressure dependence of equilibrium Si isotope fractionation between metal and silicate (Figure 2), contrary to previous work [4,5] which concluded there was no significant pressure effect.

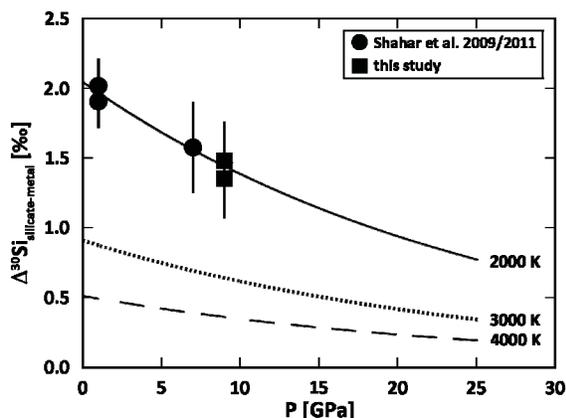


Figure 2: Pressure dependence of Si isotope fractionation between metal and silicate at different temperatures calculated on the basis of existing experimental data [4,5] and our measurements.

Implications and Outlook: A negative pressure dependence raises estimates of the Si content of Earth's core. If core-mantle equilibration occurred at 25 GPa and 2500 K, the model shown in Figure 2 suggests the core contains between 11 and 29 wt% Si depending on the value of $\Delta^{30}\text{Si}_{\text{BSE-Chondrites}}$. Higher core formation pressures and temperatures would raise these estimates even further. We conclude there is an increasing discrepancy between the Si content derived from Si isotopic data and estimates of the Si content of the core based on elemental Si partitioning studies.

To improve the accuracy of the Si isotope fractionation model, additional experimental data are required at even higher-pressure conditions. Additionally, the Si isotope fractionation behavior at higher pressures and temperatures with changing silicate structures needs to be assessed.

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