

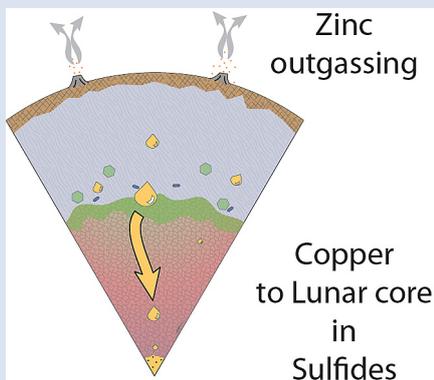
# The effect of core segregation on the Cu and Zn isotope composition of the silicate Moon

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doi: 10.7185/geochemlet.1928

## Abstract



Compared to elements of similar volatility, such as Rb, Ga and K, the bulk silicate Moon (BSM) exhibits significant enrichment in the heavy isotopes of Zn and Cu. However, both elements display a greater affinity for lunar sulfide phases than the other volatiles, suggesting their isotopic abundance in the BSM may also reflect their sequestration to the lunar core. Experimentally determined Cu and Zn isotopic fractionation between liquid metal, sulfide and silicates reveals carbon-bearing iron melts to be isotopically heavier than the silicate melt, and sulfide melts the lightest. During sulfide sequestration from a cooling lunar magma ocean, Cu, unlike Zn, partitions strongly into sulfides ( $100 < D_{\text{Cu}}^{\text{Sulfide/Melt}} < 200$ ), leaving the BSM both elementally depleted in Cu, and isotopically heavier. Sulfide sequestration therefore explains the larger offsets in the Cu isotope compositions of lunar rocks and the silicate Earth relative to other moderately volatile elements. The lunar Zn isotopic inventory is best explained by volatility driven surface processes. Irrespective of the elemental loss mechanism, the Cu isotopic content of the BSM rules out carbon as a significant light element of the lunar core.

Received 2 July 2019 | Accepted 24 September 2019 | Published 19 November 2019

## Introduction

The elemental composition of the bulk silicate Earth and Moon (BSE and BSM respectively) provides insight into the accretion processes and subsequent differentiation of the Earth-Moon system. Lunar rocks and the BSE express many similarities which support a genetic link between the Earth and Moon. These include the proportions of refractory elements and the stable isotope compositions of elements with half-mass condensation temperatures ( $T_{50}$ ) higher than 1100 K, such as Si (Fitoussi and Bourdon, 2012), Cr (Mougel *et al.*, 2018), and W (Touboul *et al.*, 2007). The Moon does, however, display a notable elemental depletion in the moderately volatile elements, such as Zn, Rb, Ga, K, and Cu, coupled with an enrichment of their heavy isotopes with respect to the BSE (Fig. 1). Although this condensation sequence is for deposition from a reducing nebula gas to solid phases, evaporation from melt at the more oxidising conditions of lunar formation results in Zn and Cu exhibiting similar volatilities (Norris and Wood, 2017), making explanations of their lunar isotopic variability problematic.

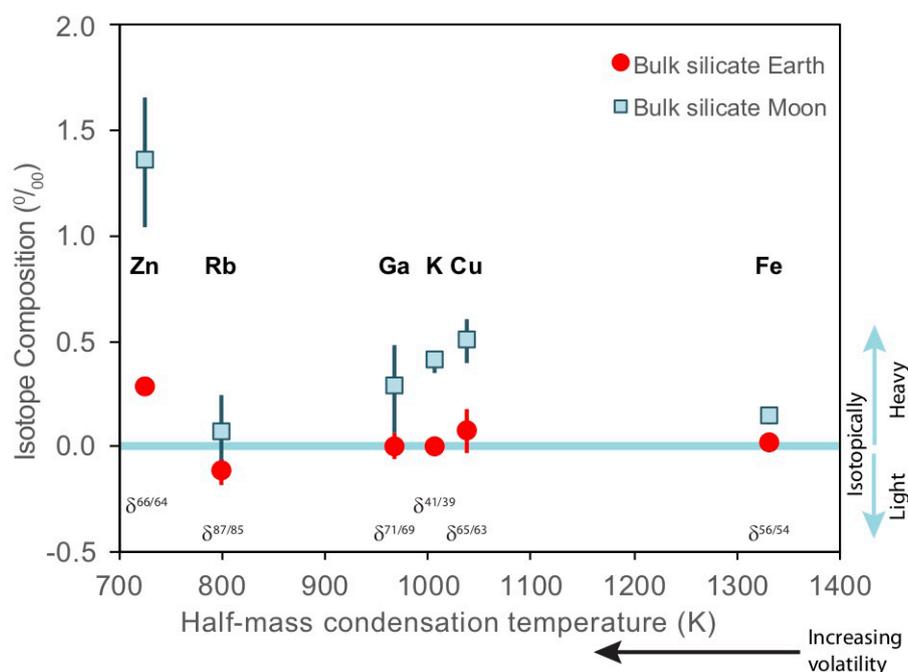
These features have been interpreted as resulting from a global scale evaporation event associated with either the giant impact (Wang and Jacobsen, 2016), and/or the differentiation

of the Lunar Magma Ocean (LMO) (Day and Moynier, 2014; Kato *et al.*, 2015) and localised degassing of the mare basalt lavas (Sharp *et al.*, 2010). Cu and Zn, however, exhibit larger isotopic variations between mare basalts and the BSE ( $1.07 \pm 0.34$  ‰ for Zn,  $0.43 \pm 0.14$  ‰ for Cu) than other volatile isotopes of comparable condensation temperatures (*e.g.*,  $0.18 \pm 0.21$  ‰ for Rb,  $0.28 \pm 0.25$  ‰ for Ga,  $0.40 \pm 0.06$  ‰ for K) (Fig. 1). Although element volatility during lunar formation and degassing of the LMO undoubtedly played a role in setting the Moon's elemental and isotopic budget, the disparity between the isotopic and elemental abundances and element condensation temperatures remains enigmatic, suggesting that more than one mechanism may be responsible. We propose that this disparity arises from the segregation of sulfides to the lunar core, exacerbated by the cooling LMO and the consequent decrease in sulfide solubility in silicate melts.

Zinc and copper exhibit both siderophile and chalcophile behaviours, evidenced both by metal-silicate-sulfide partitioning experiments (Siebert *et al.*, 2011; Mahan *et al.*, 2017), and by enrichment in meteorite hosted sulfides (*e.g.*, Williams and Archer, 2011). Geochemical and geophysical studies support the existence of a lunar core exhibiting an extant liquid outer component (Weber *et al.*, 2011), and hence the presence of a significant light element core component.

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**Figure 1** Half-mass condensation temperatures (Lodders, 2003) for a solar system composition gas versus isotope composition. Data reference for the isotopic compositions are detailed in the Supplementary Information. It should be noted, however, that the condensation temperatures displayed are for deposition from gas to solid in a nebula gas, not for evaporation from a liquid at the more oxidising conditions pertinent to Moon formation.

Segregation of a metal-rich core from the LMO during lunar core-mantle differentiation, and subsequent mantle cooling and sulfide precipitation (Mavrogenes and O'Neill, 1999), can sequester significant amounts of Cu and, to a lesser extent, Zn, without noticeable influence on lithophile volatiles such as Rb, K, Li, and Ga (Siebert *et al.*, 2011). Given significant Cu isotope fractionation among metallic, silicate, and sulfide melts (Savage *et al.*, 2015), this process will inevitably fractionate lunar Cu isotopes, and, potentially, Zn isotopes. The role of core segregation in shaping the isotope composition of the silicate Moon is, as yet, unclear because equilibrium isotope fractionation factors of Zn and Cu between phases associated with lunar core formation (metal, sulfide, and silicate), remain poorly constrained. Hence, we experimentally explored the equilibrium Zn and Cu isotope fractionation among metallic, sulfide, and silicate melts at conditions relevant to lunar core formation.

## Zinc and Copper Isotope Experiments to Simulate LMO Differentiation

We conducted a series of experiments in graphite capsules at 1.5 GPa using piston cylinder apparatus (Tables S-1 to S-4, Fig. S-1 and Methods, see Supplementary Information). The experimental charges contained approximately 50 % silicate of a basaltic composition, equilibrated with ~50 % metal or sulfide with variable Ni content, under fully molten conditions (Tables S-1 to S-5 and Fig. S-1).

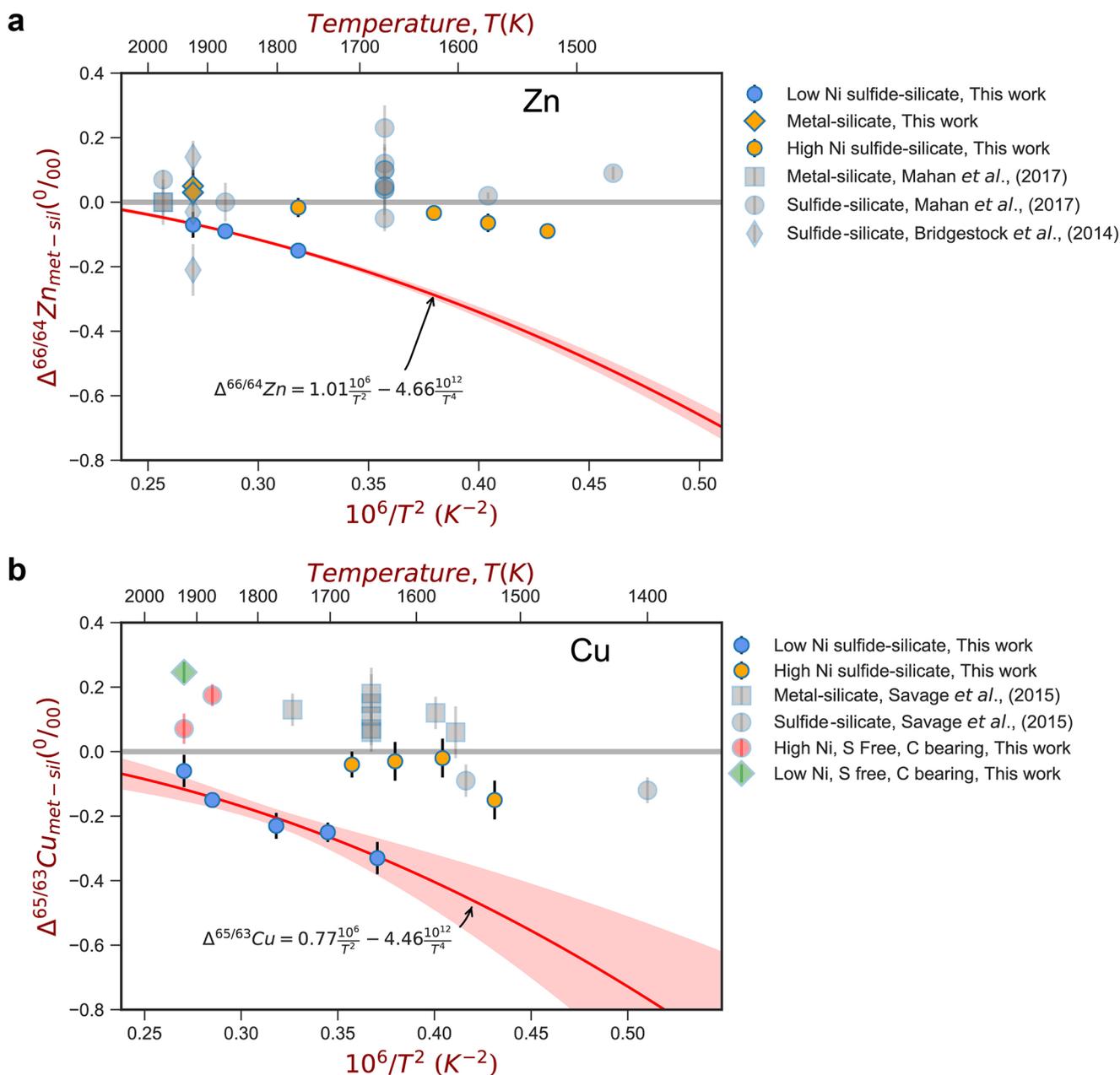
For both Cu and Zn isotopes, the iron-rich liquids are slightly enriched in heavier isotopes relative to the silicate melts. In contrast, sulfide melts exhibit demonstrably lighter isotope compositions than the silicate (Fig. 2), with measured Cu isotope fractionation factors consistent with both previous studies of iron meteorites (Williams and Archer, 2011) and experimentally determined Cu isotope fractionation for metal/silicate and sulfide/silicate liquids (Savage *et al.*, 2015) (Table S-6). Zn isotopes display a smaller degree of fractionation than Cu isotopes (Fig. 2). Overall, the isotope fractionation of both

elements decreases with increasing temperature. The nickel sulfide content affects the fractionation of both Cu and Zn isotopes (Fig. 2), with high Ni (~25 wt. % Ni in sulfide) experiments exhibiting less fractionation than those with low Ni (0.1 to 1.2 wt. % Ni in sulfide, Table S-1).

## Discussion

During lunar core-mantle differentiation, a carbon-bearing, iron-rich core will preferentially sequester isotopically heavy Cu and, potentially Zn, leading to the BSM exhibiting lower (lighter) values in  $\delta^{66}\text{Zn}$  and  $\delta^{65}\text{Cu}$ . This is contrary to observations; the BSM is isotopically heavier than the BSE in both Cu and Zn. Importantly this precludes carbon as a significant light element component of the lunar core. In contrast, sequestration of sulfide to the lunar core would leave the BSM isotopically heavy in both Cu and, potentially Zn, in accordance with the observed offset between silicate Moon and Earth (Fig. 1). It has been proposed that the proto-Moon initially accreted from the outermost volatile-rich disk generated by the giant impact, and is thus less volatile-depleted than the observed lunar rocks from the surface (Canup *et al.*, 2015). Although subsequent degassing of the LMO would result in a significant loss of volatiles from the BSM, its extent would have been mitigated by the presence of an early-formed lunar crust (Elkins-Tanton and Grove, 2011). The lunar interior may therefore have retained abundant volatiles, including sulfur, through inefficient degassing, as evidenced by the comparable sulfur content of lunar magmas and terrestrial mid-ocean ridge basalts (Hauri *et al.*, 2017). In comparison to analogous terrestrial basalts, the solubility of sulfide in the melt decreases as the BSM undergoes secular cooling, exacerbated by the lunar mantle's lower oxygen fugacity (O'Neill and Mavrogenes, 2002), promoting the formation of an immiscible sulfide liquid.

To explore this mechanism and its effect on Zn and Cu isotopic signatures, we calculated the  $\delta^{66/64}\text{Zn}$  and  $\delta^{65/63}\text{Cu}$  content of the BSM by considering the scenario of sulfide



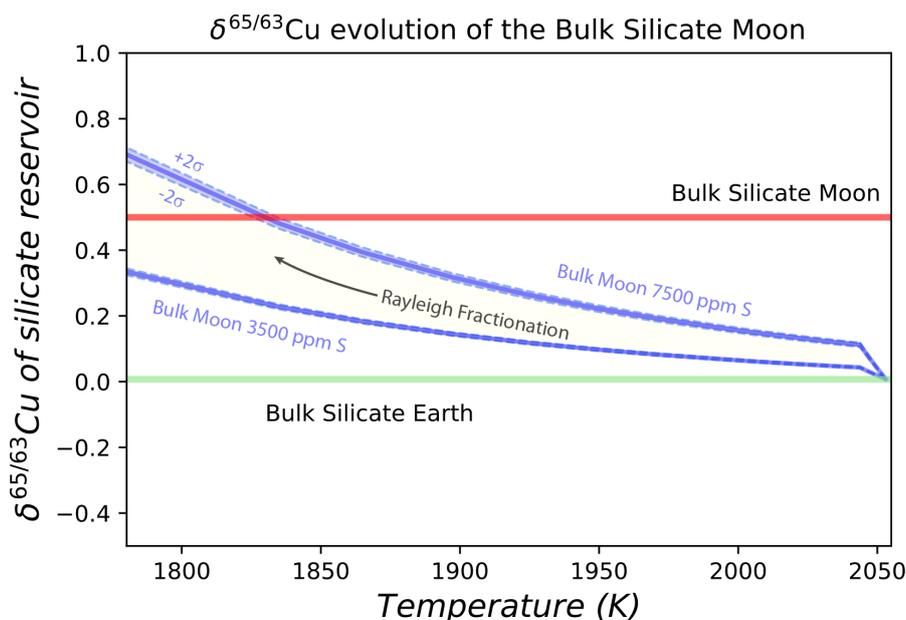
**Figure 2** (a,b) Zn and Cu isotope fractionation factors between liquid metal-silicate and sulfide-silicate as a function of temperature. Both increasing temperature and Ni content of sulfide decrease the Zn and Cu isotope fractionation, with the result that low Ni sulfides all exhibit a temperature dependent excess of isotopically light Cu and Zn. The pale-red band is the 95 % confidence interval for the regression shown.

segregation from an ambient basaltic magma ocean and assuming the bulk Moon is predominantly comprised of material derived from the Earth’s mantle (Canup, 2012; Wade and Wood, 2016).

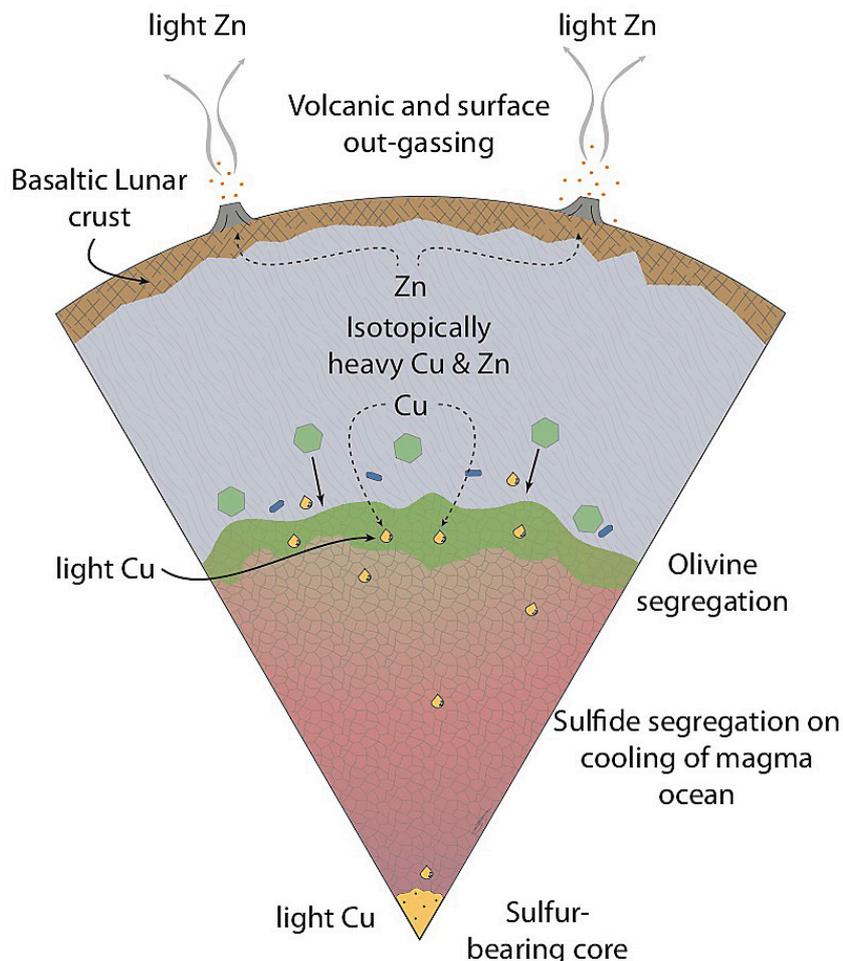
Under the conditions of lunar sulfide sequestration, Cu, unlike Zn, exhibits a strong preference for the sulfide phase; the lunar Cu sulfide/silicate partition coefficient,  $D_{Cu-Moon}^{Sulfide/Silicate}$ , ranges from 100 to 200, in contrast to Zn, which is ~1 (Kiseeva and Wood, 2015). This results in a sulfide liquid, initially in equilibrium with the silicate LMO prior to its sequestration to the lunar core, enriched in isotopically light Cu. This leads to a BSM exhibiting a significant depletion in Cu and becoming isotopically heavy in Cu. The result is a divergence of Cu isotopes between the BSE and BSM, with a negligible effect on isotopes of lithophile elements (e.g. Rb, Ga,

and K). Zn, however, exhibits negligible elemental and isotopic fractionation upon lunar sulfide extraction; a consequence of both its lower isotopic fractionation and chalcophile behaviour. The limited Zn isotope fractionation that occurs during the evolution of mafic magma (Chen *et al.*, 2013), coupled with the uniform  $\delta^{66/64}Zn$  in high Ti ( $1.50 \pm 0.54 \text{ ‰}$ ,  $n = 17$ ) and low Ti lunar basalts ( $1.35 \pm 0.43 \text{ ‰}$ ,  $n = 17$ ), suggest their Zn isotope compositions reflect that of the primitive lunar magmas (Kato *et al.*, 2015). During terrestrial mantle melting, high degrees of melt extraction (>30 %) may fractionate Zn isotopes up to 0.16 ‰ (Doucet *et al.*, 2016). The significantly lower melt extraction (~5-11 %) expressed by the mare basalts (Day and Walker, 2015) will consequently yield only subtle isotopic variations in Zn, negligible relative to the large offset between the BSE and lunar rocks.





**Figure 3** The Cu isotope evolution of the silicate Moon during lunar sulfide segregation. Assuming the Moon is derived from the precursor BSE, and the Moon’s core is predominantly FeS (equating to a bulk Moon of ~7500 ppm S), or just the outer core (3500 ppm S) and sulfide sequestration occurs by Rayleigh fractionation, the silicate Moon becomes progressively lighter in Cu. Horizontal lines represent values of the BSM estimated by lunar basalts (red) and the BSE (green) (Herzog *et al.*, 2009). The pale blue band represents 2 standard deviations of the error on the mean of the fractionation regression.



**Figure 4** Cu is hosted in lunar sulfides as a consequence of its significantly higher preference for the sulfide phase over silicate during LMO cooling and the consequent decreasing solubility of sulfide in the melt. Zn, however, is little affected implying the BSM Zn isotopic content is set by element volatility during Moon formation and LMO degassing. The BSM’s Cu isotopic composition reflects sulfide loss to the lunar core.

Modelling sulfide segregation by Rayleigh fractionation reveals that sulfur-rich lunar core formation cannot be responsible for the isotopically heavy  $\delta^{66/64}\text{Zn}$  BSM, nor for its elemental depletion. Given the limited mineralogical host phases for Zn, the most likely mechanism of lunar Zn depletion is that of volatility during lunar formation (Paniello *et al.*, 2012) or magma ocean degassing (Kato *et al.*, 2015). In contrast, the silicate Moon's high  $\delta^{65/63}\text{Cu}$  can be explained as a direct consequence of sulfide sequestration to the core (Fig. 3), a result of the initially molten Moon saturated in FeS and exacerbated by the subsequent drop in the sulfide content of lunar magmas on cooling (Mavrogenes and O'Neill, 1999). In addition, sulfide sequestration depletes the silicate Moon in the chalcophile elements Cu and Ni (Walter *et al.*, 2000), without significantly disturbing the W isotopic age of the Moon (Wade and Wood, 2016), an element that displays little affinity for the sulfide phase.

Sulfide retained in the deep Moon may therefore be an important reservoir for isotopically light Cu, but not Zn, which is best explained by its volatility during the Moon forming impact and subsequent degassing from the Lunar crust (Fig. 4). The silicate Earth and Moon share almost identical Cr isotope compositions (Mougel *et al.*, 2018), an element marginally more volatile than Fe (1296 K and 1334 K half-mass condensation temperatures respectively (Lodders, 2003)), but which exhibits a similar sulfide/melt partitioning behaviour to Zn (Kiseeva and Wood, 2015). Therefore, the segregation of sulfide (Brenan and Mungall, 2017) can drive the silicate Moon to Cu isotopic compositions, but this process has little effect on elements which display a lower preference for lunar sulfides, such as Zn and Cr. Compared to the BSE, the silicate Moon exhibits around a threefold depletion in Ni (Walter *et al.*, 2000), an observation consistent with its extraction during lunar core formation *via* sulfide segregation (Wade and Wood, 2016). Assuming the Moon's Ni content is inherited primarily from the silicate Earth, this suggests the Moon's core contains around 7.5 wt. % Ni. Increasing metallic Ni contents implies higher core sulfur contents for a given Cu isotope content exhibited by the silicate Moon.

Sulfide saturation may arise from the secular cooling of a LMO containing excess sulfide derived from the Moon forming impactor, and/or the late addition of S to the lunar mantle. Because of the higher density of sulfide relative to the ambient magma, and the initially completely molten lunar mantle, excess or precipitating sulfide will sink into the lunar interior. The near-chondritic  $^{187}\text{Os}/^{188}\text{Os}$  and chondrite-relative HSE abundance in high MgO mare basalts (Day and Walker, 2015) implies that this sulfide component is efficiently extracted from the silicate Moon to the Lunar core, with little stranded in the source region of the Mare basalts (Brenan and Mungall, 2017). This addition of sulfide liquid to lunar core is in line with the studies that propose sulfur as a dominant light element in the lunar core (Rai and van Westrenen, 2014).

## Acknowledgements

This work is supported by the Strategic Priority Research Program (B) of Chinese Academy of Sciences (Grant No. XDB18000000), the National Science Foundation of China (41325011, 41630206). ESK was supported by NERC grant NE/L010828/1. JW acknowledges receipt of a NERC Independent Research Fellowship NE/K009540/1. We thank Huimin Yu and Xingchao Zhang for the help of Zn and Cu isotope analyses.

Editor: Helen Williams

## Author Contributions

FH and ESK conceived the experimental study. ESK performed the high pressure experiments. ESK and YX conducted the electron probe measurement. YX and FH processed the samples and performed the SEM, LA-ICP-MS, and MC-ICP-MS analyses. JW performed EPMA/SEM analysis on the C-bearing samples, conceived the application, performed the data modelling and presentation. All authors contributed to interpretation of the data and writing the paper.

## Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article1928>.



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**Cite this letter as:** Xia, Y., Kiseeva, E.S., Wade, J., Huang, F. (2019) The effect of core segregation on the Cu and Zn isotope composition of the silicate Moon. *Geochem. Persp. Let.* 12, 12–17.

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