Elemental partitioning and isotopic fractionation of Zn between metal and silicate and geochemical estimation of the S content of the Earth's core

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Abstract

Zinc metal–silicate fractionation provides experimental access to the conditions of core formation and Zn has been used to estimate the S contents of the Earth's core and of the bulk Earth, assuming that they share similar volatility and that Zn was not partitioned into the Earth's core. Therefore, Zn provides both direct and indirect information into the origin and eventual fate of volatile and siderophile elements on Earth. However, the partitioning of Zn between metal and silicate – as well as the associated isotopic fractionation – is not well known. We have conducted a suite of partitioning experiments to characterize Zn elemental partitioning and isotopic fractionation between metal and silicate as a function of time, temperature, and composition. Experiments were conducted at 2 GPa and temperatures from 1473 K to 2273 K in a piston cylinder apparatus, with run durations from 5 to 240 min for four distinct starting materials. Chemical and isotopic equilibrium is achieved within 10 min of experimental outset. Zinc metal–silicate isotopic fractionation displays no resolvable dependence on temperature, composition, or oxygen fugacity within the data set. Therefore, the Zn isotopic composition of silicate phases can be used as a proxy for bulk telluric bodies. Partitioning results from this study and data from literature were used to robustly parameterize Zn metal–silicate partitioning as a function of temperature, pressure, and redox state. Using this parametric characterization and viable formation conditions, we have estimated a range of Zn contents in the cores of iron meteorite parent bodies (i.e. iron meteorites) of ∼0.1–150 ppm, in good agreement with natural observations. We have also calculated the first geochemical estimates for the Zn contents of the Earth's core and of the bulk Earth, at 242 ± 107 ppm and 114 ± 34 ppm (respectively), that consider the slightly siderophile behavior of Zn. These estimates of the Zn contents of the Earth's core and bulk Earth are significantly higher than previous estimates 0–30 ppm and 24–47 ppm, respectively. Assuming similar volatility for S and Zn, a chondritic S/Zn ratio, and considering our new estimates, we have calculated a geochemical upper bound for the S content of the Earth's core of 6.3 ± 1.9 wt%. This indicates that S may be a major contributor to the density deficit of the Earth's core or that the S/Zn ratio for the Earth is non-chondritic.

1. INTRODUCTION

Earth's formation and subsequent differentiation is thought to have occurred by the accretion of large planetes-imals (Kleine et al., 2002; Chambers, 2004; Wood et al.,

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2006). The impact energy of these coalescing planetary embryos combined with the radioactive decay of short-lived radioactive elements melted a substantial fraction of the proto-Earth (possibly multiple times), creating a deep magma ocean (up to 1100 km depth) (Tonks and Melosh, 1993; Li and Agee, 1996; Chabot et al., 2005; Wade and Wood, 2005; Halliday and Wood, 2009). The canonical view of core formation holds that during this melting event, gravitational separation of immiscible silicate and metallic melts occurred along with the isotopic fractionation of constituent elements at high temperature and high pressure (HT-HP) between metal and silicate (core and mantle) phases (Wood et al., 2006; Georg et al., 2007; Shahar et al., 2011; Hin et al., 2013). In this scenario, metallic droplets form in the deep magma ocean in chemical and isotopic equilibrium and sink to the bottom under their own weight. This metallic downpour accumulates at the base of the magma ocean (the last point of metal–silicate equilibration), subsequently coalescing via cohesive forces to form large, inverted diapers that then rapidly descend to the continuously growing core without any further equilibration, making core formation the single largest chemical fractionation event in Earth's history (e.g. Li and Agee, 1996; Siebert et al., 2011). Although this generic scenario is well accepted, the physical conditions at which the process happened and therefore the composition of the Earth's core (especially with regard to residing light elements), as well as the origin and fate of its volatile elements, are still highly debated (Dreibus and Palme, 1996; Li and Agee, 1996; Wade and Wood, 2005; Corgne et al., 2008; Albarède, 2009; Brenan and Mcdonough, 2009; Siebert et al., 2011; Hin et al., 2013; Savage et al., 2015).

Zinc is a moderately volatile element with a 50% condensation temperature (T_{50}) of 726 K (Lodders, 2003). It is comprised of five stable isotopes – ^{64}Zn (48.6%), ^{66}Zn (27.9%), ^{67}Zn (4.1%), ^{68}Zn (18.8%) and ^{70}Zn (0.6%). The Zn isotopic composition is usually given as the per mil (‰) deviation of the $^{66}Zn/^{64}Zn$ ratio from the JMC-Lyon standard ($\delta^{66}Zn$). The abundance of Zn in most planetary materials is high enough, even in the most volatile depleted samples, for precise elemental abundance and isotopic measurements in meteorites, lunar, and terrestrial samples from Earth; therefore Zn elemental and isotopic systematics have been used as a gauge of volatile depletion and a tracer of evaporation in planetary materials (e.g. Day and Moynier, 2014). Additionally, Zn has only one dominant oxidation state (2+) in the silicate fraction of planets, which limits the source of isotopic fractionation and renders Zn partitioning largely insensitive to the composition of the silicate melt (Siebert et al., 2011), thereby making interpretations of both Zn elemental partitioning and stable isotope data more straightforward. Therefore, Zn is very useful for understanding various planetary processes (evaporative loss, planetary differentiation) through direct study and also provides indirect insight into the behavior of similarly volatile elements, which are often more complicated and technically challenging to investigate independently. Sulfur (T_{50} of 664 K) is a possible – though largely debated – light element in the Earth's core (e.g. Badro et al., 2007; Morard et al., 2013). One of the first estimate of the S content of Earth's core was derived via its rel-

ative abundance to Zn in meteorites (Dreibus and Palme, 1996), wherein estimates of the Zn and S contents of the Earth's mantle and a chondritic S/Zn ratio were used, along with the assumption that Zn is completely lithophile, to calculate the S content of the core.

In order to study the Zn isotopic composition of a differentiated planetary body through surface rocks, it has been assumed that the Zn isotopic composition represents the bulk planetary body. Chen et al. (2013b) have shown that igneous differentiation (on Earth) could not cause large Zn isotopic fractionation (<0.1‰) and assumed that core formation would have a negligible isotopic effect as well. Chen et al. (2013b) considered that no Zn entered the Earth's core, however Zn may be slightly siderophile, especially at high temperature (Siebert et al., 2011), and therefore a fraction of the Zn budget of a differentiated planetary body could reside in its core. Bridgestock et al. (2014) investigated the effect of metal–silicate partitioning on Zn isotope fractionation. From three metal–silicate partitioning experiments (high purity oxide and metal powder starting materials; 1.5 GPa and 1650 K) in MgO capsules, no resolvable Zn isotope fractionation between metal and silicate phases was found within a 0.1‰ range, and an estimated Zn metal–silicate partition coefficient of $D_{met-sil}^{Zn} \sim 0.7$ was found for the experiments. This interesting first look into Zn metal–silicate isotopic fractionation invites further investigation, as these observations are at static conditions and therefore do not remark on the sensitivity of Zn metal–silicate isotopic fractionation to temperature or composition, and likewise the sensitivity of Zn metal–silicate partitioning to temperature, pressure, fO$_2$, and composition.

Several studies (e.g. Siebert et al., 2011; Bridgestock et al., 2014; Wood et al., 2014) have indicated that Zn in fact displays a slight affinity for the metallic phase (slightly siderophile behavior) in metal–silicate partitioning experiments, and each have contributed facets of understanding to the overall systematics of Zn metal–silicate partitioning in regards to temperature, pressure, fO$_2$, and the influence of other elements (e.g. carbon and sulfur). However, a more holistic and systematic approach is necessary to provide a better understanding of Zn metal–silicate partitioning and isotopic fractionation as a function of these varying conditions.

Here we present a suite of experiments to simultaneously determine Zn metal–silicate elemental partitioning and isotopic fractionation as a function of multiple influential parameters. By coupling experimental petrology and stable isotope geochemistry, this work explores the minimum chemical and isotopic equilibration time for metal–silicate differentiation (at 1673 K) through an experimental time series, as well as the temperature dependence of Zn metal–silicate partitioning and isotopic fractionation across a range of temperatures from 1473–2273 K. The effect of S on partitioning and isotopic fractionation has been investigated through a comparison of S-bearing and non S-bearing experimental series, as well as the effect of Sn through a comparison of Sn-bearing and non Sn-bearing experimental series. The effect of silicate composition on isotopic fractionation, namely Si content, has been investigated through a series of experiments with a haplogranitic