



# The selenium isotopic variations in chondrites are mass-dependent; Implications for sulfide formation in the early solar system



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## ABSTRACT

Element transfer from the solar nebular gas to solids occurred either through direct condensation or via heterogeneous reactions between gaseous molecules and previously condensed solid matter. The precursors of altered sulfides observed in chondrites are for example attributed to reactions between gaseous hydrogen sulfide and metallic iron grains. The transfer of selenium to solids likely occurred through a similar pathway, allowing the formation of iron selenides concomitantly with sulfides. The formation rate of sulfide however remains difficult to assess. Here we investigate whether the Se isotopic composition of meteorites contributes to constrain sulfide formation during condensation stages of our solar system. We present high precision Se concentration and  $\delta^{82/78}\text{Se}$  data for 23 chondrites as well as the first  $\delta^{74/78}\text{Se}$ ,  $\delta^{76/78}\text{Se}$  and  $\delta^{77/78}\text{Se}$  data for a sub-set of seven chondrites. We combine our dataset with previously published sulfur isotopic data and discuss aspects of sulfide formation for various types of chondrites.

Our Se concentration data are within uncertainty to literature values and are consistent with sulfides being the dominant selenium host in chondrites. Our overall average  $\delta^{82/78}\text{Se}$  value for chondrites is  $-0.21 \pm 0.43\text{‰}$  ( $n = 23$ , 2 s.d.), or  $-0.14 \pm 0.21\text{‰}$  after exclusion of three weathered chondrites ( $n = 20$ , 2 s.d.). These average values are within uncertainty indistinguishable from a previously published estimate. For the first time however, we resolve distinct  $\delta^{82/78}\text{Se}$  between ordinary ( $-0.14 \pm 0.07\text{‰}$ ,  $n = 9$ , 2 s.d.), enstatite ( $-0.27 \pm 0.05\text{‰}$ ,  $n = 3$ , 2 s.d.) and CI carbonaceous chondrites ( $-0.01 \pm 0.06\text{‰}$ ,  $n = 2$ , 2 s.d.). We also resolve a Se isotopic variability among CM carbonaceous chondrites. In addition, we report on  $\delta^{74/78}\text{Se}$ ,  $\delta^{76/78}\text{Se}$  and  $\delta^{77/78}\text{Se}$  values determined for 7 chondrites. Our data allow evaluating the mass dependency of the  $\delta^{82/78}\text{Se}$  variations. Mass-independent deficits or excesses of  $^{74}\text{Se}$ ,  $^{76}\text{Se}$  and  $^{77}\text{Se}$  are calculated relative to the observed  $^{82}\text{Se}/^{78}\text{Se}$  ratios, and were observed negligible. This rules out poor mixing of nucleosynthetic components to account for the  $\delta^{82/78}\text{Se}$  variability and implies that the mass dependent Se isotopic variations were produced in a once-homogeneous disk.

The mass-dependent isotopic difference between enstatite and ordinary chondrites may reflect the contribution of a kinetic sulfidation process at anomalously high  $\text{H}_2\text{S}$ – $\text{H}_2\text{Se}$  contents in the region of enstatite chondrite formation. Experimental studies showed that high  $\text{H}_2\text{S}$  contents favor the formation of compact sulfide layers around metallic grains. This decreases the reactive surface, which tends to inhibit the continuation of the sulfidation reaction. Under these conditions sulfide growth likely occurs under isotopic disequilibrium and favors the trapping of light S and Se isotopes in solids; This hypothesis provides an explanation for our Se isotope as well as for previously published S isotope data. On the other hand, high  $\delta^{82/78}\text{Se}$  values in carbonaceous chondrites may result from sample heterogeneities generated by parent body aqueous alteration, or could reflect the contribution of ices carrying photo-processed Se from the outer solar system.

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## 1. Introduction

Isotope variations among different classes of meteorites indicate that multiple sources have contributed to the origin of elements in the solar nebula. For example, mass independent isotopic

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signatures of chondrites for elements such as chromium, zirconium or molybdenum reflect the contribution of multiple stellar sources to our proto-planetary disk (Dauphas, 2017; Trinquier et al., 2009). Variable isotopic signatures across chondrite groups also imply that chromium, zirconium and molybdenum (and other refractory elements) were poorly mixed before their incorporation in solids (Dauphas, 2017 and references therein). On the other hand,

bulk chondrites show negligible mass independent isotopic signatures for elements such as iron, zinc, or silicon (Luck et al., 2005; Moynier et al., 2007; Savage and Moynier, 2013). This is remarkable since these latter elements were also provided by multiple stellar sources with mass-independent signatures (Bisterzo et al., 2011; Moynier et al., 2009). Taken together, isotopic patterns of various elements in chondrites can help to describe how an element was homogenized in the proto-planetary disk before condensation.

In addition, chondrites display mass-dependent isotopic variations for various isotopic systematics including zinc, silicon and cadmium (Luck et al., 2005; Moynier et al., 2007; Pringle et al., 2017; Savage and Moynier, 2013; Wombacher et al., 2004). This requires isotopic fractionations to occur after mixing in the nebular gas, possibly during condensation itself (Moynier et al., 2007). For instance, various chondrites groups show mass dependent zinc (Zn) isotopic variations. Zinc is carried in metals, sulfides and silicates, and since these phases have distinct Zn isotopic signatures, heterogeneous distribution (e.g. mineral sorting) can account for the isotope observation (Moynier et al., 2007). The mass dependent isotopic variations of the volatile element sulfur (S) is another example: enstatite chondrites show depletions of heavy S isotopes relative to ordinary chondrites (Defouilloy et al., 2016; Gao and Thieme, 1993b). This observation, however, is still poorly understood since S in ordinary and enstatite chondrites is almost exclusively hosted in sulfides, ruling out inter-mineral fractionation or sorting to account for the observed S isotopic variations. In contrast to most other elements, sulfur is trapped in solids not through direct condensation of a cooling nebula, but via a heterogeneous reaction (i.e. reaction between gas and solids) between gaseous H<sub>2</sub>S and iron grains in a given temperature range – between 700 and 500 K – (Lauretta et al., 1996), following the reaction (1).



This so-called sulfidation reaction allowed the first iron sulfides to form (Zolensky and Thomas, 1995), although they likely underwent subsequent modification by parent body processes and/or chondrule formation (Rubin et al., 2007; Tachibana and Huss, 2005; Zanda et al., 1995). A turbulent nebula (Ciesla and Sandford, 2012) could allow the physical separation of sulfide and metal grains before their accretion in the meteorite parent bodies: This would provide fresh metal surfaces for further reaction with the residual H<sub>2</sub>S reservoir, allowing the reaction (1) to occur as in a multitude of sulfidation events.

Thermodynamic data predict that selenium (Se) is trapped in solids via a heterogeneous reaction analogous to sulfidation: Gaseous H<sub>2</sub>Se would react with metallic iron leading to the formation of iron selenides (Lodders, 2003) following reaction (2).



This reaction is predicted to be efficient over a similar temperature range than sulfidation (Lodders, 2003) which would lead selenides to be hosted in the sulfides (Dreibus et al., 1995). Here, we investigate the Se isotopic composition of chondrites and discuss whether the Se isotopic systematic combined with pre-existing S isotopic data can help describing the completion of reaction (1) and (2).

In the first report of Se isotope compositions of a range of undifferentiated meteorites,  $\delta^{82/78}\text{Se}$  values were indistinguishable for the different chondrite groups within a 2 standard deviation (s.d.) external reproducibility of  $\pm 0.37\%$  (Vollstaedt et al., 2016). Here, we report  $\delta^{82/78}\text{Se}$  values for 23 bulk chondrites (H, L, LL, EL, EH, CO, CM, CV, and CI) and show that these objects display significant isotope variations outside our external reproducibility of  $\pm 0.10\%$  (2 s.d.). We also report values for  $\delta^{74/78}\text{Se}$ ,  $\delta^{76/78}\text{Se}$  and

of  $\delta^{77/78}\text{Se}$  for a subset of seven bulk chondrites and show that the Se isotopic variations are mass dependent within external reproducibility for these ratios.

## 2. Analytical techniques

### 2.1. Sample digestion and chemical purification of Se

The 23 chondrites investigated in this study cover a range of alteration, metamorphism and oxidation features (Table 1). The sample set includes nine observed falls and two hot-desert finds for carbonaceous chondrites, seven observed falls and two hot-desert finds for ordinary chondrites, two observed falls and one hot-desert find for enstatite chondrites (Table 1). Samples were obtained as chips from the interiors of the meteorites taken well away from the fusion crust to minimize the effects of terrestrial contamination and modification during atmospheric entry. All samples except the CI and CO chondrites were prepared for previous studies (Schoenberg and Blanckenburg, 2006; Schoenberg et al., 2016). Between 100 and 500 mg of rock chips were crushed and ground to powder in an agate mortar. Here, about 5–50 mg of sample powder was weighed into quartz glass digestion tubes and digested in reverse aqua regia (3:1 HNO<sub>3</sub>:HCl molar ratio) for 16 h at 220 °C and 100 bar in a high-pressure asher (Anton Paar<sup>TM</sup>). For the determination of stable Se isotope ratios an adequate amount of our <sup>74</sup>Se–<sup>77</sup>Se double spike was weighted into the glass tubes together with the sample powder to achieve sample-spike equilibration during sample digestion. No spike was added for sample aliquots on which potential mass-independent effects were to be determined. The procedural blanks associated with the glass vessels were roughly 1 ng Se, which is insignificant compared to the amounts of sample Se  $\geq 100$  ng. For some samples, duplicates were digested in 5 ml of reverse aqua regia in closed teflon beakers placed on a hot plate for 24 h at 100 °C, where the procedural blanks were below detection limit (<0.1 ng Se).

After digestion, sample solutions were evaporated to dryness at 65 °C and further dried twice with 0.2 ml 9 M HCl at 65 °C to ensure complete conversion of the residues to chloride form. Samples were then taken up in 4 ml 6 M HCl and heated at 80 °C for 2 h to ensure quantitative conversion of Se<sup>6+</sup> to Se<sup>4+</sup> (Elwaer and Hintelmann, 2008; Pogge von Strandmann et al., 2014). Although solutions can be purified with the thiol cotton fiber method (Elwaer and Hintelmann, 2008; Rouxel et al., 2002), we followed a ion-exchange resin protocol recently developed (Kurzawa et al., 2017). The solutions were loaded onto polypropylene columns containing 3 ml pre-cleaned Eichrom AG1-X8 (100–200 mesh) anion resin. The pre-cleaning involved treatment with 8 ml 1 M HNO<sub>3</sub> and 4 ml high-purity water (18 M $\Omega$  cm) followed by conditioning the resin with 8 ml 6 M HCl. Se<sup>4+</sup> does not exchange with the resin and was directly collected during loading of the sample and elution of additional 8 ml of 6 M HCl. Our approach allowed quantitative elimination of iron from the solutions otherwise depressing the potential of hydride generation (see below and supplementary online material). Sample solutions were then evaporated to dryness at 65 °C and dissolved in 1 ml 2 M HCl. The solutions were then introduced to a multi-collector inductively coupled plasma mass spectrometer (Neptuneplus<sup>TM</sup> MC-ICP-MS) through a hydride generator which allows only hydride-forming elements to be transported to the instrument plasma source.

### 2.2. Mass spectrometry

A detailed description of our instrumental setup, data treatment and correction is given in the supplementary online file and in Kurzawa et al. (2017). Briefly, a CETAC HGX-200 hydride generator was used as sample introduction system, where acidic sample

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