

The isotope composition of selenium in chondrites constrains the depletion
mechanism of volatile elements in solar system materials

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25 **Abstract**

26 Solar nebula processes led to a depletion of volatile elements in different chondrite groups when
27 compared to the bulk chemical composition of the solar system deduced from the Sun's
28 photosphere. For moderately-volatile elements, this depletion primarily correlates with the
29 element condensation temperature and is possibly caused by incomplete condensation from a hot
30 solar nebula, evaporative loss from the precursor dust, and/or inherited from the interstellar
31 medium. Element concentrations and interelement ratios of volatile elements do not provide a
32 clear picture about responsible mechanisms. Here, the abundance and stable isotope composition
33 of the moderately- to highly-volatile element Se are investigated in carbonaceous, ordinary, and
34 enstatite chondrites to constrain the mechanism responsible for the depletion of volatile elements
35 in planetary bodies of the inner solar system and to define a $\delta^{82/78}\text{Se}$ value for the bulk solar
36 system. The $\delta^{82/78}\text{Se}$ of the studied chondrite falls are identical within their measurement
37 uncertainties with a mean of -0.20 ± 0.26 ‰ (2 s.d., $n = 14$, relative to NIST SRM 3149) despite
38 Se abundance depletions of up to a factor of 2.5 with respect to the CI group. The absence of
39 resolvable Se isotope fractionation rules out a kinetic Rayleigh-type incomplete condensation of
40 Se from the hot solar nebula or partial kinetic evaporative loss on the precursor material and/or
41 the parent bodies. The Se depletion, if acquired during partial condensation or evaporative loss,
42 therefore must have occurred under near equilibrium conditions to prevent measurable isotope
43 fractionation. Alternatively, the depletion and cooling of the nebula could have occurred
44 simultaneously due to the continuous removal of gas and fine particles by the solar wind
45 accompanied by the quantitative condensation of elements from the pre-depleted gas. In this
46 scenario the condensation of elements does not require equilibrium conditions to avoid isotope

fractionation. The results further suggest that the processes causing the high variability of Se concentrations and depletions in ordinary and enstatite chondrites did not involve any measureable isotope fractionation. Different degrees of element depletions and isotope fractionations of the moderately-volatile elements Zn, S, and Se in ordinary and enstatite chondrites indicate that their volatility is controlled by the thermal stabilities of their host phases and not by the condensation temperature under canonical nebular conditions.

1. Introduction

Moderately- and highly-volatile elements are depleted in almost all materials of the inner solar system including the carbonaceous chondrites (e.g., Davis and Richter (2014) and Palme (2001)). Only the CI chondrites closely match solar abundances for all elements except the extremely volatile elements such as the rare gases, H, C, O, N, and Li (e.g., Palme and O'Neill (2003)). Specifically, abundances of moderately-volatile elements show a positive correlation with condensation temperature (T_C), indicating that T_C is the primary factor controlling volatile element concentrations in chondrites (Palme and O'Neill, 2003; Wasson and Kallemeyn, 1988). The moderately-volatile elements comprise elements with 50% T_C between 1060 and 664 K, ranging between the condensation of Mg-silicates and FeS from a gas of solar composition (Palme and O'Neill (2003); Table 1). With the exception of S, all elements in this group are trace elements and condense by dissolution into already condensed major phases such as silicates, metal, and sulphides (Palme and O'Neill, 2003). Several processes have been proposed to explain the depletion of volatile elements in chondrites with respect to the bulk solar system. These processes may have occurred prior to or during condensation and/or during evaporation caused by a heating event. Since depletion of moderately- to highly-volatile elements is observed

in all meteorite groups except CI chondrites, this depletion must be a very early and universal process. To record the characteristic volatile element fractionation observed in chondrites, a physical separation of gas and dust in the solar nebula must have taken place. The nebular temperature at which the meteoritic and planetary volatile-element depletion was established is estimated to be higher than 1400 K (Humayun and Cassen, 2000).

Yin et al. (2005) studied the moderately-volatile element depletion in interstellar dust and rocky material of the inner solar system and argues for an inheritance of the depletion pattern from the interstellar medium (ISM). In his conceptual model, interstellar dust grains acquired an outer layer of condensed ice and other volatiles in the cold and dense molecular cloud stage. During the collapse of the dense molecular cloud and the formation of the early solar system, adiabatic compression or passage of shock waves take off and vaporize/sublimate the icy mantle. The re-condensation and re-equilibration of the gas with the entrained dust grains was prohibited by rapid grain growth in the solar nebula, reducing the surface area per unit mass and removing them from contact with the gas before complete recondensation occurs. The variable proportions of refractory grains and volatile-rich mantle constitute the ultimate chemical heterogeneities observed in different reservoirs of the solar nebula at different scales (Yin et al., 2005). However, different extents of volatility-related element fractionation in grains from the ISM and carbonaceous chondrites as well as a uniform isotopic composition of the solar system argues against an element and isotope record in chondrites produced by dust and gas fractionation in the ISM (Palme, 2001).

Models for a loss of volatile elements prior to or during condensation from the solar nebula suggest a progressive removal of gas as condensation and aggregation proceeded leading to a higher depletion of volatile elements with low T_C . Different mechanisms have been proposed

describing the possible separation of the gas from dust. Similar to the model of Yin et al. (2005), Larimer (1967) suggested that the limitation of surface area by grain aggregation may lead to a kinetic limitation of volatile-element condensation that depends on the diffusion of the elements into grains. In this scenario, volatile elements condense partially from the solar nebula. Wasson and Chou (1974) and Wai and Wasson (1977) proposed that the separation occurred continuously during the cooling of the solar nebula and consequent condensation due to one or a combination of processes including i) the shrinkage of particle orbital radii due to solid-gas interactions and induced deceleration of particles, ii) the removal of gas from the surface of the solar nebula by wind and photons whereas particles were retained and settled towards the midplane, and iii) the entrainment of gaseous and/or fine dust condensates of volatile elements with the nebula gas during the final dissipation of gases from the nebula. These qualitative arguments have been supported and quantified in model simulations (e.g., Cassen (2001)). Here, the chemical fractionation patterns are the natural result of the inherently coupled evolution of condensing and coagulating solids from a nebula of diminishing mass cooling from a hot initial state. However, to exactly reproduce the moderately- to highly-volatile element abundances with $T_C < 800$ K as observed in meteorites, mixing with material having a composition similar to that of CI chondrites is additionally required (Humayun and Cassen, 2000; Larimer, 1967; Wolf et al., 1980).

The latter observation led other authors to explain the element pattern in chondrites by a two- or multi-component model where a volatile-depleted phase, devoid of all highly-volatile elements < 700 K T_C , variously depleted in moderately-volatile elements, and completely retaining the refractory elements > 1200 K T_C , is mixed with a CI-like phase to explain the chemical fractionation in chondrites (Alexander, 2005; Anders, 1964). The amount of the CI-like

115 component roughly correlates with the amount of matrix in chondrites whereas the volatile-
116 depleted component originates from the coarse grained fraction, mainly consisting of chondrules
117 (Wolf et al., 1980). The partial loss of gaseous volatiles during the chondrule formation process
118 then explains the smooth relationship between CI-normalized moderately-volatile element
119 abundance and T_C (Alexander, 2005). Bulk meteorites are therefore considered to represent a
120 mixture of undepleted matrix and volatile-depleted chondrules, which are thought to be residues
121 from partial vaporization of CI-like material (Alexander, 2005). Also impacts on the chondrite
122 parent bodies have been considered to result in a redistribution and depletion of volatile elements
123 (Kadlag and Becker (2015) and references therein). However, heating experiments on fragments
124 of the Allende CV and Murchison CM chondrites showed depletions of volatile elements in the
125 residues that are inconsistent with the origin by thermal processing of CI-like material (Wulf et
126 al., 1995). Also, other studies argued that Mn/Na ratios are constant and CI-like within $\pm 15\%$ (1
127 r.s.d.) in all chondrite groups, that Se/Zn ratios are constant and CI-like within $\pm 5\%$ (1 r.s.d.) in
128 all carbonaceous chondrites despite significant absolute variations in element abundances, and
129 that Au/Co significantly correlates with Ga/Co ratios in carbonaceous chondrites (Dreibus and
130 Palme, 1996; Palme and O'Neill, 2003; Xiao and Lipschutz, 1992). The authors from these
131 studies inferred from the data that no net evaporative loss of these elements could have occurred
132 under oxidising conditions on the chondrite parent bodies. Further, Bland et al. (2005) studied
133 minor and trace element abundances in the fine-grained matrix of a variety of carbonaceous
134 chondrites and found that matrix elements are characteristic for a given chondrite group and
135 depleted with respect to CI but enriched relative to bulk compositions, particular in volatile
136 siderophile and chalcophile elements. They inferred that complementary and non-monotonic
137 depletions of volatile elements with decreasing T_C between matrix and chondrules best explain

138 the monotonic trace element pattern observed in bulk carbonaceous chondrites. Accordingly,
139 Bland et al. (2005) proposed that matrices of carbonaceous chondrites formed from material that
140 has been volatile-depleted before the chondrule formation process. According to Alexander
141 (2005) the non-CI-like matrix compositions may also be explained by an addition of about 10-
142 30% of a refractory element-rich and volatile element-depleted component.

143 The depletion pattern in ordinary and enstatite chondrites differs for some elements so that there
144 is not always a smooth decrease in abundances with decreasing T_C (Dreibus and Palme, 1996;
145 Wasson and Kallemeyn, 1988). Volatile elements show much larger variability in concentrations
146 and ratios than refractory elements among the different chondrite groups, including
147 unequilibrated samples. Partly, these variations could result from aqueous alteration on the
148 chondrite parent bodies and/or from terrestrial weathering. Wasson and Kallemeyn (1988)
149 interpreted this element pattern primarily as a result of metamorphic heating. However, the
150 constant Mn/Na ratios in all chondrite groups argue against net evaporative loss of Na and
151 similar volatile elements, such as K and Rb, under oxidising conditions on the chondrite parent
152 bodies (Palme and O'Neill, 2003). Also, chemical equilibrium calculations were used to model
153 abundance trends of moderately-volatile elements in ordinary chondrites as a function of thermal
154 metamorphism. These models are able to explain most element concentrations, but fail to explain
155 abundances of Ag or Zn (Schaefer and Fegley Jr, 2010). The element concentrations and
156 interelement ratios alone therefore do not provide a clear picture on the mechanism responsible
157 for the volatile element depletion and variability in chondrites.

158 Under certain conditions, mass-dependent isotope fractionation is caused by incomplete
159 condensation of volatile elements from the solar nebula or net evaporative loss of volatile
160 elements from the chondrite precursor material and/or the chondrite parent bodies (Davis and

Richter, 2014). Therefore, the isotope composition of volatile elements in chondrites provides additional constraints on the volatile element depletion processes and/or their environmental conditions (Humayun and Clayton, 1995).

Selenium is a moderately- to highly-volatile element with chalcophile and siderophile behaviour. At nebula pressures of 10^{-4} bar Se is expected to condense from a gas of solar composition by reactions with already condensed sulphides to form FeSe at about 697 K (Lodders, 2003; Palme and O'Neill, 2003). Due to the low T_C , Se is expected to be depleted in the early inner solar system relative to refractory and main component elements such as Fe, Mg or Si. The similar cosmochemical behaviour of Se and S results in a constant chondritic ratio of $S/Se = 2565 \pm 314$ in carbonaceous and ordinary chondrites despite significant absolute variations in S and Se concentrations (Dreibus et al. (1995), Wang et al. (2015); see also Table 2, Table A4, and Figure A1). However, Se and S are affected differently by oxidative weathering processes (particularly during terrestrial weathering) and meteorites with non-chondritic S/Se ratios should be regarded with caution (Dreibus and Palme, 1996). Thus, for a study involving element concentrations or isotope compositions of S and Se, meteorite falls should be preferred over meteorite finds.

Presently, no data is available for the Se isotope composition of chondrites, but troilites from five iron meteorites indicate a limited range of $<0.3\%$ in $\delta^{82/78}Se$ and absolute values that are indistinguishable from the isotope composition of the Earth (Rouxel et al., 2002). Here, the Se isotope composition of chondrites was measured to constrain the possible mechanism(s) responsible for the depletion of moderately- to highly-volatile elements in chondrites. The results will further serve to determine the Se isotope composition of the bulk solar system.

2. Methods

A physical separation of pristine sample fragments followed by acid digestion, chemical purification of Se, and isotope measurements on a MC-ICP-MS using a double spike technique was conducted. The details of these techniques may be found in the appendix. The Se isotope variations, expressed as $\delta^{82/78}\text{Se}$ relative to the NIST standard SRM 3149 are calculated via:

$$\delta^{82/78}\text{Se} = \left(\frac{\left(\frac{{}^{82}\text{Se}}{{}^{78}\text{Se}} \right)_{\text{sample}}}{\left(\frac{{}^{82}\text{Se}}{{}^{78}\text{Se}} \right)_{\text{SRM 3149}}} - 1 \right) * 1000$$

3. Results

A literature compilation for the Se abundances in chondrites is provided in Table 2, Table A4, and Figure 1. The methods used for determining Se concentrations include instrumental neutron activation analysis (INAA), radiochemical neutron activation analysis (RNAA), and ICP-MS measurements (external calibration or isotope dilution). Selenium concentrations measured in this study by isotope dilution are consistent with the literature data (Figure 1). The Se concentrations for each chondrite group given in Table 2 are calculated by averaging the average Se concentrations of single meteorites falls (except CK and CH) of the respective meteorite group. From the literature compilation in Table 2 it can be seen that Se concentrations in carbonaceous chondrites are depleted by up to a factor of 6 compared to CI, while S/Se ratios are almost indistinguishable in CI, CM, CO, CV, and CK chondrites with a mean of 2565 ± 314 (Dreibus et al. (1995) and Wang et al. (2015) and references therein). Meteorite finds often show lower S/Se ratios most probably due to S loss during terrestrial oxidative weathering (Figure A1). Ordinary chondrites are depleted in Se by a factor of 2.2 to 2.5 compared to CI and also

have S/Se ratios similar to CI. According to the limited database in Table 2, the variability in Se concentrations for different ordinary chondrites falls is considerably higher than for carbonaceous chondrites. The highest variability in Se concentrations is observed in EH and EL chondrites that overlap in their Se concentrations. Interestingly, the average Se concentration of EH chondrites is 25.7 ± 11.1 $\mu\text{g/g}$ ($n=7$), which is even higher than for the CI group.

The $\delta^{82/78}\text{Se}$ values for carbonaceous, ordinary, and enstatite falls are indistinguishable within the measurement uncertainty with a mean of -0.20 ± 0.26 ‰ ($n=14$; Figure 1; Table 3). The Se isotope composition of the five measured meteorite finds also agrees with this value, indicating that for these finds weathering has only very little (if any) effect on the Se isotopic ratios. Troilites from five IAB iron meteorites have a $\delta^{82/78}\text{Se}$ of -0.08 ± 0.27 ‰ (Table 3), and are thus indistinguishable from the average of 0.00 ± 0.27 ‰ for troilites and also from the chondritic value, both reported by Rouxel et al. (2002).

4. Discussion

4.1. Isotope fractionation during condensation and evaporation

Depending on the physical and chemical conditions during condensation, the chemical fractionation of volatile elements can imprint characteristic isotope signatures on the volatile-depleted materials from the inner solar system. Specifically, the maintenance of the thermodynamic equilibrium between the volatile-depleted liquid or solid phase and the volatile-enriched gas phase determines the degree of isotope fractionation (Davis and Richter, 2014). Equilibrium isotope mass fractionation of heavy elements is expected to be negligible at high temperatures. As isotope exchange is a time-dependent process it requires slowly changing environmental conditions as well as a homogeneous liquid/solid phase. Both requirements may

not always be fulfilled, potentially resulting in large isotope fractionations even in a closed system that is only subsequently subject to a separation of the gas from the partially condensed phases (Davis and Richter, 2014). On the other hand, kinetic (disequilibrium) isotope fractionation requires, beside the existence of a well-mixed liquid/solid reservoir, the complete separation of the evaporating or condensing phase. For evaporation, this generally occurs during slow heating in vacuum. In this case the isotopic composition of the evaporative flux differs from that at the surface of the evaporating material, expressed by the fractionation factor $\alpha = \sqrt{m_1/m_2}$ where m_i is the atomic or molecular weight of the isotopes or isotopologues involved. Any recondensation of the vapour reduces the net effect of isotope fractionation.

Vacuum evaporation experiments on chondritic meteorites and calcium-aluminium-rich inclusions (CAIs) show changes in isotopic compositions of Mg and Si in the remaining solid phase following Rayleigh curves with α being closer to 1 than expected from the relation

$\sqrt{m_1/m_2}$ (Davis and Richter, 2014). Later experiments showed that the results of the experiments

were not affected by recondensation or limited diffusion in the evaporation liquid but probably by different evaporation coefficients of the isotopes (Davis and Richter, 2014). Specifically, Mg isotope fractionation was found to be different from those predicted by any of the commonly used mass fractionation laws (Davis et al., 2015). Quantitative condensation experiments are difficult to conduct and no well-controlled experiments are available on chondritic or CAI compositions (Davis and Richter, 2014). However, zoned metal grains found in several chondrite groups exhibit correlated Fe and Ni isotopic compositions, which were explained by condensation (Richter et al., 2009). Overall, the laboratory experiments and observations on iron meteorites demonstrate that condensation and evaporation cannot *a priori* be considered as

equilibrium or disequilibrium processes. The absence of isotope fractionation is therefore not diagnostic of whether the path involved condensation or evaporation but rather a measure of the degree to which the system maintained thermodynamic equilibrium (Davis and Richter, 2014).

Therefore, measuring the isotope composition of the highly depleted moderately- to highly-volatile element Se in chondrites may provide constraints on the environmental conditions during its depletion. Specifically, the degree of Se isotope fractionation and its relation to Se abundances constrains predictions on the homogeneity of the solar nebula and maintenance of thermodynamic equilibrium during the depletion of volatile elements.

4.2. Carbonaceous chondrites

Carbonaceous chondrites are the most primitive meteorites in the solar system found on Earth as extraterrestrial samples. The similar $\delta^{82/78}\text{Se}$ values of CI, CM, CO, and CV chondrites argue against a kinetically controlled isotope fractionation during partial evaporation or condensation (Table 3; Figure 1). Assuming similar evaporation/condensation coefficients for ^{82}Se and ^{78}Se and a maximum $\delta^{82/78}\text{Se}$ difference between CI and CV chondrites of 0.52 ‰ (4 s.d. of the mean of all chondrite groups), the maximum fractionation factor α between the volatile-depleted CV

and CI is 1.0009. This value is distinctly lower than $\sqrt{\frac{m_{^{82}\text{Se}}}{m_{^{78}\text{Se}}}} = 1.0253$ theoretically leading

to a $\delta^{82/78}\text{Se}_{\text{CV}}$ of 14.5 ‰ applying the Rayleigh fractionation law. Even by considering different evaporation/condensation coefficients for ^{82}Se and ^{78}Se resolvable differences in $\delta^{82/78}\text{Se}$ are expected. Similar observations were made for other moderately- to highly-volatile elements, like S, Tl, Te, Zn, Cd, K, and B, that all also show no evidence for a disequilibrium between gas and

267 dust during volatile depletion (Baker et al., 2010; Fehr et al., 2005; Gao and Thiemens, 1993a;
 268 Humayun and Clayton, 1995; Luck et al., 2005; Wombacher et al., 2008; Zhai et al., 1996).
 269 The lack of Se isotope fractionation in carbonaceous chondrites therefore leaves four scenarios to
 270 explain the observed chemical fractionation in chondrites: i) the element patterns might have
 271 been inherited from the ISM, ii) volatile loss during partial condensation or evaporation occurred
 272 under thermodynamic equilibrium conditions, iii) nearly all Se present in carbonaceous
 273 chondrites represents the admixture of a CI-like component to a component strongly depleted in
 274 volatile elements, iv) a fraction of the volatile elements was already removed without any
 275 significant effect on their isotope composition prior to their incorporation into existing phases.
 276 Scenarios i) and ii) require the existence of thermodynamic equilibrium between the solid/liquid
 277 and the gas phase for all moderately-volatile elements to explain the stable isotope data from
 278 carbonaceous chondrites. Humayun and Cassen (2000) argued that it is not possible to produce
 279 the chemical fractionation of moderately-volatile elements recorded in chondrites by partial
 280 volatilization and simultaneously not producing a distinct and measureable change in the isotope
 281 composition of volatile elements. Further confirmation comes from the finding of solar Mn/Na,
 282 Se/Zn, and Ga/Co ratios in carbonaceous chondrites, which are highly sensitive to evaporative
 283 loss of elements under oxidising conditions (Dreibus and Palme, 1996; Palme and O'Neill, 2003;
 284 Xiao and Lipschutz, 1992). Chemical without isotopic fractionation might be, however, also
 285 explained by the equilibration of solids with the nebula gas in a region with a high dust to gas
 286 ratio (Alexander, 2005). However, the chondrule forming processes likely were short-term
 287 events, which would have increased the likelihood of disequilibrium effects on isotopes of
 288 volatile elements, except if nearly everything re-condensed and re-equilibrated. Scenario iii), e.g.
 289 the two-component mixing model, predicts that almost the complete inventory of the

290 moderately-volatile elements with $T_C < 700$ K was inherited from the volatile-rich CI-like phase.
291 This is also consistent with the similar Se isotope composition of all carbonaceous chondrites
292 investigated. However, moderately-volatile elements with $T_C > 700$ K, like K and B, which are
293 supposed to be partly retained in the volatile-depleted phase, also show no indications for a
294 Rayleigh-type kinetic isotope fractionation (Humayun and Clayton, 1995; Zhai et al., 1996).
295 Accordingly, the two-component-model also requires the existence of thermodynamic
296 equilibrium during devolatilization of the volatile element-depleted phase. Scenario iv) also
297 predicts homogeneous stable isotope compositions of moderately-volatile elements as the
298 continuous separation of gas from dust during cooling of the nebula due to a change in the
299 particle orbital radius, removal by the solar wind and photons, or by entrainment with gases
300 during the final dissipation of nebula gases is not expected to result in any isotope fractionation.
301 The degree of volatile element depletion may be a function of the radial distance to the proto-sun
302 and/or the vertical distance from the midplane, explaining differences in volatile abundances
303 between the chondrite groups. However, this scenario requires that the condensation of volatiles
304 into their individual host phases occurs in narrow temperature windows to ensure quantitative
305 condensation of volatile elements from the pre-depleted nebula gas. In this scenario the
306 characteristic volatile element depletion pattern in chondrites is established without any
307 significant isotope fractionation of volatile elements in chondrites. These constraints seem to be
308 supported by literature data that infer a cooling time of the nebula being in the range of 10^5 years
309 to cool down to temperatures of about 200-600 K at 1 AU (Humayun and Cassen, 2000). In
310 contrast, coagulation is capable to change the nebula opacity by one order of magnitude at 1 AU
311 in 10^3 - 10^4 years (Humayun and Cassen, 2000). However, experimental data also show that
312 cooling rates of the nebular environment were also strongly non-uniform and possibly varying

several orders of magnitude (Berg et al., 2009). Nevertheless, the rather constant abundances of some moderately- and highly-volatile elements in carbonaceous chondrites require an additional explanation like the admixture of a CI-like component (Humayun and Cassen, 2000; Larimer, 1967; Wolf et al., 1980). Ultimately, the homogeneous Se isotope composition in chondrites does not preclude any of the scenarios mentioned above but places some constraints on their environmental conditions. If volatile depletion was inherited from the ISM, produced by partial condensation and/or by evaporative loss, it must have occurred under near equilibrium conditions to prevent any isotope fractionation. If the nebula was depleted in volatile elements during cooling due to the entrainment of gas and fine particles by solar wind the condensation of phases had to occur fast compared to the gas removal to ensure a quantitative condensation of elements. Importantly, the latter scenario also tolerates the condensation of phases under disequilibrium conditions.

4.3. Ordinary chondrites

The depletion patterns of moderately-volatile elements in ordinary chondrites show a non-monotonic decrease with decreasing T_C . For example, Mn and Na are only slightly depleted, while F, Zn, S, and Se are more strongly depleted in all types of ordinary chondrites compared to carbonaceous chondrites (Dreibus and Palme, 1996; Palme and O'Neill, 2003). Wasson and Kallemeyn (1988) ascribed the non-monotonic decrease of siderophile and chalcophile elements with increasing volatility to the presence of a variety of nebular siderophile components during the formation of the ordinary chondrite parent bodies. Ordinary chondrites also show a higher variability in volatile element concentrations compared to carbonaceous chondrites (see also Table 2). These variations were not found to be a function of the petrographic grade among type

3-6 H, L, and LL chondrites (Kallemeyn et al., 1989). However, Friedrich et al. (2004) observed lower concentrations of highly mobile trace elements in strongly shocked (S4-S6) compared to mildly shocked (S1-S3) L4-6 chondrites. Our dataset does not contain any strongly shocked meteorites, thus the impact of shock metamorphism on the Se isotope composition cannot be evaluated. Sulfur and Se are not significantly fractionated in bulk samples compared to CI (Table 2) but partitioning between metal-sulphide and silicate melts, most probably during chondrule formation, were found to influence S/Se ratios between different components in unequilibrated ordinary chondrites (Kadlag and Becker, 2016). Additional minor variations in element abundances might come from thermal metamorphism that is supposed to have large effects on some highly-volatile elements like Cs, In, Bi, Tl, and Cd, but not on moderately-volatile elements, like Zn, Rb or K (Wombacher et al. (2008) and references therein).

Despite the variability of Se concentrations there is no detectable Se isotope fractionation in ordinary chondrites (Table 3; Figure 1). Therefore, any processes involved in the formation and evolution of the ordinary chondrite parent body did not lead to a significant loss of Se under disequilibrium conditions. Explicitly, it is not observed that $\delta^{82/78}\text{Se}$ varies as a function of the Se concentration, metal content or petrographic grade in the eight analysed ordinary chondrite falls (Table 3). The effect of oxidative weathering of troilite on the Se isotope composition has not yet been studied but large isotope fractionations in the range of several per mill are known for Se redox transformations (e.g., Mitchell et al. (2013)). However, data from ordinary chondrites meteorite finds (one equilibrated LL, one unequilibrated L from Antarctica, and equilibrated L from a desert area) show no significant evidence for the influence on terrestrial weathering on bulk rock abundances of S, Se, and Te (Dreibus et al., 1995; Kadlag and Becker, 2016). This

358 interpretation is supported by indistinguishable Se concentrations and S/Se ratios of H, L, and LL
359 chondrite falls and finds (Table A4).

360 Other moderately-volatile elements like S, K, Zn, and Ag also show no or only minor isotope
361 variability among ordinary chondrites with different petrologic or shock grades (Gao and
362 Thiemens, 1993b; Humayun and Clayton, 1995; Luck et al., 2005; Schönbachler et al., 2008;
363 Tachibana and Huss, 2005). Specifically, the variability of isotopes of the moderately-volatile Zn
364 and S in different bulk ordinary chondrites and their components is ≤ 1 ‰/amu (Gao and
365 Thiemens, 1993b; Luck et al., 2005; Tachibana and Huss, 2005). Contrarily, the highly-volatile
366 element Cd shows concentration variations of up 4 orders of magnitude and isotope variations of
367 up to 6 ‰/amu, which are not correlated, indicating that this highly-volatile element is more
368 strongly affected by thermal metamorphism on the ordinary chondrite parent body (Wombacher
369 et al., 2008).

370 The small but significant negative correlation of $\delta^{66/64}\text{Zn}$ with Cr/Zn ratios in carbonaceous and
371 unequilibrated ordinary chondrites was explained by the reaction of refractory materials, having
372 a heavy Zn isotopic composition, with a gas phase enriched in the lighter Zn isotopes (Luck et
373 al., 2005). Although Se and Zn have similar T_C under canonical nebular conditions, an isotopic
374 fractionation of Se was not detected in this study. In ordinary chondrites, Zn is concentrated in a
375 variety of phases including sulphides, olivine, pyroxene, and chromite whereas Se is almost
376 exclusively hosted in sulphides (Dreibus et al., 1995; Luck et al., 2005). Possibly the differences
377 in the carrier phases contribute to the different behaviour of Se and Zn.

378 The heterogeneity of moderately-volatile elements in bulk ordinary chondrites may therefore be
379 ascribed either to i) the presence of a large variety of nebular components and/or a more variable

thermal processing of nebular components in the ordinary chondrite formation regions (Wasson and Kallemeyn, 1988). This might be due to the larger gravitational field of the ordinary chondrite parent bodies due to their larger sizes compared to the carbonaceous chondrites parent bodies. Alternatively, ii) metal-silicate partitioning during chondrule formation (Kaczaral et al., 1988; Kadlag and Becker, 2016) and/or iii) volatilization caused by shock-heating on the parent bodies (Friedrich et al., 2004) could have led to the high variability in moderately-element concentrations in ordinary chondrites. Importantly, any significant loss or partitioning of Se during these processes seems to have occurred under closed system equilibrium conditions that prevented significant Se isotope fractionation.

4.4. Enstatite chondrites

Enstatite chondrites are volatile-depleted and highly reduced, as seen from the oxidation state of their Fe (mostly 0), indicating an evolution in a distinct solar nebula region (Krot et al., 2014; Palme and O'Neill, 2003). Since their oxygen isotope composition plots on the terrestrial fractionation line, enstatite chondrites probably formed in the innermost part of the solar system (Clayton et al., 1984). Element fractionation patterns are complex in bulk enstatite chondrites, which could result from volatility-controlled partial condensation or evaporation, incorporation of different precursor material in chondrules, different elemental volatilities due to different redox conditions, and/or later partitioning between sulphides, silicates, and metal during chondrule formation and/or impacts on the parent bodies (Kadlag and Becker (2015) and references therein). The relative importance of these processes remains, however, unclear. Concentrations of highly-siderophile elements (HSE) in components from unequilibrated enstatite chondrites suggests the mixing of two metal carriers formed under different conditions

403 in the solar nebula. The enrichment of the moderately-volatile element Au with respect to the
404 HSE likely resulted from fractional condensation or metal-sulphide-silicate partitioning in the
405 solar nebula (Kadlag and Becker, 2015).

406 Selenium abundances are higher in EH chondrites compared to EL and CI chondrites (Table 2).
407 The cosmochemically and geochemically similar elements S and Te show the same trend but are
408 depleted relative to Se, indicating multistage chemical fractionation processes in enstatite
409 chondrite precursor dust (Kadlag and Becker, 2015; Kong et al., 1997; Wasson and Kallemeyn,
410 1988). The systematically low S/Se ratios in components from EH3 chondrites were attributed
411 primarily to the loss of S during thermal metamorphism with minor and non-systematic effects
412 contributed by terrestrial weathering (Kadlag and Becker, 2015). The element trends of ten
413 volatile/mobile trace elements, including Se, Te, and Zn, in a heated EH4 sample under 10^5 atm
414 H_2 environment are quite similar to those in unheated E4-6 chondrites, indicating that enstatite
415 chondrites represent primitive material that was thermally metamorphosed on a parent body
416 (Ikramuddin et al., 1976). Also, S and Zn concentrations, although being generally higher in EH
417 compared to EL, show lower concentrations for higher petrologic types in both EH and EL,
418 indicating that their loss is probably a result of parent body metamorphism (Defouilloy et al.,
419 2016; Moynier et al., 2011). Contrarily, Kong et al. (1997) observed, based on the chemical
420 compositions of eleven enstatite chondrites, that abundances of refractory lithophile elements,
421 such as Al, Sc, and Mg, are higher in EL compared to EH, while those of siderophile and
422 moderately-volatile elements decrease from $EH_{4,5} \rightarrow EH_3 \rightarrow EL_3 \rightarrow EL_{5,6}$, i.e., inverse with
423 petrographic type between EH and EL groups. This general trend is confirmed by Se abundances
424 in our literature compilation, showing decreasing but overlapping concentrations of 25 ± 11 $\mu\text{g/g}$
425 ($n=8$), 22 ± 8 $\mu\text{g/g}$ ($n=12$), 18 ± 4 $\mu\text{g/g}$ ($n=4$), and 13 ± 10 $\mu\text{g/g}$ ($n=14$) for $EH_{4,5}$, EH_3 , EL_3 , and

EL5,6 chondrite falls and finds, respectively (Table A4). Nevertheless, the high Se variability within the groups of different petrologic type precludes any specific conclusions concerning the genetic relationship between EH and EL chondrites but rather indicates that multiple processes were responsible for the observed element patterns.

The homogenous and CI-like Se isotope composition indicates that the processes leading to the wide range and high variability of moderately-volatile concentrations in the EL and EH meteorites did not cause a resolvable shift in the bulk Se isotope composition (Figure 1). A volatility-controlled kinetic evaporation on the enstatite parent body can therefore be excluded. Similar observations were made for S isotopes with indistinguishable $\delta^{34}\text{S}$ values in EH3, EH5, and EL3 chondrites (Defouilloy et al., 2016; Gao and Thiemens, 1993b). However, EL6 chondrites were recently found to be slightly enriched in the light S isotopes compared to average EH chondrites by $\delta^{34}\text{S} = 0.41\text{‰}$, which was interpreted to be either a result of S isotopic heterogeneities in the inner area of the solar nebula or impact-induced thermal metamorphism on a unique EL6 parent body that altered the original S isotopic composition (Defouilloy et al., 2016).

The isotopic variability of Se and S contrasts with Zn isotopes that show heavy isotope compositions of $\delta^{66/64}\text{Zn} = 2\text{--}7\text{‰}$ for EL6 chondrites and $\delta^{66/64}\text{Zn}$ of 0 ‰ for EH and EL3 chondrites and the Earth. The difference in $\delta^{66/64}\text{Zn}$ between EL6 and EL3 chondrites were explained by Zn volatilization, probably as a consequence of thermal metamorphism. Zinc is depleted by a factor of about 36 in EL5,6 chondrites compared to EL3 chondrites (Moynier et al., 2011), while other elements with a similar volatility under solar nebula conditions, including Se, S, and Ge, are only depleted by a factor of about 1-2 (Defouilloy et al., 2016; Kong et al., 1997). The large differences in depletion factors and isotope compositions for Zn, S, and Se could

potentially arise from i) different redox conditions during the condensation of EH and EL precursor dust or ii) a more effective partitioning of Zn into a different phase than S and Se on the enstatite parent body followed by a preferential breakdown of the Zn carrier phase in EL5,6 chondrites upon metamorphism. For scenario i) the extremely reducing conditions and possibly low nebula gas pressures might have led to a significant decrease in the Zn T_C , possibly explaining the depletion of Zn over Se in EL6 chondrites. This scenario, however, does not explain the different $\delta^{66/64}\text{Zn}$ values in EL3 and EL6 chondrites, because other Zn-depleted chondrites, like L or LL chondrites, do not show a substantial Zn isotope variability (Luck et al., 2005; Moynier et al., 2011). For scenario ii) the large differences in depletion factors and isotope compositions between Zn and Se, S, and Ge can be attributed to their different sulphide carrier phases. In the least metamorphosed EL3 chondrites, Zn is concentrated in sphalerite, whereas Se, S, and Ge are also present in troilite (Hertogen et al., 1983; Moynier et al., 2011). During thermal metamorphism sphalerite may have become unstable and a large amount of the incorporated elements may have been lost (e.g., 98% of Zn) and only a small fraction was redistributed into other mineral phases (Moynier et al., 2011). This leads to significant element and isotope fractionations of Zn with enrichment of the heavy isotopes in the residue. Also affected can be Cd and (partly) Tl that are also concentrated in sphalerite (Hertogen et al., 1983; Moynier et al., 2011; Palk et al., 2011; Wombacher et al., 2008). Selenium contained in sphalerite is supposed to be also largely lost and isotopically fractionated, but the bulk Se isotope composition in EL6 chondrites is then dominated by troilite, which is thermodynamically more stable. The depletion of about 20% in S and Se in EL6 chondrites (Se = 13 ± 10 $\mu\text{g/g}$; S = 2.1 ± 1.3 wt-%) compared to EL3 chondrites (Se = 17 ± 4 $\mu\text{g/g}$; S = 2.5 ± 0.8 wt-%) is consistent with this scenario (Table A4; Defouilloy et al. (2016)). This ultimately explains the different depletion factors and isotope

compositions of Se and Zn in EL3 ($\text{Se/Zn} = 0.09$; $\delta^{66/64}\text{Zn} = 0 \text{ ‰}$) and EL5,6 ($\text{Se/Zn} = 2.1$; $\delta^{66/64}\text{Zn} = 2\text{-}7 \text{ ‰}$) chondrites (Kong et al., 1997; Moynier et al., 2011). Unfortunately to our knowledge, no systematic study on S/Se variations among different petrologic types of EL chondrites has been performed so far testing the sulphide mineral control on S and Se abundances.

Zinc concentrations in mineral separates of EH chondrites show that Zn is concentrated in magnetic and silicate phases, but not in sulphides. Both Zn-bearing phases were found to have a homogeneous Zn isotope composition (Moynier et al., 2011). However, a complete separation of metals and silicates from sulphides is impossible so that Zn-bearing sulphides could have been sampled together with these phases, possibly explaining why El Goresy and Ehlers (1987) found Zn-bearing sulphides in two EH3 chondrites (Moynier et al., 2011). Nevertheless, the thermally more stable silicate host phases (such as pyroxenes) are expected to retain their element budgets during metamorphism so that no isotope fractionation of Zn is observed between EH4 and EH6 chondrites (Hertogen et al., 1983; Moynier et al., 2011).

Parent body thermal metamorphism is therefore considered to be an important process for the redistribution of volatile elements on the enstatite parent bodies. The degree of element volatilization during parent body metamorphism is a function of the thermal stabilities of its host phases and not of the T_C under canonical nebular conditions. Therefore, the isotope mass balance of phases present in the sample determines the isotope composition of the bulk sample.

5. Conclusions

This study of the Se isotope composition of bulk chondrites constrains the mechanism responsible for the depletion of moderately- to highly-volatile elements in planetary bodies of the

494 inner solar system and defines the $\delta^{82/78}\text{Se}$ value for the bulk solar system. The $\delta^{82/78}\text{Se}$ of all
495 bulk samples of carbonaceous, ordinary, and enstatite chondrite falls are identical within
496 analytical uncertainties and define a mean of -0.20 ± 0.26 ‰ despite variable Se depletion of the
497 investigated samples that can be as high as a factor of 2.5. This finding argues for a
498 homogeneous Se isotopic composition of the solar nebula. The Se isotope data and homogeneous
499 S/Se ratios in carbonaceous and ordinary chondrites further argue against any significant losses
500 of Se during terrestrial weathering. The data from this study show no indications for a Rayleigh-
501 type incomplete condensation of Se from the solar nebula or partial evaporative loss on the
502 precursor material and/or the parent bodies of carbonaceous, ordinary, and enstatite chondrites.
503 Thus, the Se depletion must have occurred under near equilibrium conditions, if acquired during
504 partial condensation or evaporative loss, to prevent any measureable isotope fractionation.
505 Alternatively, the depletion relative to the more refractory elements could have occurred after the
506 condensation of the refractory elements into solids in an environment that had lost a major part
507 of the remaining gas during cooling. In this scenario the entrainment of gas and fine particles by
508 solar wind and removal from the condensation region was accompanied by a quantitative
509 incorporation of volatile elements into their host phases from the pre-depleted gas. In this
510 situation condensation of the remaining volatile elements results in an increasing depletion with
511 decreasing T_C but no isotope fractionation irrespective if the depletion occurred under
512 equilibrium or disequilibrium conditions. Thus the constant Se isotope ratio combined with the
513 strong depletion of Se in all chondrite classes, save CI chondrites, is a reflection of the
514 condensation sequence of elements in a cooling solar nebula that changed its surface density as a
515 function of time and temperature.

The high variability of Se concentrations and depletions in ordinary and enstatite chondrites have been proposed to be a consequence of a variety of nebular components present in the parent body formation regions, thermal metamorphism, metal-sulphide and metal-silicate partitioning, and/or shock metamorphism (Ikramuddin et al., 1976; Kaczaral et al., 1988; Kadlag and Becker, 2015, 2016; Kong et al., 1997; Wasson and Kallemeyn, 1988). The findings from this study suggest that these processes did not involve any significant isotope fractionation, possibly due to the high temperatures involved. Different degrees of element depletions and isotope fractionations of elements with similar volatility under solar nebula conditions, including Zn, S, Se, in different petrologic types of EL and EH chondrites are likely caused by the different thermal stabilities of their host phases. This indicates that thermal metamorphism is an important process for the redistribution of volatile elements on the enstatite chondrite parent bodies. The isotope mass balance of the host phases therefore determines the isotope composition of the bulk sample.

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537 **6. Tables**

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Table 1 – Moderately-volatile elements and calculated 50% equilibrium condensation temperatures (T_C) for a gas of solar composition (Lodders, 2003; Palme and O'Neill, 2003).

| Element | 50% T_C [K] |
|---------|---------------|
| Au | 1060 |
| Cu | 1037 |
| K | 1006 |
| Ag | 996 |
| Ga | 968 |
| Na | 958 |
| Cl | 948 |
| B | 908 |
| Ge | 883 |
| Rb | 800 |
| Cs | 799 |
| Bi | 746 |
| F | 734 |
| Pb | 727 |
| Zn | 726 |
| Te | 709 |
| Sn | 704 |
| Se | 697 |
| S | 664 |

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543 Table 2 - Se concentrations and S/Se ratios of major chondrite groups obtained from literature data and this study for
 544 observed falls (except CK and CH groups for which no Se concentration data exists for observed falls). S/Se ratios of LL
 545 and EH chondrites are from meteorite finds.

| Meteorite group | Se [$\mu\text{g/g}$] | 2 s.d. | $n_{\text{meteor.}}$ | $n_{\text{anal.}}$ | S/Se | 2 s.d. | $n_{\text{meteor.}}$ | $n_{\text{anal.}}$ |
|--------------------------------|------------------------|--------|----------------------|--------------------|------|--------|----------------------|--------------------|
| <i>Carbonaceous chondrites</i> | | | | | | | | |
| CI | 21.2 | 0.6 | 3 | 18 | 2552 | 66 | 2 | 5 |
| CM | 12.8 | 1.1 | 6 | 20 | 2458 | 246 | 4 | 5 |
| CO | 8.8 | 1.5 | 5 | 9 | 2771 | 217 | 2 | 2 |
| CV | 8.7 | 1.5 | 4 | 14 | 2572 | 345 | 3 | 5 |
| CK (finds) | 5.6 | 3.5 | 7 | 8 | 255 | | 1 | 1 |
| CR | 5.6 | | 1 | 1 | 1963 | | 1 | 1 |
| CH (finds) | 3.7 | 0.6 | 2 | 2 | 1166 | | 1 | 1 |
| <i>Ordinary chondrites</i> | | | | | | | | |
| H | 8.3 | 3.9 | 22 | 24 | 2456 | 372 | 2 | 2 |
| L | 9.6 | 3.0 | 73 | 79 | 2278 | 51 | 2 | 2 |
| LL | 9.2 | 6.4 | 17 | 25 | 2346 | | 1 | 1 |
| <i>Rumuruti chondrites</i> | | | | | | | | |
| R | 14.6 | | 1 | 2 | 2795 | | 1 | 2 |
| <i>Enstatite chondrites</i> | | | | | | | | |
| EH | 25.7 | 11.1 | 7 | 22 | 1788 | 238 | 2 | 2 |
| EL | 15.7 | 8.7 | 5 | 16 | | | | |

546 $n_{\text{meteor.}}$ = number of measurements on different meteorites included in mean Se calculation. $n_{\text{anal.}}$ = number of total
 547 analyses including independent measurements on the same meteorite. A table with the comprehensive data set,
 548 including meteorite names and sources for Se and S concentrations, can be found in Table A4.

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Table 3 – List of samples investigated for Se abundances and isotope compositions. All samples are meteorite falls and finds. Finds are indicated by an asterisk next to the sample name. Information on meteorite classes were gained from Meteoritical Bulletin Database (<http://www.lpi.usra.edu/meteor/>)

| <i>Sample name</i> | <i>Class</i> | <i>Shock stage</i> | <i>Material analyzed [g]</i> | <i>Se [μg/g]</i> | <i>δ^{82/78}Se [‰]</i> |
|--|--------------|--------------------|------------------------------|------------------|--------------------------------|
| <i>Carbonaceous chondrites</i> | | | | | |
| Orgueil | CI1 | | 0.035 | 22.78 | -0.08 |
| Murchison | CM2 | 1-2 | 0.093 | 12.32 | -0.14 |
| Cold Bokkeveld | CM2 | 1 | 0.110 | 13.39 | 0.06 |
| Kainsaz | CO3.2 | 1 | 0.148 | 7.49 | -0.14 |
| Leoville* | CV3 | 3 | 0.159 | 7.00 | -0.34 |
| Allende | CV3 | 1 | 0.167 | 7.95 | -0.26 |
| <i>Ordinary chondrites</i> | | | | | |
| Dimmitt (Be-200)* | H3.7 | 3 | 0.199 | 6.97 | 0.13 |
| Dimmitt (Be-201)* | H3.7 | 3 | 0.111 | 8.08 | -0.09 |
| ZAG | H3-6 | 3 | 0.200 | 7.07 | -0.21 |
| Mezö-Madaras light pieces | L3.7 | | 0.106 | 9.50 | -0.20 |
| Mezö-Madaras dark pieces | L3.7 | | 0.101 | 10.41 | 0.06 |
| Jiddat al Harasis 091* | L5 | | 0.201 | 8.97 | -0.15 |
| Semarkona | LL3.00 | 2 | 0.121 | 13.41 | -0.22 |
| Chainpur | LL3.4 | 1 | 0.115 | 10.39 | -0.47 |
| Parnallee | LL3.6 | | 0.113 | 8.11 | -0.08 |
| <i>Enstatite chondrites</i> | | | | | |
| Qingzhen | EH3 | 3 | 0.122 | 26.05 | -0.24 |
| Indarch | EH4 | 3 | 0.108 | 33.16 | -0.34 |
| Pillistfer | EL6 | 2 | 0.135 | 12.13 | -0.36 |
| Hvittis | EL6 | 2 | 0.238 | 10.86 | -0.22 |
| Happy Canyon* | EL6/7 | 2 | 0.125 | 3.21 | 0.11 |
| <i>Iron meteorites, troilite phase</i> | | | | | |
| Canyon Diablo | IAB-MG | | 0.019 | 86.78 | -0.15 |
| Odessa | IAB-MG | | 0.018 | 165.17 | 0.12 |
| Toluca | IAB-sLL | | 0.020 | 47.51 | -0.22 |
| Mundrabilla | IAB-ung | | 0.020 | 102.10 | -0.13 |
| Nantan | IAB-MG | | 0.016 | 121.29 | -0.01 |

7. Figures

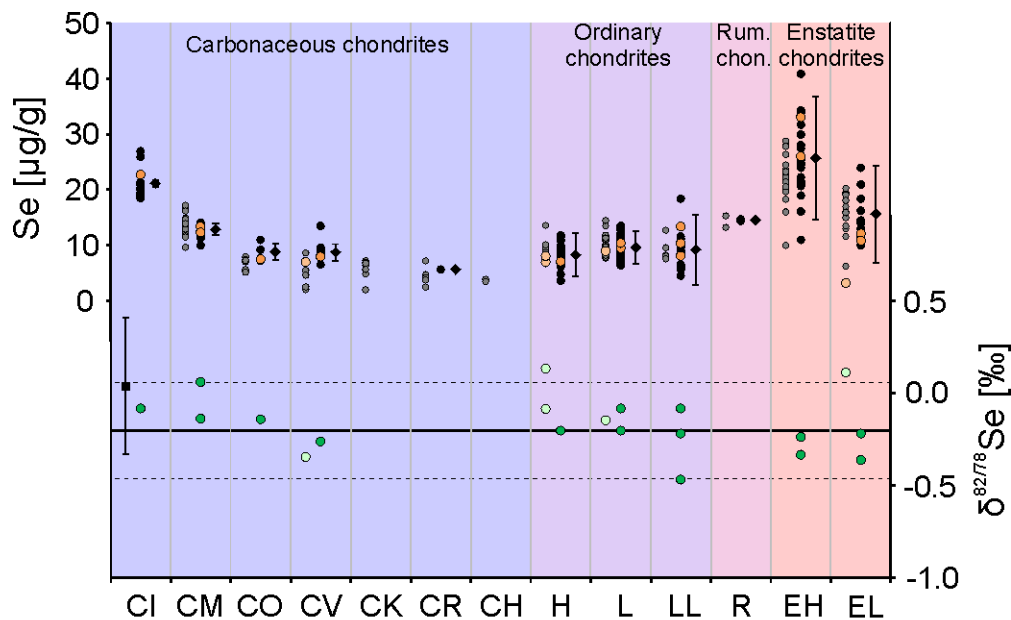


Figure 1 – The Se abundance and isotope composition of chondrites. Selenium concentrations from literature data include meteorite falls and finds and are indicated by black and grey circles, respectively. The source for Se concentrations can be found in Table A4. Selenium concentrations of meteorite falls and finds from this study are indicated by orange and light orange circles, respectively. The average Se concentration and uncertainty is taken from Table 1 and is indicated by black diamonds. $\delta^{82/78}\text{Se}$ for meteorite falls and finds are indicated by green and light green circles, respectively. The long-term reproducibility of the shale standard SGR-1 of $\pm 0.37\text{‰}$ (2 s.d., $n = 8$; black square) is taken as a representative for the analytical uncertainty. Black solid and dashed horizontal lines represent the average $\delta^{82/78}\text{Se}$ and uncertainty of all meteorites falls, which is $-0.20 \pm 0.26 \text{‰}$ (2 s.d., $n = 14$).

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