Silver contents and Cu/Ag ratios in Martian meteorites and the implications for planetary differentiation

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Abstract:

Silver and Cu show very similar partitioning behavior in sulfide melt-silicate melt and metal-silicate systems at low and high pressure-temperature (P-T) experimental conditions, implying that mantle melting, fractional crystallization and core-mantle differentiation have at most modest (within a factor of 3) effects on Cu/Ag ratios. For this reason, it is likely that Cu/Ag ratios in mantle-derived magmatic products of planetary bodies reflect that of the mantle and, in some circumstances, also the bulk planet composition. To test this hypothesis, new Ag mass fractions and Cu/Ag ratios in different groups of Martian meteorites are presented and compared with data from chondrites and samples from the Earth's mantle.

Silver contents in lherzolitic, olivine-phyric and basaltic shergottites and nakhlites range between 1.9 and 12.3 ng/g. The data display a negative trend with MgO content and correlate positively with Cu contents. In spite of displaying variable initial ε^{143}Nd values and representing a diverse spectrum of magmatic evolution and physiochemical conditions, shergottites and nakhlites display limited variations of Cu/Ag ratios (1080±320, 1s, n=14). The relatively constant Cu/Ag suggests limited fractionation of Ag from Cu during the formation and evolution of the parent magmas, irrespectively of whether sulfide saturation was attained or not. The mean Cu/Ag ratio of Martian meteorites thus reflects that of the Martian mantle and constrains its Ag content to 1.9±0.7 ng/g (1s).

Carbonaceous and enstatite chondrites display a limited range of Cu/Ag ratios of mostly 500-2400. Ordinary chondrites show a larger scatter of Cu/Ag up to 4500, which may have been caused by Ag redistribution during parent body metamorphism. The majority of chondrites have Cu/Ag ratios indistinguishable from the Martian mantle value, indicating that Martian core formation strongly depleted Cu and Ag contents, but probably did not significantly change the Cu/Ag ratio of the mantle compared to bulk Mars. Bulk Mars is richer in moderately volatile elements than Earth, however, the Martian mantle displays a much stronger depletion of the moderately volatile elements Cu and Ag, e.g., by a factor of 15 for Cu. This observation is consistent with experimental studies suggesting that core formation at low P-T conditions on Mars led to more siderophile behavior of Cu and Ag than at high P-T conditions as proposed for Earth. In contrast, Cu/Ag ratios of the mantles of Mars and Earth (Cu/Ag_{Earth}=3500±1000) display only a difference by a factor of 3, which implies restricted fractionation of Cu and Ag even at high P-T conditions. The concentration data

45 support the notion that siderophile element partitioning during planetary core formation scales
46 with the size of the planetary body, which is particularly important for the differentiation of
47 large terrestrial planets such as Earth. Collectively, the Ag and Cu data on magmatic products
48 from the mantles of Mars and Earth and the data on chondrites confirm experimental
49 predictions and support the limited fractionation of Cu and Ag during planetary core
50 formation and high-temperature magmatic evolution, and probably also in early solar nebular
51 processes.
52
53 Keywords: Mars, shergottites, Cu/Ag ratio, core formation, planetary differentiation
54

1. Introduction

During planetary core formation, siderophile elements were distributed between the cores and mantles of differentiated planetesimals and planets according to their metal-silicate and sulfide-silicate partition coefficients (e.g., Jones and Drake, 1986; O'Neill, 1991). Experimental studies of siderophile element partitioning between metal, sulfide and silicate melt at low- and high-pressure (P) - temperature (T) conditions now permit to constrain the P-T-fO_2 conditions of planetary accretion and core formation of different planetary bodies, such as Earth, Moon and Mars (e.g., Corgne et al., 2008; Fischer et al., 2015; Laurenz et al., 2016; Li and Agee, 1996; Li and Agee, 2001; Mann et al., 2009; Righter, 2011; Rubie et al., 2011; Rubie et al., 2015; Rubie et al., 2016; Siebert et al., 2011; Wade and Wood, 2005; Wood, 2008). Accurate estimates of the contents of siderophile elements in the mantle and in the core are essential for a successful application of this approach.

The contents of siderophile elements in the mantle can be constrained directly by rock samples from planetary mantles if such samples are available, for instance, mantle peridotites in the case of the Earth. However, planetary cores are inaccessible and thus the contents of siderophile elements in planetary cores are often calculated by subtraction of mantle element inventories from assumed chondritic model compositions of the bulk planet (McDonough, 2014). This approach appears to be valid for refractory elements with uncertainties of approximately a few percent (such as rare earth elements and refractory siderophile elements, e.g., Dauphas and Pourmand, 2015; Palme and O'Neill, 2014). For volatile elements (the elements with the 50% condensation temperature at 10^{-4} bar total pressure less than those of

76 Mg, Si and Fe, Lodders, 2003), uncertainties in the exact composition of the building
77 materials of the planets may be much larger, because chondritic materials display much larger
78 variations in volatile element abundances (e.g., Wasson and Kallemeyn, 1988) and the
79 behavior of these elements in chondrites is decoupled from refractory elements (e.g., Davis,
80 2006; Kadlag and Becker, 2015). Furthermore, it cannot be excluded that the fractionation of
81 volatile elements in the building materials of the terrestrial planets was different from that in
82 chondrites (e.g., Dauphas, 2017; Wang et al., 2016) and that additional volatile loss processes
83 may have occurred during planetary accretion (e.g., Canup et al., 2015; Wang and Jacobsen,
84 2016). The high contents of volatile S and K on Mercury (Nittler et al., 2011; Peplowski et al.,
85 2011) are also not easily reconciled with models that predict that the volatile depletion of
86 planetary bodies increases as heliocentric distances decrease (McCubbin et al., 2012).
87 Experimentally determined high P-T metal-silicate partitioning data (e.g., 5-20 GPa
88 and 2000-2300 °C) can be applied directly to Mars-size planetary bodies (e.g., Corgne et al.,
89 2008; Fischer et al., 2015; Laurenz et al., 2016; Li and Agee, 2001; Mann et al., 2009; Righter,
90 2011; Rubie et al., 2011; Siebert et al., 2011; Wade and Wood, 2005). In forward models,
91 such experimental results and data on the concentration of siderophile volatile elements
92 (volatile elements with metal affinity during metal-silicate partitioning) in planetary mantles
93 may provide independent constraints on the likely composition of accreted materials (e.g.,
94 Wang et al., 2016). The core formation history of planetary bodies likely involves changes in
95 P-T-fO_2 conditions (e.g., Wade and Wood, 2005; Rubie et al., 2011; 2015). Thus, it is best to
96 first consider the siderophile volatile elements whose siderophile element ratios are little

affected by core formation. In such cases, the ratios of siderophile elements in the mantle should reflect the ratios in the bulk planetary body.

Experimental data on metal-sulfide-silicate partitioning suggest that Ag and Cu very likely display such behavior (Vogel, 2015; Wood et al., 2014). Sulfide melt-silicate melt partitioning data have also indicated no systematic fractionation of Cu from Ag in sulfide melt-silicate melt systems, in spite of the large variations of partition coefficients at different physicochemical conditions (Kiseeva and Wood, 2013; Kiseeva and Wood, 2015; Li and Audetat, 2012). Therefore, magmatic products originating from the mantle likely retain the Cu/Ag ratio of their mantle source and also the value of the bulk planetary body. In order to test this hypothesis, we present Ag concentration data on Martian meteorites and new Ag and Cu data on some ordinary chondrites obtained by isotope dilution ICP-MS. The data on Martian meteorites are compared with terrestrial samples and chondrites and the behavior of Cu and Ag in these objects is discussed.

2. Samples and methods

About 0.2-0.25 gram fragments of 15 Martian meteorites were obtained (Table 1). Except for Sau 005, these samples are falls and finds from the cold desert of Antarctica, with negligible terrestrial alteration (Wang and Becker, 2017). The meteorites consist of diverse groups of lherzolitic (n=2), olivine-phyric (n=8) and basaltic (n=1) shergottites, nakhlites (n=3) and the orthopyroxenite cumulate ALH 84001, with a large range of presumed formation ages from 4.1 Ga to 150 Ma (Lapen et al., 2010; Nyquist et al., 2001). Based on lithophile incompatible elements and radiogenic isotopes of Sr, Nd and Os, they reflect a

118 range of geochemical characteristics with substantial differences in mantle source
119 compositions of lithophile incompatible elements, variations in the degrees of Martian crustal
120 contamination and magmatic evolution at variable oxygen fugacity (e.g., Brandon et al., 2012;
121 Herd et al., 2002; Lapen et al., 2010; Meyer, 2013; Mittlefehldt, 1994; Treiman, 2005;
122 Wadhwa, 2008).

123 These samples have been used to measure Cu, S, Se and Te contents by isotope
124 dilution ICP-MS after digestion in Parr digestion bombs (Wang and Becker, 2017). In the
125 present study, the Ag contents were determined by isotope dilution ICP-MS from the same
126 digested sample aliquots (Tables 1 and 2). Obtaining both Cu and Ag contents from the same
127 sample aliquots reduces the effect of separation of small-scale monosulfide solid solution
128 (MSS)-sulfide liquid (if they occur at all) and the effect of the heterogeneous distribution of
129 trace sulfides, which cause scatter in abundances and ratios of chalcophile elements if the
130 latter are analyzed in different aliquots of bulk rocks.

131 The Ag and Cu abundances in nine ordinary chondrites were also determined from
132 the same sample aliquots in order to compare with literature Ag and Cu data on ordinary
133 chondrites which display a large range of Cu/Ag. The analyzed chondrites are mostly
134 meteorite falls, with negligible terrestrial contamination, and include the H, L and LL groups
135 with different degrees of parent body metamorphism (Table 3,
136 https://www.lpi.usra.edu/meteor/metbull.php). Because the literature data show a larger range
137 of Cu/Ag ratios in ordinary chondrites than in carbonaceous and enstatite chondrites and
138 alteration potentially affects Ag contents (and thus Cu/Ag, see below), the new data from

139 ordinary chondrites falls may constrain whether the scatter of Cu/Ag of ordinary chondrites
140 from the literature reflects a pristine feature or is due to terrestrial alteration.

141 Sample preparation and digestion have been described before (Wang and Becker,
142 2017; Wang et al., 2015) and only a brief outline of the method is given here. Fragments of
143 Martian meteorites were crushed to smaller fractions using an agate mortar and then
144 processed to fine powder in a Retsch® oscillating ball mill MM 200 with agate cups.
145 Ordinary chondrites were crushed to powder in an agate mortar. After addition of spike
146 solutions containing ^{109}Ag-^{65}Cu and spikes of other elements such as S, Se and Te, sample
147 powders were digested in a mixture of concentrated HF-HNO_3 in Parr digestion bombs at
148 190°C for 3 days. The digestion solution was dried down and converted to chloride form. The
149 sample solution was dissolved in 4.5 mol l^{-1} HCl and then loaded on 2 ml 100-200 mesh
150 pre-cleaned Eichrom 1-X8 anion resin to remove matrix elements and elements that may form
151 interferences (Wang et al., 2015).

152 Martian meteorites have low Ag contents (Tables 1 and 2) and very high Zr/Ag and
153 Nb/Ag ratios, particularly in incompatible element-enriched samples (e.g., Meyer, 2013;
154 Yang et al., 2015). In order to reduce the effect of the oxide interferences on Ag isotopes, 9
155 mol l^{-1} HCl was used to exclusively collect Ag after elution of matrix in 4.5 mol l^{-1} HCl, 0.4
156 mol l^{-1} HCl and 0.05 mol l^{-1} HCl. Because of low Zr/Ag and Nb/Ag in chondrites, the Ag
157 fraction of ordinary chondrites was collected with other elements of interest (Cd and Tl) in a
158 mixture of 0.7 mol l^{-1} HNO_3 and 1 vol.% H_2O_2 (Wang et al., 2015). After conversion to nitric
159 acid form, the samples were dissolved in 0.28 mol l^{-1} HNO_3 and analyzed at Freie Universität
160 Berlin on the Element XR sector field ICP-MS (Thermo Scientific) coupled to an Aridus-I

desolvator to limit oxide formation (CeO^+/Ce^+ < 0.002). At such conditions, a 20 ng/g Nb standard solution yielded $^{93}NbO^+/^{93}Nb^+$ of < 0.0002. The monitored $^{91}Zr/^{107}Ag$ and $^{93}Nb/^{109}Ag$ in Martian meteorites were low and mostly < 0.1, indicating negligible effects of these metal-oxide interferences. Different reference materials (e.g., NIST SRM 612 glass, BHVO-1, BHVO-2 and others) and the replicates have yielded reproducible results (< 5%, 2s, Wang et al., 2015). During the period of sample measurements, the total procedural blanks (also by isotope dilution, n=5, 2s) were 0.022 ± 0.015 ng Ag and 4 ± 4 ng Cu. Procedural blank corrections were applied, and blank contributions range from mostly < 3% to 8% for the largest correction for Ag and 28% for Cu (Table 1).

3. Results

3.1.1. Martian meteorites

The new data on Martian meteorites are listed in Table 1 and plotted in Figure 1. Overall, the Ag contents in shergottites increase from lherzolitic, olivine-phyric to basaltic types, with a range of 1.9 ng/g to 12.3 ng/g (Figure 1). Three nakhlite samples have 7.8 ng/g to 10.5 ng/g Ag. ALH84001 has an Ag content of 7.2 ng/g.

Silver data in the Martian meteorites have been reported before (Biswas et al., 1980; Kong et al., 1999; Laul et al., 1972; Laul et al., 1986; Lodders, 1998; Meyer, 2013; Smith et al., 1984; Treiman et al., 1986; Wang et al., 1998; Yang et al., 2015). Our new Ag data are within the range of literature data but tend to be lower, even in the same samples. For example, Zagami has 8.1 ng/g in this work, compared to 14.2 ng/g (Treiman et al., 1986), 31 ng/g (Wang et al., 1998) or 12.4 ng/g (Kong et al., 1999) in previous work (Table 2). A

similar behavior was observed for Nakhla, with 32 ng/g (Wang et al., 1998), 40 ng/g (Laul et al., 1972) or 246 ng/g (Kong et al., 1999) in previous work compared to 7.8 ng/g in the present study. The different aliquots of ALHA 77005 have similar values at 4-5 ng/g (Table 2), whereas our Ag concentration of 7.2 ng/g in ALH 84001 is much higher than the previous values of 0.22-0.35 ng/g (Wang et al., 1998) and < 0.9 ng/g (Kong et al., 1999).

The observation that different studies obtained different Ag concentrations in different aliquots of the same samples has also been noted for other chalcophile elements, e.g., S (e.g., Ding et al., 2015; Franz et al., 2014; Wang and Becker, 2017), Cu (Meyer, 2013; Wang and Becker, 2017) and the highly siderophile elements (HSE, e.g., Brandon et al., 2012; Jones et al., 2003; Yang et al., 2015). The scatter of data may reflect uncertainties of the applied analytical methods and sample heterogeneity as different proportions of silicate phenocrysts and sulfides may be present in different aliquots of the same sample. Some Ag concentration data on bulk rocks of shergottites from the literature were produced by laser ablation ICP-MS with a relatively high detection limit of 2 ng/g for Ag (Yang et al., 2015). Most samples analyzed by the latter method show high Ag contents (up to 651 ng/g). For example, Zagami has 651 ng/g Ag (Yang et al., 2015), far higher than our value and data obtained by others (Table 2). A possible explanation for such very high concentrations might be interferences from transition metal oxides, e.g., ^{91}ZrO and ^{93}NbO.

Similar to Cu abundances, Ag contents display a broad negative trend with MgO contents (Figure 1), and, not surprisingly, Ag and Cu are positively correlated. Because Ag and Cu contents of the present study are from the same sample aliquots, the effect of sample heterogeneity on Cu/Ag ratios is limited. If ALH 84001 is not considered, the Martian

meteorites display limited variation in Cu/Ag ratios with a mean value of 1080±320 (1s, n=14, Figure 2). Of these samples, Y-980459 and LAR 06319 are thought to be closed-system crystallization products of primitive magma from the Martian mantle (Basu Sarbadhikari et al., 2009; Mikouchi et al., 2004; Musselwhite et al., 2006; Usui et al., 2012). The Cu/Ag ratios of Y-980459 (1122±31) and LAR 06319 (1474±48) are similar to the mean value within uncertainty. Sau 005 (628±14) and Y-00593 (466±9) tend to have the lowest Cu/Ag ratios and some olivine-phyric shergottites have slightly higher values of around 1500. Olivine-phyric shergottites which were derived from mantle reservoirs with different depletion of incompatible lithophile elements show no obvious difference in Cu/Ag ratios (range from 1100 to 1500, Table 1, Figure 3).

3.1.2. Chondrites

Here we present new data on some ordinary chondrites and also compiled literature data of Cu and Ag contents in chondrites. Mean contents of Cu and Ag in different groups of chondrites display no systematic variations or differences (Wasson and Kallemeyn, 1988). Mean Cu/Ag ratios in carbonaceous (CI, CM, CV and CO), ordinary (H, L and LL) and EH chondrites are also similar, however, EL chondrites show higher Cu/Ag (Wasson and Kallemeyn, 1988, Figure 4). Literature data where both Cu and Ag contents were obtained from the same samples, indicate that Cu/Ag ratios of CI, CM, CO, CV, EH and EL chondrites range from 500 to 2400 (a mean of 1100±400, 1s, n=24, Figure 4). The mean Cu/Ag of EL chondrites in which Cu and Ag were determined on different samples (4780, Wasson and Kallemeyn, 1988) is different from Cu/Ag values of EL chondrites for which Cu and Ag concentration data were obtained from the same sample (a mean Cu/Ag of 1260±670, 1s,

n=5). This suggests that it is important to obtain Cu and Ag data on the same samples, or better, from the same sample aliquot.

Ordinary chondrites show a large scatter of Cu/Ag ratios from 200 to 4500 (mean = 1600±1000, 1s, n=39, median = 1400), however, the majority of samples have Cu/Ag similar to carbonaceous and enstatite chondrites (Figure 4). The scattered Cu/Ag is mainly due to the large variation in Ag contents (e.g., Friedrich et al., 2004; Kaczaral et al., 1989; Koblitz, 2005; Lingner et al., 1987; Schönbächler et al., 2008; Schaefer and Fegley, 2010; Wolf and Lipschutz, 1995; Wolf et al., 1997). The new Cu and Ag contents in ordinary chondrites are listed in Table 3 and are shown in Figure 4. The samples are mostly falls and vary from petrological type 3 to 6 (https://www.lpi.usra.edu/meteor/metbull.php). Our results show a range of Cu/Ag ratios similar to the literature data on ordinary chondrites. Samples of this study do not show systematic differences or changes of Cu/Ag with the petrological type or as a function of ordinary chondrite group.

4. Discussion

4.1. The effect of Martian crustal contamination and terrestrial alteration

Based on $\Delta^{33}S$ (Franz et al., 2014) and δD values (Usui et al., 2012), some Martian meteorites or their parent magmas underwent variable extents of contamination by Martian crustal materials. These contamination processes barely affected Cu, Se, Te and HSE contents but might have increased S contents because of incorporation of sulfate on Mars (Farquhar et al., 2000; Franz et al., 2014; Greenwood et al., 2000; Wang and Becker, 2017). Terrestrial alteration may increase Ag contents as indicated by Ag concentration data on serpentinized

247 peridotites and komatiites (Theis et al., 2013; Wang and Becker, 2015), probably because of
248 the mobile behavior of Ag during hydrothermal or other fluid-controlled processes (Wang and
249 Becker, 2015). Therefore, the effect of Martian crustal contamination and terrestrial alteration
250 should be evaluated for Ag contents and Cu/Ag ratios in Martian meteorites.

251 The literature values of Ag contents in ALH 84001 are 0.22 and 0.35 ng/g (Wang et
252 al., 1998), consistent with the very low contents of the other strongly chalcophile elements
253 HSE, Cu, Se and Te (Jones et al., 2003; Wang and Becker, 2017). The low contents of HSE,
254 Cu and Se in the cumulate ALH 84001 imply a very low sulfide abundance and low Ag and S
255 contents. However, the present study shows a higher Ag content of 7.2 ng/g in ALH 84001.
256 The high Ag content is coupled with a high S content of 219 µg/g in the same sample aliquot
257 (Wang and Becker, 2017), possibly indicating an effect of Martian crustal assimilation on Ag
258 as it was suggested for S. Some other SNC samples such as MIL 03346, RBT 04262 and LAR
259 06319 also display evidence from $\Delta^{33}S$ (Franz et al., 2014) and high S/Se (Wang and Becker,
260 2017) that their S budget was affected significantly by contamination with Martian crust.
261 Although the contamination affects the S budget, these samples show Cu/Ag similar to the
262 others with little or no contamination with sulfur from the Martian crust. Therefore, the effect
263 of Martian crustal contamination is likely to be also limited for Ag as for the HSE, Cu, Se and
264 Te. The specific reason for the relatively high Ag content of ALH 84001 in this study is
265 unclear.

266 Sau 005 (628±14) and Y-000593 (466±9) are both meteorite finds and have the
267 lowest Cu/Ag ratios in samples of this study, a factor of 2 lower than the mean value. The
268 lower Cu/Ag in both samples may be explained by terrestrial alteration, however, Ag contents

of these two samples display no obvious difference from other samples and are relatively low (around 9-12 ng/g) and other chalcophile element ratios did not yield clear evidence for a significant influence of terrestrial weathering on these elements (Wang and Becker, 2017). Alternatively, the range of variations of Cu/Ag recorded by the SNC meteorites reflects intrinsic variations in the parent magmas and in the Martian mantle.

4.2. Limited fractionation of Ag and Cu in magmatic processes

During high-temperature magmatic processes, Ag and Cu are mainly controlled by sulfide melt-silicate melt partitioning (e.g., Kiseeva and Wood, 2015; Li and Audetat, 2012; Wang and Becker, 2015). Experimental results have indicated no significant or systematic fractionation of Cu from Ag in sulfide melt-silicate melt systems, regardless of the physicochemical conditions (Figure 5, Kiseeva and Wood, 2013; Kiseeva and Wood, 2015; Li and Audetat, 2012). The only exception where large differences between Cu and Ag partitioning may occur is the segregation of MSS from sulfide melt (e.g., Bockrath et al., 2004; Li and Audetat, 2012), a process which is restricted to specific situations during the late cooling stage of some basic magma series (e.g., Dare et al., 2011; Patten et al., 2013), some supra-subduction zone magmatic systems (e.g., Jenner et al., 2010) and the exsolution of sulfide melts into different sulfide phases during cooling of mantle rocks (e.g., Alard et al., 2000; Luguet et al., 2004).

Many Martian meteorites of this study are magmatic cumulates with variable proportions of interstitial basic melts. Based on rare earth element patterns and Sr-Nd-Os isotopes, they originated from different mantle sources and show a large range of emplacement ages and variable magmatic evolution (e.g., Brandon et al., 2012; Herd et al.,

291 2002; Lapen et al., 2010; Meyer, 2013; Mittlefehldt, 1994; Treiman, 2005; Wadhwa, 2008).
292 Nevertheless, they display a restricted range of Cu/Ag ratios (466 to 1527 with a mean of
293 1080±320, Table 1 and Figures 2-3), similar to ratios of some other chalcophile elements (e.g.,
294 Cu/Se, Wang and Becker, 2017). These features suggest limited fractionation of Ag from Cu
295 at different magmatic conditions on Mars.

296 Recent work suggested a sulfide-understated evolution of the parent magmas of many
297 Martian meteorites (Ding et al., 2015; Wang and Becker, 2017). The increasing Ag and Cu
298 contents with decreasing MgO support a sulfide undersaturated evolution of Martian magmas
299 (Figure 1; Wang and Becker, 2007). Given such conditions, it is not surprising that different,
300 even genetically unrelated Martian meteorites show similar Cu/Ag. Because Cu and Ag are
301 incompatible elements during melting of mantle in which sulfides are not retained and during
302 the subsequent evolution of sulfide-undersaturated mantle-derived magmas (Cu and Ag are
303 incompatible in olivine and pyroxenes, e.g., Fellows and Canil 2012; Lee et al., 2012; Liu et
304 al., 2014), these elements become depleted or enriched in constant proportion in cumulates,
305 evolving silicate melts and mixtures of cumulates and melts (as in most SNC meteorites).
306 Therefore, no significant change of Cu/Ag ratios should have occurred in lherzolitic,
307 olivine-phyric, basaltic shergottites, and at least some nakhlites, even though concentrations
308 of Cu and Ag may vary (Figures 1 and 2). At sulfide-saturated conditions, Cu and Ag also
309 would display little fractionation because Ag and Cu have similar sulfide melt-silicate melt
310 partition coefficients for a large range of FeO contents in silicate magmas (Figure 5). During
311 slow cooling of silicate magma and the formation of immiscible sulfide droplets, Cu and Ag
312 may fractionate differently if MSS forms at low temperatures and separates from sulfide melt

313 (e.g., Dare et al., 2011; Patten et al., 2013). In the MSS-sulfide melt system, Ag tends to
314 enrich in the remaining sulfide liquid more strongly than Cu (Jenner et al., 2010; Li and
315 Audetat, 2012). Because sulfides in shergottites and nakhlites mainly crystallized during the
316 late stage of cooling and crustal emplacement and a limited amount of chalcopyrites exsolved
317 during cooling (e.g., Chevrier et al., 2011; Lorand et al., 2005), the petrological observations
318 and the limited Cu/Ag range of the present study indicate that MSS-sulfide melt segregation
319 likely did not play a significant role in the fractionation of Cu/Ag and other chalcophile
320 elements in bulk rocks of Martian meteorites.

321 Although factors such as FeO content in the silicate melt and sulfide composition
322 strongly affect partition coefficients, this is not the case for Cu and Ag during sulfide
323 melt-silicate melt partitioning (Kiseeva and Wood, 2013; Kiseeva and Wood, 2015; Li and
324 Audetat, 2012, Figure 5d). The mean Cu/Ag ratios in fresh terrestrial lherzolites, MORB from
325 different ocean basins and sulfide droplets in MORB are similar (Figure 2). Although
326 MORBs undergo substantial sulfide melt-silicate melt fractionation and display variable Cu
327 contents, existing data indicate limited changes in Cu/Ag during partial melting,
328 melt-peridotite reaction and fractional crystallization processes in the Earth's convecting
329 mantle and predominant control of Cu/Ag and other chalcophile element ratios by sulfide
330 melt-silicate melt partitioning (e.g., Jenner and O'Neill, 2012; Jenner et al., 2010; Patten et al.,
331 2013; Wang and Becker, 2015). We note that in some terrestrial peridotites (notably those
332 with low Cu and Ag abundances), Cu/Ag ratios are substantially lower (Figure 2), which may
333 reflect preferential enrichment of Ag during serpentinization and other forms of alteration

334 (Wang and Becker, 2015). This is the main reason why some peridotites show low Cu/Ag
335 ratios relative to those with similar MgO contents (Figure 2).

336 The mantles of Earth and Mars are characterized by different oxygen fugacity
337 conditions, FeO, Ni and Cu contents. In particular, because of the higher FeO contents of
338 Martian magmas (e.g., 18 wt.%) relative to terrestrial magmas (e.g., 10 wt.%), sulfur contents
339 at sulfide saturation of mantle-derived magmas on Mars are much higher than those on Earth
340 at similar P-T conditions (e.g., 3500-4000 μg/g S versus 1500-2000 μg/g, Ding et al., 2015;
341 Liu et al., 2007; Righter et al., 2009; Smythe, et al., 2017; references therein). This leads to a
342 different role of sulfide melt-silicate melt partitioning in these planets. On Mars, because of
343 high sulfur contents at sulfide saturation, most mantle-derived magmas were
344 sulfide-undersaturated from the source to subsequent high-temperature crystallization stage in
345 the crust (Ding et al. 2015, Wang and Becker, 2017). In contrast, most terrestrial basic
346 magmas should be sulfide-saturated during partial melting and during subsequent fractional
347 crystallization (e.g., Czamanske and Moore, 1977; Fortin et al., 2015; Liu, et al., 2007;
348 Lorand, 1989; Patten et al., 2013; Smythe et al., 2017). The limited range in Cu/Ag of
349 Martian meteorites and the coincidence in Cu/Ag of terrestrial MORB and mantle lherzolites
350 (Figure 2), respectively, support the conclusions of limited fractionation of Ag and Cu at a
351 range of magmatic conditions, consistent with experimental data. These results suggest that
352 the Cu/Ag ratios in mantle rocks and their melting products should reflect the mantle
353 composition of a planetary body, regardless of the specific compositions and magmatic
354 evolution and regardless whether silicate magmas were saturated with a sulfide melt or not.

4.3. Cu/Ag ratios in the Martian mantle and in bulk Mars

4.3.1. The Ag content and Cu/Ag in the Martian mantle

On the basis of variations in major and trace element and Sr-Nd-Os isotopic compositions, the parent magmas of Martian meteorites were interpreted to originate from incompatible element-depleted to enriched mantle sources and underwent different extents of partial melting and fractional crystallization at different physiochemical conditions (e.g., Borg and Draper, 2003; Brandon et al., 2012; Debaille et al., 2009; Herd et al., 2002; references therein). It was also argued that Sr-Nd isotopic variations may reflect strong Martian crustal contamination, particularly in enriched shergottites (Jones, 2015 and references therein). Regardless of these complexities, the Cu/Ag ratios in different Martian meteorites are similar within a factor of 2 and show no correlation with La/Yb ratios and initial ε^{143}Nd (Figure 3). These observations suggest that the depletion and re-enrichment processes that resulted in substantial variations of incompatible lithophile elements and their radiogenic isotopes led to only a small and non-systematic variation of Cu/Ag in Martian mantle sources.

The limited variations in Martian meteorites yield a mean Cu/Ag of 1080±320 (1s, n=14, except ALH 84001). Because of sulfide-undersaturated conditions, both Cu and Ag should enter silicate melts quantitatively after a few percent partial melting (Ding et al., 2015; Wang and Becker, 2017), and thus, the mean ratio of the Martian meteorites is interpreted to reflect that of the Martian mantle. Because the value is calculated from all shergottites and nakhlites of this study, the uncertainty includes the possible effect of crustal contamination and primordial heterogeneity of the mantle. Within uncertainty, the mean value is similar to Cu/Ag of Y-980459 and LAR 06319, which were interpreted to have crystallized from

377 primitive mantle-derived magma (e.g., Basu Sarbadhikari et al., 2009; Mikouchi et al., 2004;
378 Musselwhite et al., 2006; Usui et al., 2012). The Cu content in the Martian mantle has been
379 estimated at 2.0±0.4 µg/g (1s) (Taylor, 2013; Wang and Becker, 2017), thus based on Cu/Ag,
380 the Ag content of the Martian mantle is 1.9±0.7 ng/g (1s). The latter value overlaps with a
381 previous estimate of 2.6 ng/g Ag in the Martian mantle, which was estimated from Ag/La in a
382 limited set of Martian meteorites (Kong et al., 1999). Another recent estimate of the Ag
383 content of the Martian mantle was based on Ag/Dy and is twice as high (4.2±1.2 ng/g, 1s,
384 Taylor, 2013).

385 ***4.3.2. The effect of core formation on Cu/Ag in planetary mantles***

386 The current Martian core-mantle boundary may be at a pressure of 20-23 GPa and a
387 temperature of about 2000 K (Fei and Bertka, 2005; Khan and Connolly, 2008; Konopliv et
388 al., 2011; Stewart et al., 2007). Data on metal-silicate partitioning experiments for a variety of
389 non-volatile siderophile elements such as W, Mo, Ni, Co, and the abundances of these
390 elements in model compositions of the Martian mantle suggest that the Martian mantle may
391 have equilibrated with the core at 14±3 GPa and 2000-2300 K (Rai and van Westrenen, 2013;
392 Righter and Chabot, 2011; Yang et al., 2015).

393 Experimental studies have covered this P-T range for metal-silicate partitioning of Cu
394 and Ag and the influence of other parameters (Corgne et al., 2008; Righter, 2011; Righter and
395 Drake, 2000; Vogel, 2015; Wheeler et al., 2011; Wood et al., 2014). Silver and Cu become
396 less siderophile with increasing P and T and more siderophile with increasing S content in the
397 metal (Corgne et al., 2008; Vogel, 2015; Wood et al., 2014). In contrast, Si contents in the
398 metal and oxygen fugacity appear to have very weak effects (Vogel, 2015). Copper tends to

399 become slightly less siderophile with increasing oxygen fugacity (Corgne et al., 2008).
400 Remarkably, although the absolute partition coefficients may change dramatically with
401 variable conditions (a factor of tens or more), the relative siderophile behavior of Cu and Ag
402 changes little (Figure 5). For instance, metal-sulfide-silicate partitioning data from the same
403 experiments at 1.5 GPa and 1460-1650 °C (Wood et al., 2014) show only a factor of 1-3
404 variations, with a modest decrease in the ratios of exchange coefficients K_{Cu}/K_{Ag} (about 1.8 to
405 about 0.6, a mean of 1.2 ± 0.6, 1s, n=10) from the metal-silicate system to the sulfide-silicate
406 system (Figure 5b). Data at higher P-T conditions (11-21 GPa, 2000-2600 °C, ΔIW of -4.7
407 to -1.6) also show limited fractionation of Cu and Ag, although Cu and Ag data are not from
408 the same experiments (Vogel, 2015). Therefore, experimental data predict that core formation
409 should have yielded low Cu and Ag abundances in the Martian mantle (as observed), but
410 should have had a limited effect on the Cu/Ag ratio of the mantle, compared to the bulk
411 planet.

412 Different domains of the Martian mantle are not homogenous and likely underwent
413 different extents of equilibration with the core, as indicated by ^{182}W isotopic heterogeneities
414 (e.g., Lee and Halliday, 1997). These heterogeneities preserve a memory of Hf-W
415 fractionations within the first 60 Ma since formation of the solar system, and indicate that the
416 early Martian mantle was not fully homogenized by convection and melting processes after
417 accretion and core formation were completed. We note that the Cu/Ag in different mantle
418 domains is similar (maximum difference by a factor of 2), reflecting the limited fractionation
419 of Cu and Ag during metal-silicate partitioning. Thus, as expected from data on partition

coefficients of Cu and Ag, incomplete core-mantle equilibration hardly affected Cu/Ag ratios in the Martian mantle.

Besides metal-silicate segregation, it was also proposed that segregation of iron sulfide melt into the core ("Hadean matte") may have occurred during the final stages of core formation of some planetary bodies. In case of Earth, this process is necessary to explain the depletion of some siderophile elements in the mantle and possibly the isotopic variations of some chalcophile elements such as Cu (e.g., Laurenz et al., 2016; O'Neill, 1991; Rubie et al., 2016; Savage et al., 2015; Wood et al., 2008). However, due to the high FeO content of the Martian mantle of 18 wt. % (Taylor, 2013), the sulfur content at sulfide saturation in Martian magmas may be too high to facilitate exsolution of sulfide melt at high temperatures. Experimental results at 5 GPa and 1600 °C indicated a required S content at saturation of about 3000 µg/g S in melts with 14 wt.% FeO (Ding et al., 2014) and the S content could be even higher for high FeO Martian magmas (e.g., Smythe et al., 2017). The Martian mantle likely has a low S content of 360±120 µg/g (Wang and Becker, 2017), far lower than the values of > 2000 µg/g at sulfide saturation for conditions of the Martian magma ocean at 14±3 GPa (Ding et al., 2014; Laurenz et al., 2016). Thus, considering the present state of knowledge, an immiscible sulfide melt appears to be an unlikely ingredient during Martian core formation and magma ocean evolution (Wang and Becker, 2017). Formation of the Martian core by metal-silicate or sulfide melt-silicate segregation should have strongly fractionated and depleted the HSE contents in the mantle (e.g., Laurenz et al., 2016; Mann et al., 2012). However, the HSE and Os isotopes in many Martian meteorites display chondritic or nearly chondritic ratios, thus, late accretion, very likely also occurred after core formation

on Mars (e.g., Brandon et al., 2012; Dale et al., 2012), although other workers proposed that the HSE contents in the Martian mantle can be explained by core formation (Righter et al., 2015). CI chondrite normalized Cu/Pd and Ag/Pd ratios are > 3, indicating that the dominant fraction of Cu and Ag in the Martian mantle was accreted during the main stages of accretion, rather than by late accretion (Figure 6). Sulfide melt-silicate segregation would not have affected the Cu/Ag ratios as variable S contents during metal-silicate or sulfide melt-silicate partitioning of Cu and Ag hardly affected their relative behavior (Figure 5).

4.3.3. Comparison of Cu/Ag ratios in Mars and chondrites

Because metal-silicate and sulfide melt-silicate melt fractionation cause relatively limited fractionation of Cu from Ag (within a factor of 3, Figure 5), we evaluate abundance variations of Cu and Ag in primitive solar system objects, as such materials may represent potential building materials of terrestrial planets. In Figure 4, we have compiled Cu and Ag data of different groups of chondrites, including our new data. The compilation includes data on samples for which both Cu and Ag contents are available (H, L, L/LL, LL chondrites: this work, Friedrich et al., 2004; Friedrich et al., 2003; CI, CM, CV, CO chondrites: Friedrich et al., 2002; Wang et al., 2015; and EH and EL chondrites: Kong et al., 1997; Wang and Lipschutz, 2005). The mean Cu/Ag ratios of most groups of chondrites (CI, CM, CV, CO, H, L, LL and EH) are similar (mean Cu/Ag = 1100±400, 1s, Wasson and Kallemeyn, 1988, Figure 4) and close to the solar ratio of about 600 (Lodders, 2003).

The ordinary chondrites analyzed in this study are mostly falls, which show negligible terrestrial contamination. The Cu/Ag ratios of these chondrites are within the range of literature data on ordinary chondrites (Figure 4). Overall, ordinary chondrites show a larger

464 scatter of Cu/Ag ratios (ranging from 200 to 4500) than other chondrite classes. The larger
465 range in Cu/Ag is mainly due to the large variation in Ag contents (e.g., Friedrich et al., 2004;
466 Schönbächler et al., 2008; Schaefer and Fegley, 2010). Terrestrial contamination likely is not
467 the main reason of the scatter of Ag concentrations as the data obtained in this study on falls
468 show a similar scatter as literature data. A possible reason for the scatter of Ag abundances
469 may be impact-induced shock heating, which appears to mobilize Ag at higher shock intensity
470 (Friedrich et al., 2004) and thus only the data of ordinary chondrites with shock stages S1-3
471 (Friedrich et al., 2004) are shown in Figure 4. Parent body metamorphism of ordinary
472 chondrites also may have an effect on Ag contents as indicated by our new data and the
473 compiled data (Figure 1 in Schaefer and Fegley, 2010). Previous studies on Ag isotopes and
474 volatility calculations have suggested the possibility of volatility-controlled loss or
475 redistribution of Ag during open-system parent body thermal metamorphism (Schönbächler et
476 al., 2008; Schaefer and Fegley, 2010). The specific reasons for the larger variations of Ag
477 contents in ordinary chondrites relative to carbonaceous and enstatite chondrites need further
478 detailed work. Nevertheless, most ordinary chondrites (mean Cu/Ag = 1600±1000, 1s, n=39,
479 median = 1400) have Cu/Ag in the range of carbonaceous and enstatite chondrites (mean
480 Cu/Ag = 1100±400, 1s, n=24, median = 1000, Figure 4).

481 The similar mean Cu/Ag in different groups of chondrites (mean Cu/Ag = 1100±400,
482 1s) indicates similar volatility of Cu and Ag in the different formation regions of these
483 chondrites in the solar nebula. The limited fractionation of Cu and Ag in chondrites is
484 consistent with the very similar condensation behavior of these elements in solar gas ($T_{50\%}$
485 near 1000 K at P = 10^{-4} atm, Lodders, 2003). Recently, Kiseeva and Wood (2015) proposed

that Ag may have a significantly lower 50% condensation temperature ($T_{50\%}$ near 700 K) compared to previous estimates, assuming that Ag should condense mainly into FeS, whereas Cu ($T_{50\%}$ near 1000 K) condenses into metal and FeS. Enstatite chondrites and carbonaceous chondrites contain different proportions of metal and sulfides. For instance, EH chondrites are enriched in metal and sulfides relative to most other chondrites and the proportions of metal to sulfides vary widely in carbonaceous chondrites. The similar Cu/Ag ratios in different groups of enstatite and carbonaceous chondrites are inconsistent with a different condensation behavior of Cu and Ag. The similarity of Cu/Ag ratios in the majority of chondrites may imply only a small range of Cu/Ag ratios in the building materials of terrestrial planets. The Cu/Ag ratio of the Martian mantle (1080±320, 1s) is indistinguishable from the majority of chondrites (except some ordinary chondrites) and only slightly higher than the ratio of about 600 in CI chondrites. This observation thus is consistent with models that Mars was built from materials with chondritic Cu/Ag ratios and with a limited change in Cu/Ag during Martian metal-silicate segregation (at most a factor of 2).

To conclude, Martian core formation has led to low Cu and Ag contents in the mantle, but likely with little change of Cu/Ag, which thus retained a value indistinguishable from most chondrites. This conclusion is consistent with available metal-sulfide-silicate partitioning experimental data (Figure 5). Consequently, the mean Cu/Ag of Martian meteorites reflects the ratio of the mantle and of bulk Mars. Given the less than a factor of 2 change in the relative siderophile and chalcophile behavior of Cu and Ag at different core formation and magmatic conditions, this conclusion should be robust and applicable to other planetary bodies, at least for those with a size equivalent to Mars or smaller.

4.4. Comparison between the mantles of Mars and Earth

The late stages of metal-silicate and sulfide-silicate segregation during the formation of Earth's core is now believed to have taken place at very high P-T conditions (presumably P > 40 GPa and T > 2300°C), which requires extrapolation of partition coefficients from available experimental conditions (e.g., Fischer et al., 2015; Mann et al., 2009; Rubie et al., 2015; Rubie et al., 2016; Siebert et al., 2011; Wade and Wood, 2005). Comparison of Cu/Ag ratios in the mantles of Mars and Earth might reveal the effects of low (< 2000°C and corresponding pressures near the liquidus curve of the mantle) vs. high P-T core formation on Cu and Ag concentrations and on Cu/Ag in planetary mantles. Mars and Earth likely accreted from different proportions of primitive material of variable composition as differences in their $\Delta^{17}O$ suggest (Franchi et al., 1999; Lodders and Fegley, 1997). These planets also underwent different accretion and core formation histories, because Mars is smaller than Earth and the Martian core likely formed much earlier than Earth (Kleine et al., 2004; Kleine et al., 2009; Lee and Halliday, 1997; Righter, 2011; Righter and Chabot, 2011; Righter et al., 1998; Rubie et al., 2011; Rubie et al., 2004; Wade and Wood, 2005; Yang et al., 2015). Here we will discuss how these differences affect the relative depletion of Cu and Ag and Cu/Ag ratios in the mantles of Mars and Earth.

The Cu contents in the mantles of both Mars and Earth are lower than in chondrites which show a predominant range of 80-200 µg/g Cu (Figure 4). The Cu and Ag contents in the Martian mantle are lower than in the Earth's mantle, by a factor of 15 for Cu and of 4-5 for Ag (Figure 6). The Martian mantle seems to have somewhat higher abundances of lithophile volatile elements (e.g., K, Rb) compared to Earth's mantle, as K/U and Rb/Sr data

530 show (Dreibus and Wänke, 1985; Halliday et al., 2001, Figure 6). Data on other lithophile to
531 weakly siderophile elements such as Zn (Wang et al., 2016 and references therein) support
532 this view (e.g., Lodders and Fegley, 1997). This difference is commonly interpreted to
533 indicate that bulk Mars is somewhat less depleted in volatile elements (compared to CI
534 chondrites) than the Earth (e.g., Dreibus and Wänke, 1985).

535 If we conservatively assume that Mars is at least similarly depleted in moderately
536 volatile elements as Earth, the larger depletion of Cu and Ag in the Martian mantle must be a
537 consequence of core formation. Both Ag and Cu become less siderophile with increasing P
538 and T and many core formation models have explained the depletion of Cu in the mantle of
539 Earth and Mars by metal segregation (Corgne et al., 2008; Righter, 2011; Righter and Drake,
540 2000; Vogel, 2015; Wood et al., 2014; Yang et al., 2015). The greater depletion of Cu and Ag
541 in the Martian mantle is consistent with the partitioning behavior of Cu and Ag at lower P-T
542 core formation conditions because Mars' mass is equivalent to only about 1/10 of the Earth's
543 mass. Figure 7 is a simple illustration of the changes of metal-metal oxide exchange
544 coefficients K_D(Cu-Fe) and Cu contents in the silicate mantle of an Earth-size body during
545 accretion. The curves in Figure 7 are based on the parameterization of K_D(Cu-Fe) with P-T
546 (Corgne et al., 2008) and a single-stage equilibrium core formation model with a mean Cu
547 content of 100 μg/g assumed for accreted materials. Given the limited variation of Cu
548 contents in different chondrites, a somewhat different Cu content would not change the result
549 significantly. Other factors such as light element abundances in the metal and the details of
550 accretion processes also affect K_D(Cu-Fe) and the Cu content in the mantle, thus Figure 7 is
551 schematic for the overall evolution of K_D(Cu-Fe) and Cu abundances as a function of the size

552 of the body (i.e., P-T), provided metal and silicates predominantly equilibrate during
553 accretion (Note the purpose is not to explain the specific Cu contents in the mantles of Mars
554 and Earth, but to show the trend of K_D (Cu-Fe) with increasing P-T). Because the function of
555 Corgne et al. (2008) is based on P-T conditions far lower than those believed to be relevant
556 for the formation of Earth's core, the extrapolation of K_D (Cu-Fe) to very high P-T conditions
557 may have a large uncertainty.

558 As shown for the case of Mars, core formation on small planetary bodies leads to a
559 strong depletion of Cu and Ag in the silicate fraction because of high K_D (Cu-Fe) at low P-T
560 conditions (Figure 7). For example, Cu in the Martian mantle is depleted by a factor of
561 50-100 relative to chondrites (Figure 4). During accretion of larger terrestrial planets such as
562 Earth (i.e., higher mean P-T of core formation), K_D (Cu-Fe) tends to decrease, thus leading to
563 a higher Cu content in the mantle (e.g., Corgne et al., 2008; Righter, 2011; Righter and Drake,
564 2000; Vogel, 2015; Yang et al., 2015). It follows that the contents of moderately siderophile
565 Cu and Ag in Earth's mantle mainly reflect the late stage history of accretion and core
566 formation when the proto-Earth already accreted most of its mass. The actual accretion
567 history of volatile elements is difficult to assess. The abundances of Cu and Ag are consistent
568 with suggestions that more volatile-rich material was accreted during the final high P-T stage
569 of Earth's main accretion phase (e.g., Rubie et al., 2011; Schönbächler et al., 2010; Wade and
570 Wood, 2005). However, accretion of volatile-rich material is also possible during the early
571 stages of Earth's accretion (e.g., Rubie et al., 2015).

572 During accretion, a fraction of metallic cores of differentiated bodies may not
573 equilibrate with the mantle and directly merge during collisions (Halliday, 2004; Jacobsen

574 and Harper, 1996; Rubie et al., 2011). Disequilibrium metal-silicate segregation would
575 preserve the effects of low P-T metal-silicate partitioning from smaller differentiated bodies.
576 The high Cu and Ag contents in the Earth's mantle indicate high extents of
577 metal-sulfide-silicate equilibration during late terrestrial core formation (e.g., Rudge et al.,
578 2010), otherwise, the Earth's mantle would contain much less Cu and Ag.

579 In comparison to the large differences in the depletion factor of Cu in the mantles of
580 Mars and Earth relative to CI chondrites (a factor of 50-100 and 3-6, respectively), the Cu/Ag
581 ratios in the mantles show only a small difference, e.g., 1080±320 in the Martian mantle
582 (similar to most chondrites) and 3500±1000 in the Earth's mantle (Figure 4). The factor of 3
583 higher Cu/Ag in Earth's mantle reflects either metal-sulfide-silicate equilibration during core
584 formation at very high P-T conditions or, a nonchondritic composition of Earth's building
585 materials, or volatility-controlled processes such as preferential volatilization of Ag during
586 giant impacts. Given the limited variations of Cu/Ag in different groups of chondrites (Figure
587 4) and the reported effects of impact-induced shock heating on Ag (Friedrich et al., 2004), the
588 non-chondritic Cu/Ag of Earth more likely reflects fractionation of Cu/Ag during high P-T
589 core formation and possible volatile element loss during giant impacts. Because Ag is slightly
590 more chalcophile than Cu during high P-T sulfide-silicate partitioning relative to
591 metal-silicate partitioning (K_{Cu}/K_{Ag} show about a factor of 3 variation with a mean of 1.2±
592 0.6, Figure 5b), late segregation of sulfide matte into Earth's core may have removed slightly
593 more Ag and led to the higher Cu/Ag in Earth's mantle. However, it should be noted that the
594 behavior of chalcophile elements in liquids and gases at extreme P-T conditions, as might be
595 relevant for the final stages of accretion of Earth, is still quite uncertain.

5. Conclusions

This study has presented Ag contents obtained by isotope dilution ICP-MS and Cu/Ag ratios in shergottites and nakhlites and new data on ordinary chondrites. The parent magmas of the Martian meteorites originated from different mantle sources and underwent different magmatic evolution, but display a limited variation in Cu/Ag ratios (1080±320, 1s, n=14). The new results and data from terrestrial mantle rocks and mantle-derived magmas indicate limited fractionation of Cu from Ag during high temperature magmatic evolution at variable physicochemical conditions as experimentally determined sulfide melt-silicate melt partitioning data predict, regardless whether sulfide saturation was reached or not. Thus, the relatively constant Cu/Ag value in the Martian meteorites likely is representative of the Martian mantle, and based on Cu/Ag, the Ag content of the Martian mantle is estimated at 1.9±0.7 ng/g (1s).

The low concentrations of Cu and Ag in the Martian mantle are in contrast to the relatively high abundances of lithophile volatile elements and indicate that Cu and Ag were controlled by core formation. The very different concentrations of Cu and Ag in the Martian and in Earth's mantle support the notion that the partitioning of some siderophile and chalcophile elements during planetary core formation scales with the size of the planetary body, which is particularly important for the differentiation of large terrestrial planets such as Earth. Experimental studies of metal-silicate segregation at low- and high P-T conditions indicate that core formation may lead to no or at most only a moderate (< factor 3) increase of Cu/Ag in mantle compositions, compared to bulk planet compositions. The Cu/Ag in the Martian mantle is indistinguishable from values in most chondrites, indicating no significant

618 fractionation of this ratio during core formation on Mars. The Cu/Ag ratio in the Martian
619 mantle thus reflects that of bulk Mars. The Cu/Ag of Earth's mantle is a factor of 2-3 higher
620 than in most chondrites and in the Martian mantle, which may reflect the effects of very high
621 P-T core formation and/or segregation of sulfide matte into Earth's core. Alternative
622 explanations include a slightly non-chondritic volatile element composition of Earth's
623 building materials (Wang et al., 2016), or volatility-controlled loss of Ag during accretion of
624 Earth. These explanations are considered less likely given the relatively high abundances of
625 Cu and Ag in Earth's mantle, which are consistent with results from high-P-T experimental
626 studies.
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637
638

Figure caption

Figure 1. Silver contents versus MgO and Cu contents in Martian meteorites. a) Ag contents in shergottites from the present study show a broadly negative correlation with MgO contents. b) Ag and Cu contents show a positive correlation for data of the present study. The Ag data of this study are similar to or lower than literature values (Table 2). The difference may reflect the large analytical uncertainty of the previously applied methods or sample heterogeneity. Literature data were obtained by INAA and RNAA (Biswas et al., 1980; Kong et al., 1999; Laul et al., 1986; Lodders, 1998; Smith et al., 1984; Treiman et al., 1986; Wang et al., 1998) or laser ablation-ICP-MS (Yang et al., 2015). The Cu data on samples from the present study are from Wang and Becker (2017). The bulk circle represents the value of the Martian mantle, and the Ag content is 1.9±0.7 ng/g (1s, see Section 4.3.1) and Cu of 2.0±0.4 μg/g (1s) (Taylor, 2013; Wang and Becker, 2017). Note that the Ag values on Figure 1a are cut off at the value of 40 and there are many higher values (see Figure 1b), and due to scale ALH84001 is not shown in Figure 1b.

Figure 2. Cu/Ag ratios versus MgO contents in different groups of Martian meteorites, terrestrial MORB, Hawaiian basalts and peridotites. In the basaltic (green triangle), olivine-phyric (yellow triangle) and lherzolitic (purple triangle) shergottites and nakhlites (red square), Cu/Ag ratios overall are similar and reflect the Martian mantle (blue band). Most terrestrial peridotites (3500±1200, 1s, n=38, for fresh peridotites with $Al_2O_3 \geqslant 2$ wt.%,

661 Wang and Becker, 2015) show Cu/Ag ratios similar to global MORB glasses (3600±400, 1s,
662 n=338, Jenner and O'Neill, 2012), MORB sulfide droplets (Cu/Ag = 3000±300, 1s, n= 7, gray
663 band, Patten et al., 2013). Due to Ag enrichment during terrestrial alteration, some peridotites
664 have lower Cu/Ag contents at given MgO contents (see details in Wang and Becker, 2015).
665 Mantle-derived magmatic rocks on Mars and Earth formed at different physicochemical
666 conditions, but the Cu/Ag ratios in these rocks are relatively constant on Mars and Earth,
667 respectively. Data sources for the mantle contents of MgO and Cu/Ag: the Earth's mantle
668 (Palme and O'Neill, 2014; Wang and Becker, 2015) and the Martian mantle (Taylor, 2013;
669 this study).
670
671 Figure 3. Cu/Ag versus CI chondrite normalized La/Yb ratio (a) and initial ε^{143}Nd (b). The
672 La/Yb data (Lodders, 2003; Meyer, 2013) and initial ε^{143}Nd (Debaille et al., 2009; Jones,
673 2015; Shih et al., 2014; Shih et al., 2005; Shih et al., 1999; Shirai and Ebihara, 2009;
674 references therein) are from the literature. The lithophile incompatible element tracers display
675 no systematic variation with Cu/Ag.
676
677 Figure 4. The Cu/Ag ratios in the mantles of Mars and Earth and in different groups of
678 chondrites. Mars shows a strong depletion of Cu (and Ag, not shown) in the mantle relative to
679 chondrites (a factor of 50-100). In contrast, the depletion of Cu is much smaller for the
680 Earth's mantle (a factor of 3-5). However, Cu/Ag ratios in the mantle of Mars and Earth do
681 not show such a large difference as the concentrations (only a factor of 3). Carbonaceous
682 chondrites and EH chondrites have similar Cu/Ag ratios and overlap with ordinary chondrites,

683 which show a larger scatter. Data on chondrites with both Cu and Ag data on the same sample
684 are indicated by small symbol sizes (H, L, LL: Friedrich et al., 2004; Friedrich et al., 2003;
685 this study; CI, CM, CV, CO: Friedrich et al., 2002; Wang et al., 2015; EH and EL: Kong et al.,
686 1997; Wang and Lipschutz, 2005). The mean Cu/Ag of different groups of chondrites (H, L,
687 LL, EH, EL, CI, CM, CO and CV indicated by larger symbols than those of the individual
688 samples) are calculated from the average Cu and Ag contents of the groups (Wasson and
689 Kallemeyn, 1988). See details in the text.
690
691 Figure 5. Compiled metal-metal oxide exchange coefficients (K_D relative to Fe) and partition
692 coefficients (D, based on mass fraction) of Cu and Ag in experimental metal-sulfide-silicate
693 systems. a-b, Cu and Ag are moderately siderophile and become less siderophile with
694 increasing P-T, but more siderophile with increasing S content in the metal (Vogel, 2015;
695 Wood et al., 2014). Copper and Ag display limited fractionation in metal-sulfide-silicate
696 systems (K_{DCu}/K_{DAg} with a mean of 1.2 ± 0.6, 1s, n=10, b). The relative partitioning behavior
697 of Cu and Ag appears to slightly change from sulfide-poor to sulfur-rich metals (b). c-d,
698 during sulfide melt-silicate melt partitioning, partition coefficients $D_{Cu}^{\text{sulfide/silicate melt}}$ and
699 $D_{Ag}^{\text{sulfide/silicate melt}}$ change dramatically as a function of changing compositions, e.g., FeO
700 content in silicate melts; whereas the relative partition coefficients of Cu and Ag change little
701 (Kiseeva and Wood, 2013; Kiseeva and Wood, 2015; Li and Audetat, 2012). Experimental
702 data of Kiseeva and Wood (2013, 2015) were obtained at 1.5 GPa and a range of temperatures
703 (1300-1700°C) and Cu- and Ni- contents of sulfides, whereas experiments of the study of Li
704 and Audetat (2012) were conducted at 1.5-3.0 GPa and 1175-1300°C.

Figure 6. CI chondrite and Mg normalized contents of representative lithophile (in gray) and siderophile (in color) elements in the mantles of Mars (circle) and Earth (triangle). Note that abundances of moderately volatile elements in bulk Mars are higher than in bulk Earth as is indicated by the abundances of lithophile volatile elements (a). Panel b highlights the HSE, Cu, Ag, S, Se and Te in panel a, emphasizing the effect of P-T on Cu and Ag during core formation. Data sources: CI chondrite (Lodders, 2003); Earth's mantle (Becker et al., 2006; Palme and O'Neill, 2014; Wang and Becker, 2013, 2015); Martian mantle (this study; Taylor, 2013; Wang and Becker, 2017; Yang et al., 2015).

Figure 7. Schematic illustration of the evolution of the exchange coefficient K_D (Cu-Fe) between iron metal and silicate melts and Cu content in the mantle of a planetary body with increasing pressure-temperature during accretion. The main purpose is to show the effect of increasing P-T (Corgne et al., 2008). The large value of K_D (Cu-Fe) indicates a very low Cu content in the silicate mantle after core formation at low P-T (e.g., at Mars-size or smaller). At high P-T conditions, Cu becomes less siderophile and thus leads to a higher Cu content in the mantle. Because the function used here (Corgne et al., 2008) is based on P-T conditions far lower than those of the likely formation of Earth's core, the extrapolation of K_D (Cu-Fe) to very high P-T conditions may have large uncertainty (dashed trends shown). Because of the similar behavior of Cu and Ag (Figure 5), this may also apply to Ag.

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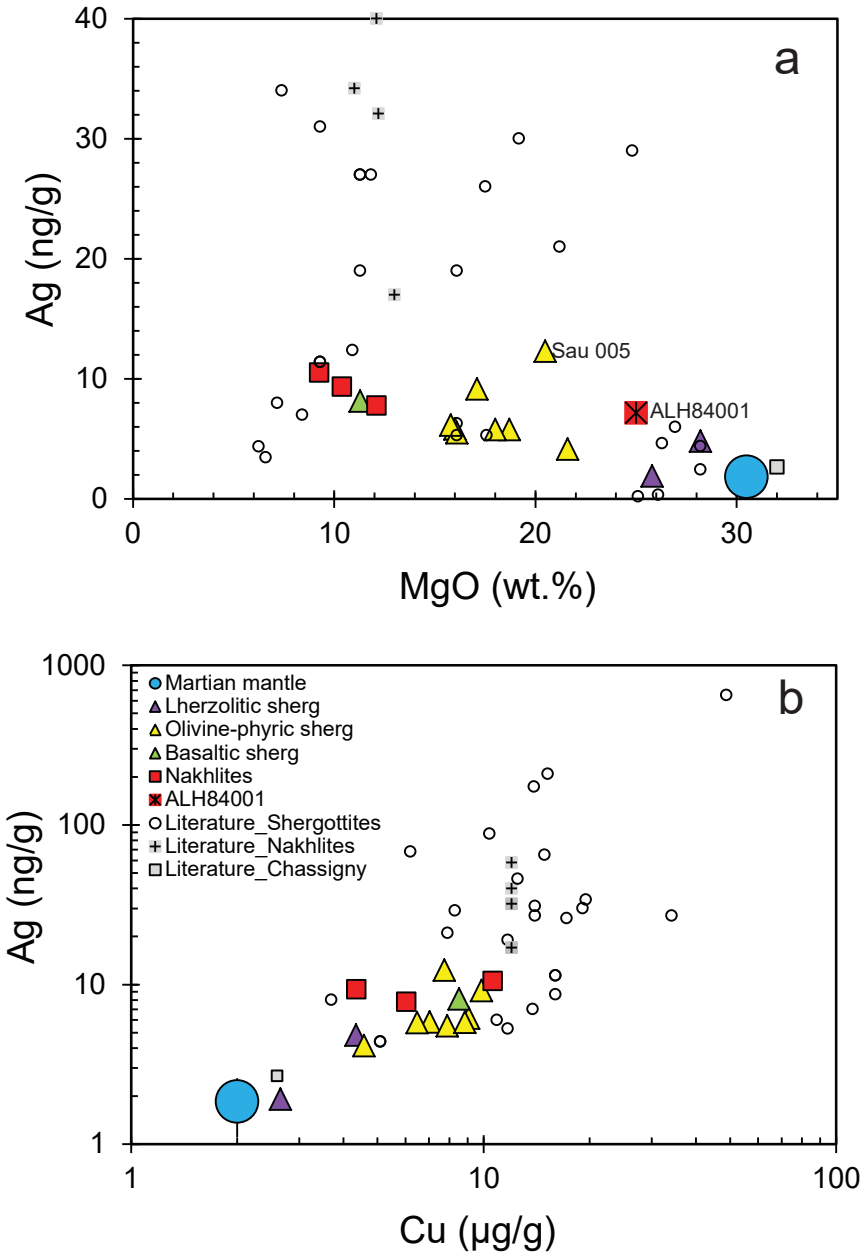
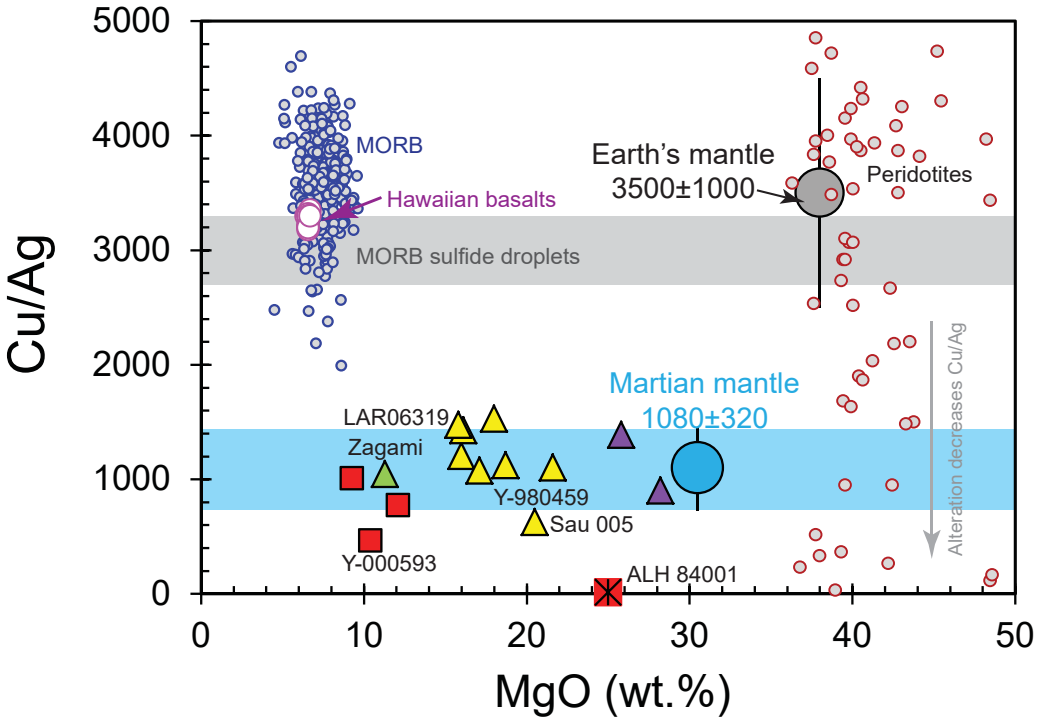
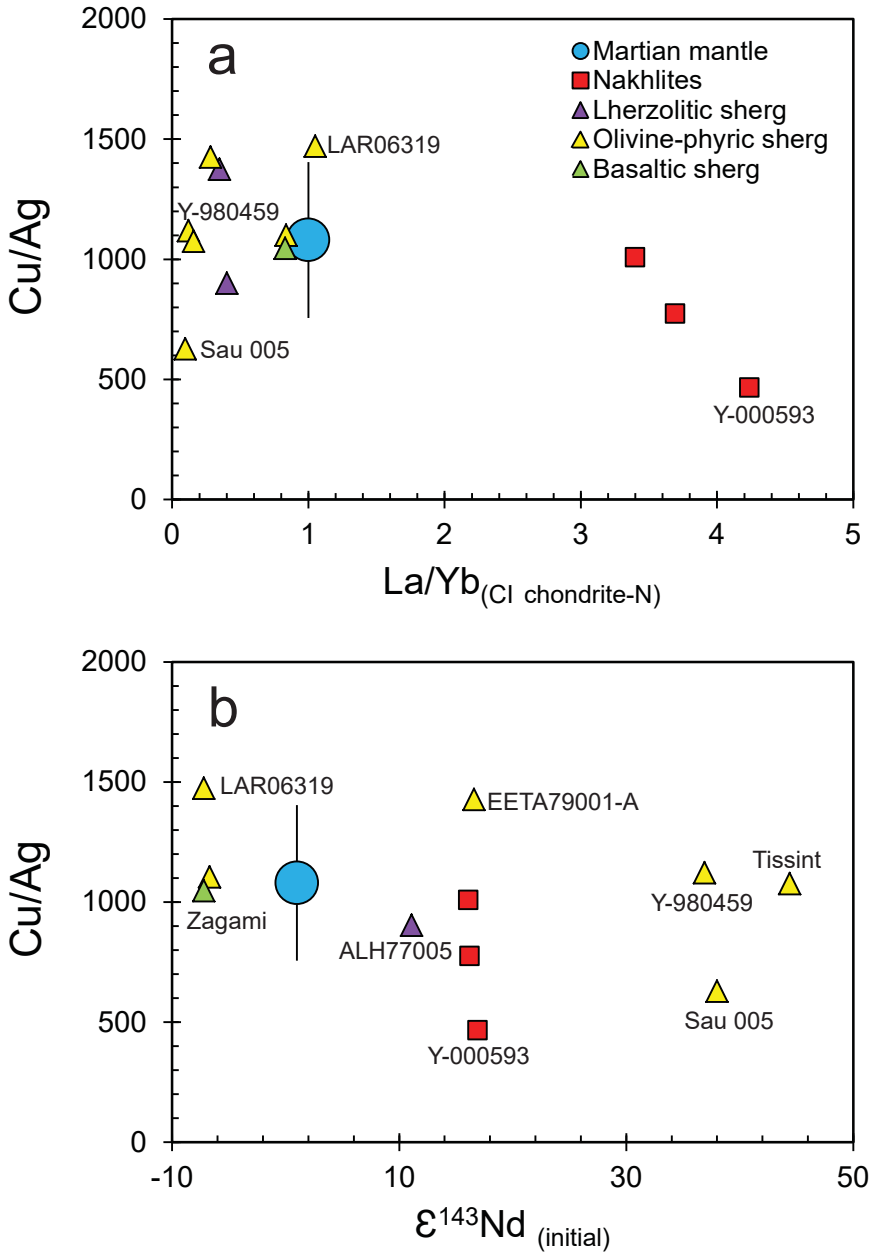
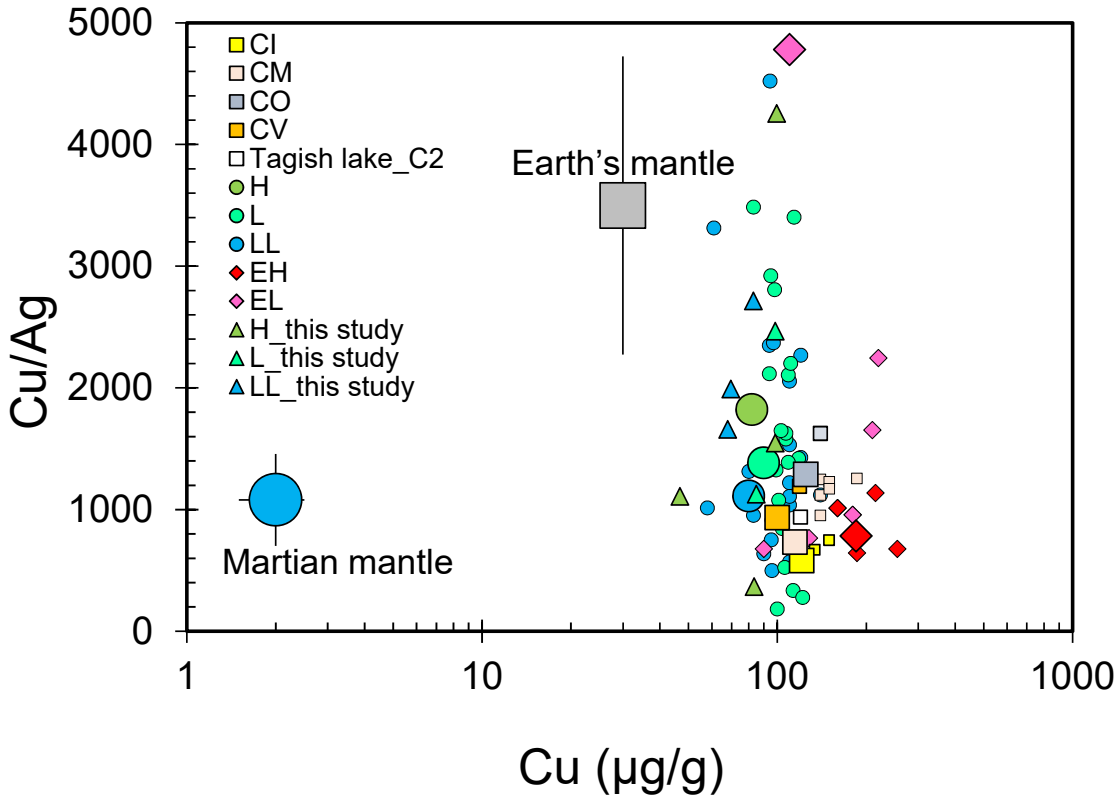
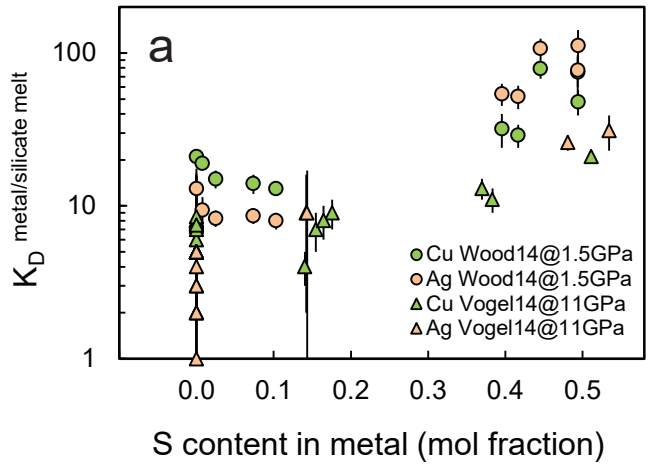
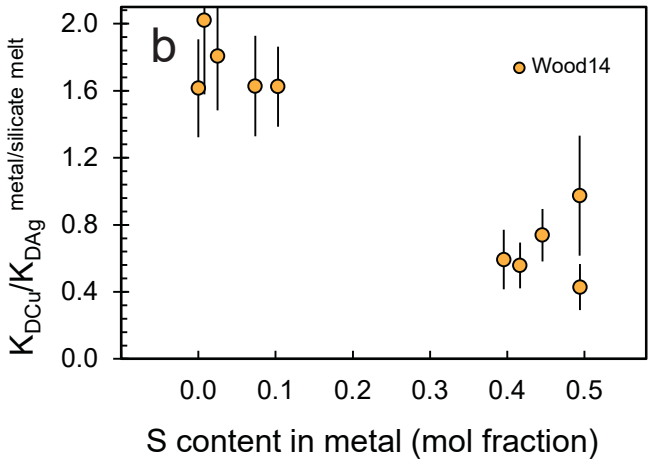

a
Ag (ng/g)
MgO (wt.%)
Sau 005
ALH84001
0
10
20
30
40
b
Martian mantle
Lherzolitic sherg
Olivine-phyric sherg
Basaltic sherg
Nakhlites
ALH84001
Literature_Shergottites
Literature_Nakhlites
Literature_Chassigny
Ag (ng/g)
Cu (µg/g)
1
10
100
1000

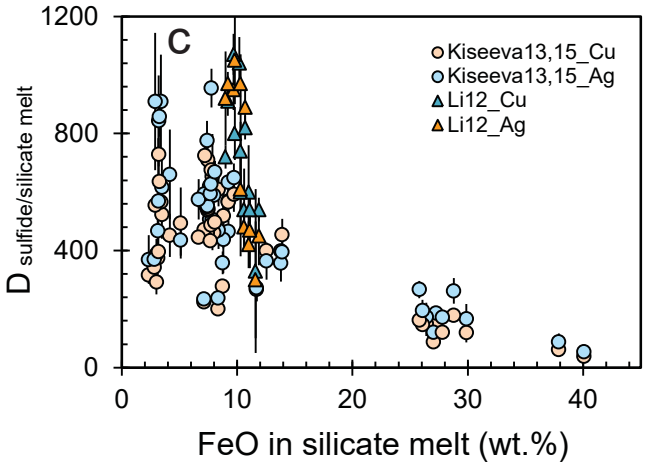

Cu/Ag
MgO (wt.%)
5000
4000
3000
2000
1000
0
0
10
20
30
40
50
MORB
Hawaiian basalts
MORB sulfide droplets
Earth's mantle
3500±1000
Peridotites
Martian mantle
1080±320
LAR06319
Zagami
Y-980459
Sau 005
Y-000593
ALH 84001
Alteration decreases Cu/Ag

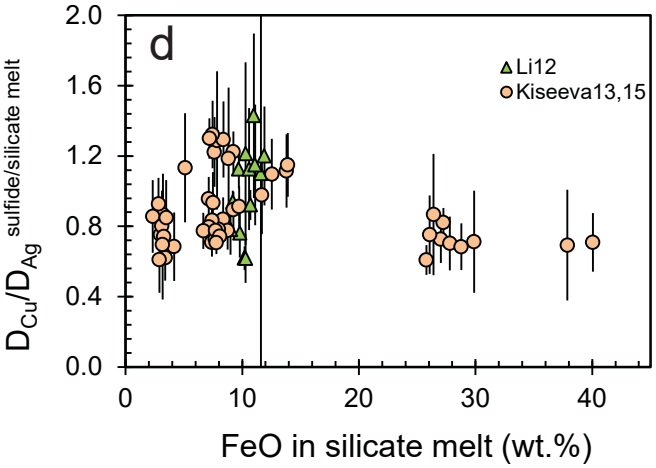

a
Martian mantle
Nakhlites
Lherzolitic sherg
Olivine-phyric sherg
Basaltic sherg
LAR06319
Y-980459
Sau 005
Y-000593
Cu/Ag
La/Yb(Cl chondrite-N)
2000
1500
1000
500
0
0
1
2
3
4
5
b
LAR06319
EETA79001-A
Tissint
Y-980459
Zagami
ALH77005
Sau 005
Y-000593
Cu/Ag
ε143Nd (initial)
2000
1500
1000
500
0
-10
10
30
50

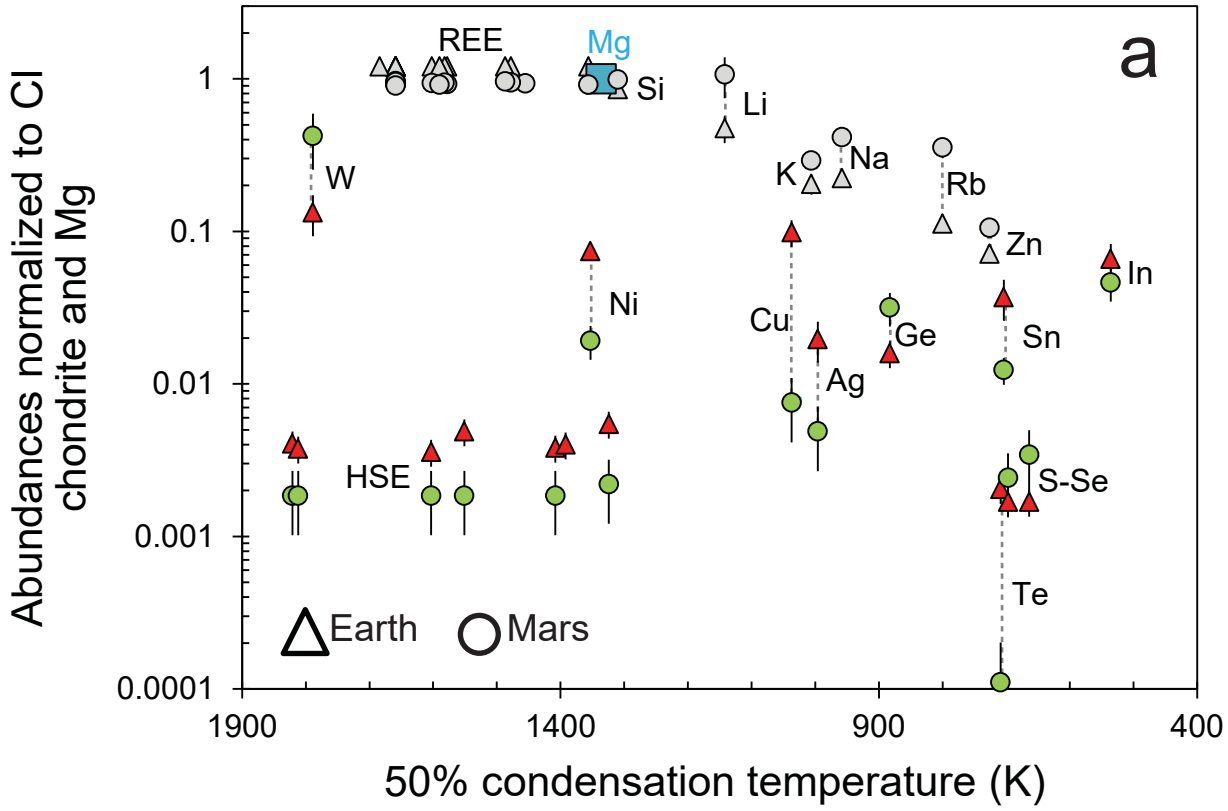

5000
4000
3000
2000
1000
0
Cu/Ag
1
10
100
1000
Cu (μg/g)
CI
CM
CO
CV
Tagish lake_C2
H
L
LL
EH
EL
H_this study
L_this study
LL_this study
Earth's mantle
Martian mantle

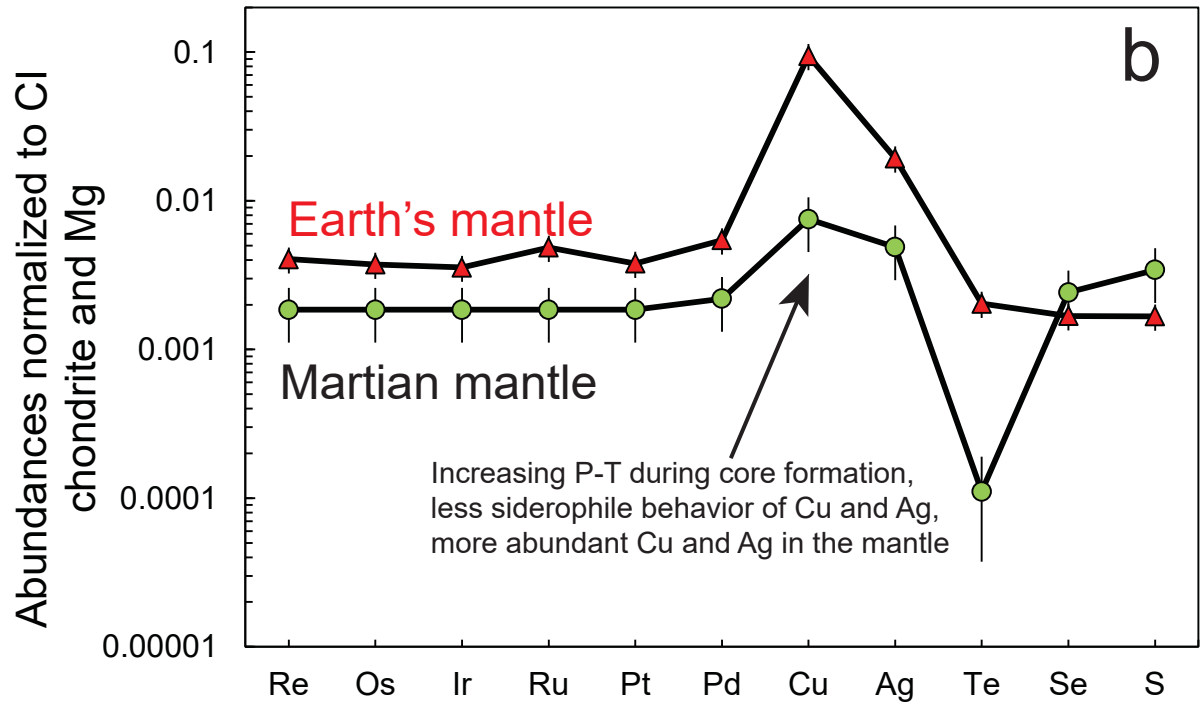

a
100
10
1
K_D metal/silicate melt
0.0
0.1
0.2
0.3
0.4
0.5
S content in metal (mol fraction)
Cu Wood14@1.5GPa
Ag Wood14@1.5GPa
Cu Vogel14@11GPa
Ag Vogel14@11GPa


b
2.0
1.6
1.2
0.8
0.4
0.0
K_{DCu}/K_{DAg} metal/silicate melt
0.0
0.1
0.2
0.3
0.4
0.5
S content in metal (mol fraction)
Wood14


c
1200
800
400
0
$D_{sulfide/silicate melt}$
0
10
20
30
40
FeO in silicate melt (wt.%)
Kiseeva13,15_Cu
Kiseeva13,15_Ag
Li12_Cu
Li12_Ag


d
2.0
1.6
1.2
0.8
0.4
0.0
D_{Cu}/D_{Ag} sulfide/silicate melt
0
10
20
30
40
FeO in silicate melt (wt.%)
Li12
Kiseeva13,15


a
Abundances normalized to CI chondrite and Mg
50% condensation temperature (K)
1900
1400
900
400
1
0.1
0.01
0.001
0.0001
REE
Mg
Si
Li
W
K
Na
Rb
Zn
In
Ni
Cu
Ge
Sn
Ag
HSE
S-Se
Te
Earth
Mars


b
Abundances normalized to CI chondrite and Mg
0.1
0.01
0.001
0.0001
0.00001
Earth's mantle
Martian mantle
Increasing P-T during core formation,
less siderophile behavior of Cu and Ag,
more abundant Cu and Ag in the mantle
Re
Os
Ir
Ru
Pt
Pd
Cu
Ag
Te
Se
S

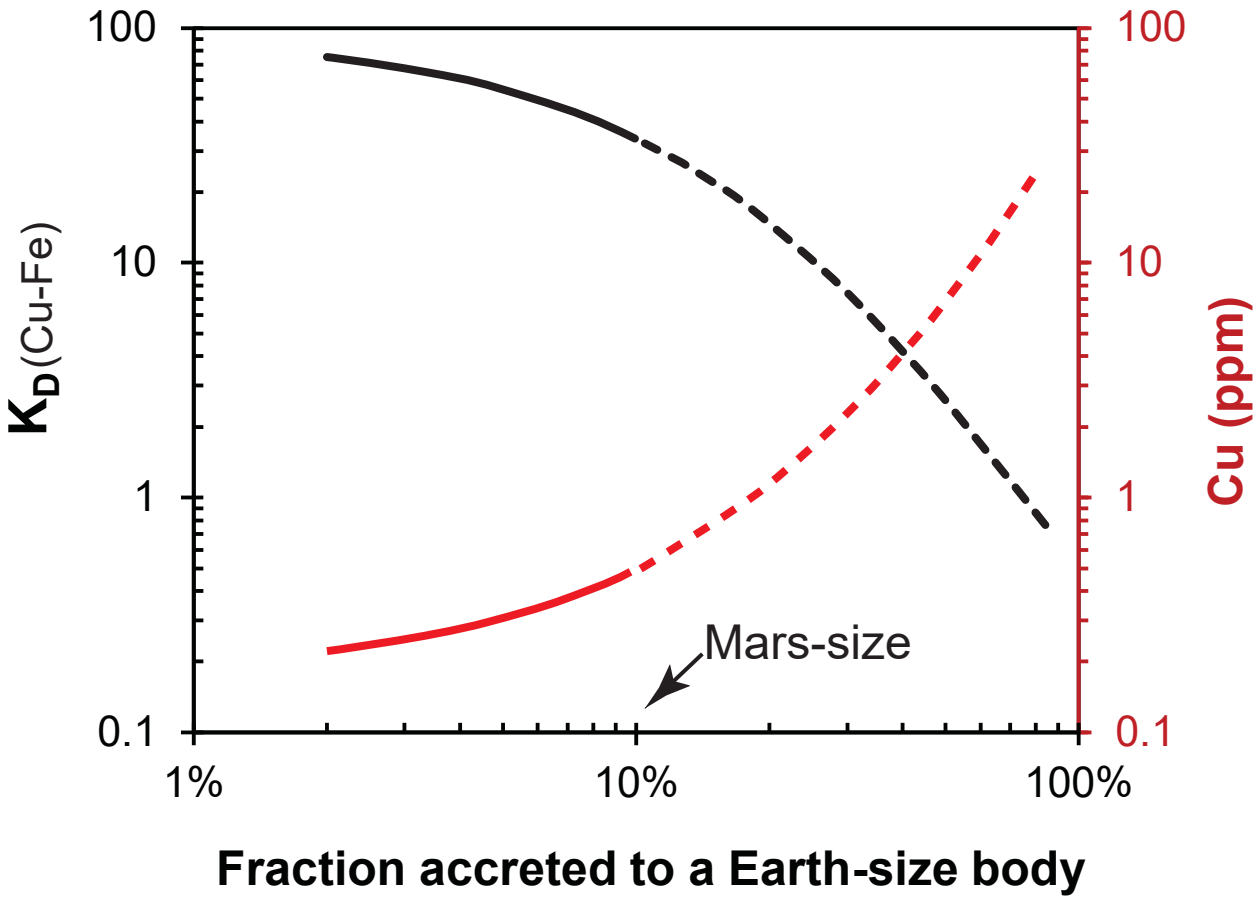

100
10
1
0.1
K_D(Cu-Fe)
100
10
1
0.1
Cu (ppm)
Mars-size
1%
10%
100%
Fraction accreted to a Earth-size body

Table 1. Silver and Cu contents in Martian meteorites and other compositional information.

Sample Name	Institution	Inventory number	Fall/Find	Classification	Chemical features	Mass (g)	MgO	SiO_2	Al_2O_3	FeO	CaO	$La/Yb_{(CI-N)}$	$\varepsilon^{143}Nd_{(initial)}$	Ag			Cu*		Cu/Ag	
							(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)			(ng/g)	±2s	Blank%	(µg/g)	±2s		±2s
ALHA77005	ANSMET	248, 82 (Specific, Parent)	Antarctica	Lherzolitic shergottite	Intermediate	0.1284	28.2	42.4	2.9	20.1	3.2	0.40	11.1	4.8	0.2	4%	4.35	0.09	903	35
Y-000097	AMRC	87	Antarctica	Lherzolitic shergottite		0.1386	25.8	45.6	2.2	19.9	4.2	0.35		1.9	0.1	8%	2.65	0.04	1386	103
Sau 005	SM	MPI 1522/3	Hot desert	Olivine-phyric shergottite	Depleted	0.0946	20.5	47.2	4.5	18.3	5.7	0.10	38.0	12.3	0.2	2%	7.74	0.09	628	14
Y-980459	AMRC	77	Antarctica	Olivine-phyric shergottite	Depleted	0.1378	18.7	49.9	5.2	17.3	6.8	0.12	36.9	5.8	0.2	3%	6.49	0.06	1122	31
Tissint	NHML	off BM.2012, M3	Fall	Olivine-phyric shergottite	Depleted	0.1471	17.1	46.2	4.9	21.2	6.5	0.16	44.4	9.2	0.2	2%	9.87	0.09	1077	21
EETA 79001-A	ANSMET	209, 22 (Specific, Parent)	Antarctica	Olivine-phyric shergottite	Intermediate	0.1873	16.1	49.9	5.9	18.4	7.3	0.28	16.6	5.5	0.1	2%	7.88	0.07	1428	33
LAR 06319	ANSMET	67, 3 (Specific, Parent)	Antarctica	Olivine-phyric shergottite	Enriched	0.1357	15.8	46.7	6.0	20.4	6.5	1.05	-7.2	6.2	0.2	3%	9.07	0.18	1474	48
LAR 12011	ANSMET	32, 11 (Specific, Parent)	Antarctica	Olivine-phyric shergottite	Enriched#	0.1253	18#							5.8	0.2	3%	8.84	0.18	1527	54
LAR 12095	ANSMET	35, 27 (Specific, Parent)	Antarctica	Olivine-phyric shergottite	Depleted#	0.1781	16#							5.8	0.1	2%	7.03	0.06	1204	28
RBT 04262	ANSMET	74, 57 (Specific, Parent)	Antarctica	Olivine-phyric shergottite	Enriched	0.1659	21.6	47.6	3.3	20.6	5.7	0.84	-6.7	4.1	0.1	3%	4.58	0.05	1104	35
Zagami	SM	MPI 632/8	Fall	Basaltic shergottite	Enriched	0.1535	11.3	50.5	6.1	18.1	10.5	0.83	-7.2	8.1	0.2	2%	8.53	0.08	1047	22
Y-000593	AMRC	131	Antarctica	Nakhlite(clinopyroxenite)		0.1835	10.4	47.6	1.9	19.7	14.3	4.24	16.9	9.3	0.1	1%	4.36	0.05	466	9
MIL 03346	ANSMET	74, 61 (Specific, Parent)	Antarctica	Nakhlite(clinopyroxenite)		0.1553	9.3	49.5	4.1	19.1	14.4	3.40	16.1	10.5	0.2	1%	10.63	0.09	1009	18
Nakhla	NHML	off BM.1913, 25	Fall	Nakhlite(clinopyroxenite)		0.1284	12.1	48.6	1.7	20.6	14.7	3.69	16.2	7.8	0.2	2%	6.03	0.12	775	23
ALH84001	ANSMET	321, 235 (Specific, Parent)	Antarctica	Orthopyroxenite		0.1217	25.0	52.8	1.3	17.5	1.8	0.46		7.2	0.2	3%	0.09	0.05	/	
Mean values																			1082	
1s																			316	
number																			n=14	

*Cu and Ag contents were obtained from the same sample aliquots. Cu data have been reported before (Wang and Becker, 2017). Blank% means the percentage of subtracted total procedual blank.

Y-980459 and LAR 06319 possibly are the most primtive sherogottites. Note their ratios are similar to the mean values.

#LAR 12011 is paired with LAR 06319 and LAR 12095 has a REE pattern similar to Sau 005 (Balta et al., 2015).

The La/Yb is CI chondrite normalized. The data source and major elements are from Herd et al (2013), Lodders (1998), Meyer (2013) and references therein. MgO with # symbol is assumed to similar in the pairs.

Initial $\varepsilon^{143}Nd$ are from the literature (Debaille et al., 2009; Jones, 2015 and references therein).

ANSMET: Antarctic Search for Meteorites Program, NASA Johnson Space Center Houston and Smithsonian Institution, Washington D.C., USA

NHML: Natrulal History Museum, London, UK

AMRC: Antarctic Meteorite Reserch Center, NIPR,Tokyo, Japan

SM: Senckenberg Museum, Frankfut am Main, Germany

Table 2. Comparison of Ag content data in the present study with literature values

Sample Name	Classification	This work			Literature			
		Ag (ng/g)	Cu (µg/g)	Cu/Ag	Ag (ng/g)	Cu (µg/g)	Cu/Ag	sources
ALHA77005	Lherzolitic shergottite	4.8	4.35	903	4.4	5.4	1227	a
					4.0			b
					3.89; 4.85	5.41; 5.52	1115	c
Y-000097	Lherzolitic shergottite	1.9	2.65	1386	29	8.3	286	g
Sau 005	Olivine-phyric shergottite	12.3	7.74	628	21	7.9	376	g
Y-980459	Olivine-phyric shergottite	5.8	6.49	1122	68	6.2	91	g
Tissint	Olivine-phyric shergottite	9.2	9.87	1077	46	12.5	272	g
EETA 79001-A	Olivine-phyric shergottite	5.5	7.88	1428	19			a
					5.3			b
					88	10.4	118	g
Zagami	Basaltic shergottite	8.1	8.53	1047	31			a
					12.4			b
					14.2			d
					37			e
					651	48.9	75	g
Nakhla	Nakhlite	7.8	6.03	775	40	5.03	126	e
					246			b
					1380			d
					32.1			f
ALH84001	Orthopyroxenite	7.2	0.09	-	<0.9			b
					0.22; 0.35			f
Shergotty	Basaltic shergottite				37; 110	54	1459	a
					203	11.9	59	e
					6.8; 10.5	26	2476	h
					16.9			d
					209	15.2	73	g

a: Smith et al. (1984); b: Kong et al. (1999); c: Biswas et al. (1980); d: Treiman et al. (1986); e: Laul et al. (1972); f: Wang et al. (1998); g: Yang et al. (2015); h: Laul et al. (1986)

Except data from Yang et al. (2015) by laser ablation ICP-MS, other Ag and Cu contents in literature were mainly determined by RNAA and INAA.

The Cu/Ag is calculated from literature data if both Ag and Cu data are available for the same sample aliquot.

Table 3. Silver and Cu contents in the analyzed ordinary chondrites.

Meteorites	WSG95300,68	Bremervorde	Ceniceros	Parnallee	Ochansk	Forest City	Mount Tazerzait	Saint Severin	Benguerir
Type	Find, H3.3	Fall, H/L3.9	Fall, L3.7	Fall, LL3.6	Fall, H4	Fall, H5	Fall, L5	Fall, LL6	Fall, LL6
Institution	ANSMET	USNM144	NHM London	NHM London	Com.	USNM 1649	Com.	USNM 6672	Com.
Mass (g)	0.0626	0.0570	0.0518	0.0463	0.0758	0.0555	0.0634	0.0553	0.0542
Cu (µg/g)	99.5	83.4	98.5	67.9	46.8	98.4	84.9	69.6	83.0
±2s	1.0	0.8	1.0	0.6	1.1	1.0	0.9	0.7	0.8
Ag (ng/g)	23.4	227	39.9	40.9	42.1	63.6	75.3	34.9	30.6
±2s	0.5	4	0.7	0.8	0.6	0.9	1.1	0.7	0.6
Cu/Ag	4257	368	2467	1660	1111	1548	1128	1992	2715
±2s	106	8	51	35	30	27	20	42	62

Com.: commercial source