An Experimental Study of Trace Element Partitioning into Troilite during Iron Meteorite Crystallization

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1 Abstract:

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Troilite is a common phase in iron meteorites, but there are limited data available for the 3 partitioning behavior of elements between troilite and solid metal. In this study, we present the 4 results of experiments with coexisting Fe-Ni solid metal, a S-rich metallic liquid, and troilite, and 5 report solid metal-troilite partition coefficients for 22 elements commonly studied in iron 6 meteorites. We find that elements with chalcophile behavior have an affinity for troilite and that 7 the majority of siderophile elements are incompatible in troilite. A notable exception to this 8 generalization is for the siderophile element Mo, which partitions roughly equally between solid 9 metal and troilite. We find that Ni and Co are largely concentrated in the solid metal, but given 10 their higher concentrations in iron meteorites, their partitioning behavior indicates that measurable 11 amounts of Ni and Co should be present in iron meteorite troilite when it forms. Our work 12 motivates the need for additional measurements of the trace element composition of iron meteorite 13 troilite and validates the assumption made in iron meteorite crystallization models that partitioning 14 into troilite can be neglected for the majority of siderophile elements, with the exception of Mo. 15

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INTRODUCTION:

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Iron meteorites provide unique information about the central cores of asteroids that crystallized 19 in the early solar system (e.g., Scott 1972; Goldstein et al., 2009). Modeling the chemical trends 20 for 18 different elements measured in all magmatic iron meteorite groups has shown that early 21 solar system cores contained a range of S contents, from being nearly S-free to potentially having 22 more than 15 wt% S (Zhang et al., 2024). Given that S is largely insoluble in solid Fe-Ni metal, a 23 metallic liquid in the Fe-Ni-S system would be expected to reach the cotectic composition as the 24 system cooled, at which point both solid Fe-Ni metal and troilite (FeS) would form (e.g., Hsieh et 25 al., 1982; Raghavan, 2004). Indeed, troilite nodules are a common component in iron meteorites 26 (e.g., Buchwald, 1971), as one would expect based on the phase relations for the solidification of 27 a S-bearing asteroidal core. 28

Despite troilite being a common and important phase for iron meteorites, there have been limited studies to examine how troilite formation has affected the elemental chemistry measured in iron meteorite samples. Recently, iron meteorite crystallization models that include the effects of melt trapped during the solidification of the core have also included a term to account for the

effect on troilite formation on the resulting elemental composition of the metallic phase (e.g., Ni 33 et al., 2020; Chabot and Zhang, 2022; Hilton et al., 2022; Zhang et al., 2022; 2024). However, 34 these models include the assumption that no elements partition into troilite during its formation. 35 This assumption is likely an appropriate one for many siderophile elements, which in systems 36 involving a solid Fe-Ni metal and a S-bearing metallic liquid strongly prefer the Fe-Ni metal, 37 sometimes by a factor of 1,000 or more (e.g. Chabot et al, 2017). Direct experimental 38 determinations of solid metal-troilite partitioning behavior are limited to one study (Jones et al., 39 1993). Jones et al. (1993) conducted experiments that determined the solid metal-troilite partition 40 coefficient (D) for six elements, finding that Pd was largely excluded from the troilite, consistent 41 with the assumption in the crystallization models. In contrast, Jones et al. (1993) also reported that 42 Pb and Tl highly favored partitioning into the troilite over the Fe-Ni solid metal, and that the troilite 43 also had measurable quantities of Ag, Mo, and Ni. Thus, the assumption that the formation of 44 troilite simply results in concentrating the elements into the solid metal phase is not necessarily a 45 valid assumption for all of the elements modeled in iron meteorites. However, without element-46 specific determinations about how each element partitions between solid metal and troilite, iron 47 meteorite crystallization models are not able to include the effect of elements partitioning into 48 troilite in their calculations. 49

With this motivation, we conducted a series of experiments at the Fe-Ni-S cotectic to determine the partitioning behavior of trace elements between coexisting Fe-Ni solid metal, troilite, and Srich liquid metal phases. We present the results of these experiments and discuss the implications for understanding the chemical signatures of iron meteorites and for modeling asteroidal core crystallization.

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EXPERIMENTS AND ANALYSIS:

In the Fe-Ni-S system, the cotectic liquid composition ranges from ~ 31 wt% S in the Ni-free 58 system to ~26 wt% S with ~20 wt% Ni (Hsieh et al., 1982; Raghavan, 2004). There is an 59 equilibrium field where the three phases of Fe-Ni solid metal, FeS troilite, and a S-bearing metallic 60 liquid can co-exist, with the temperature ranging from roughly 750–970°C. While the motivation 61 for our experiments is based on determining partitioning behavior between solid metal and troilite, 62 conducting experiments in the three-phase field that also contains liquid metal has many benefits. 63 First, achieving equilibrium compositions is faster at higher temperatures and in the presence of a 64 liquid. Second, extensive previous experimental studies (which are tabulated in Chabot et al. 65 (2017)) have examined solid metal-liquid metal partitioning behavior in the Fe-Ni-S system, 66 providing a valuable dataset for us to compare our new results to and to verify that partitioning 67 behavior is consistent with these previous studies. Third, the three-phase field allows us the 68 opportunity to explore a range of temperatures and resulting solid metal Ni-contents, and to 69 evaluate if such parameters have an effect on the solid metal-troilite portioning behaviors. The 70 previous study by Jones et al. (1993) that determined solid metal-troilite partitioning for 6 elements 71 also conducted experiments in this three-phase field in the Fe-Ni-S system. 72

To conduct the experiments, mixtures of powders of Fe, Ni, and FeS were prepared with bulk compositions that fell within the three-phase cotectic field given by the Fe-Ni-S phase diagram. The starting powders were doped with 21 trace elements at roughly ~100 ppm levels, using commercially purchased powders of: Co, Cu, Zn, Ga, Ge, As, Mo, Ru, Rh, Pd, Ag₂O, Sn, Sb, H₂WO₄, Re, Os, Ir, Pt, Au, PbO and Bi. Experiments were run from 800–925 °C in an evacuated silica tube in a 1 atm vertical tube furnace at the Johns Hopkins University Applied Physics Lab, following established procedures (e.g., Chabot et al., 2009; 2017). The work of Jones et al. (1993) demonstrated that equilibrium was achieved in their experiments conducted at 970°C for 3-day durations. To evaluate the obtainment of equilibrium in our experiments, we conducted a time series set of experiments at 850°C with durations that varied from 1–7 days, and all runs produced consistent results, as discussed in more detail in the next section. In total, nine runs that each contained three coexisting phases, with each phase being large and distinct, were produced.

Figure 1 shows a run product with coexisting Fe-Ni solid metal, solid troilite, and a phase that 85 was a S-bearing metallic liquid at the run conditions. Upon quenching of the experiment, the liquid 86 solidified to a mixture of Fe-Ni dendrites surrounded by FeS. Experiments were first characterized 87 and analyzed for major elements at the Johns Hopkins University Applied Physics Lab using a 88 Hitachi TM3000 SEM equipped with a Bruker Quantax 70 EDS (Chabot et al., 2017). Next, the 89 abundances of major elements, Fe, Ni and S, in each phase were analyzed by a JEOL 8530F+ 90 Hyperprobe at the Smithsonian Institution National Museum of Natural History using a beam size 91 of 50 µm. The solid phases of Fe-Ni metal and troilite were homogenous, and their major element 92 93 compositions were determined by averaging ≥ 10 points together, and using the standard deviation to calculate the uncertainty in the measurement. The quenched metallic liquid phase was not 94 homogeneous, composed of Fe-Ni dendrites and surrounding FeS, and hence ≥40 points were 95 averaged together to determine the bulk liquid composition. The error in the measurement of the 96 liquid metal composition was calculated using the standard error of the mean. Table 1 provides the 97 major element compositional results obtained for the nine different experiments. 98

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Figure 1. Back-scattered electron images of run #N8-3, held at 925°C for 6 days. (a) The run product consists of three equilibrium phases, with the Fe-Ni solid metal and solid troilite separated from the phase that was a S-bearing metallic liquid at the run conditions. (b) The three phases are shown in more detail, showing solid metal, solid troilite, and S-bearing metallic liquid that has quenched to a texture of Fe-Ni dendrites surrounded by FeS.

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Trace element abundances were measured by laser ablation inductively coupled plasma mass spectrometry (LA ICP-MS) at the University of Maryland, using the same approach as applied to the analysis of Fe-Ni-S system experimental run products in previous studies (e.g., Chabot et al., 2017). Analyses were conducted using a single-collector ICP-MS (Element 2, Thermo Finnigan)

coupled to a laser ablation system with an output wavelength at 213 nm (UP213, New Wave 111 Research). The laser was operated at ~3 Jcm⁻². Ablation sampling was done using a spot diameter 112 ranging from 55 to 100 µm and flash rate of 5 to 10 Hz, with 3 to 9 analyses acquired for each of 113 the solid metal, liquid metal, and troilite phases. Data were collected for the following masses: 114 ⁵⁷Fe, ⁵⁹Co, ⁶¹Ni, ⁶²Ni, ⁶³Cu, ⁶⁶Zn, ⁶⁷Zn, ⁶⁹Ga, ⁷¹Ga, ⁷²Ge, ⁷³Ge, ⁷⁵As, ⁹⁵Mo, ⁹⁷Mo, ¹⁰¹Ru, ¹⁰³Rh, 115 ¹⁰⁵Pd, ¹⁰⁷Ag, ¹⁰⁸Pd, ¹¹⁸Sn, ¹²¹Sb, ¹⁸⁴W, ¹⁸⁵Re, ¹⁸⁹Os, ¹⁹³Ir, ¹⁹⁵Pt, ¹⁹⁷Au, ²⁰⁸Pb and ²⁰⁹Bi. Analyses 116 were carried out in blocks of 9 to 19 runs. Two runs of each of two standard reference materials 117 bracketed the analyses: Coahuila (Walker et al., 2008) and either NIST 610 glass (Jochum and 118 Stoll, 2008) or Hoba (Walker et al., 2008), all with an 80 µm spot size. These standard reference 119 materials provided the basis for determining calibration curves to constrain instrument drift and 120 provide element concentrations. In general, element concentrations for Fe, Co, Ni, Cu, Ga, Ge, As, 121 Mo, Ag, Sn, Sb, Pb and Bi were standardized using the NIST 610 standard, and element 122 concentrations for Ru, Rh, Pd, W, Re, Os, Ir, Pt, and Au were standardized using the Coahuila iron 123 meteorite standard. For runs using Hoba as the standard instead of NIST 610, all elements were 124 standardized using Coahuila except for Mo, Sn and Sb, which were standardized according to the 125 Hoba standard. 126

Laser ablation inductively coupled plasma mass spectrometry data were processed using the 127 LAMTRACE (Van Achterberg et al., 2001) software program, which determines element 128 concentrations using ratios of count rates for samples and standards, known concentrations in the 129 standards, and the known concentration of an internal standard in the sample, in this case Ni or Fe 130 as determined by the Smithsonian JEOL 8530F+ Hyperprobe measurements. For elements 131 measured by two isotopes, the results were compared to confirm consistency in the measurements, 132 and in general, the measurement from the isotope with the lower detection limit was used. In 133 particular, ⁹⁵Mo and ¹⁰⁵Pd were used for all runs. In the case of Zn, ⁶⁶Zn was used for all runs 134 except for #N12-1 where only ⁶⁷Zn data were available. The measurement of ⁶⁹Ga was used for all 135 runs except for #S32-5, where troilite measurements for ⁷¹Ga were statistically significant but 136 those for ⁶⁹Ga were not, and for #N12-1, where ⁶⁹Ga was not measured for most troilite or liquid 137 metal analysis points but ⁷¹Ga measurements were obtained. For Ge measurements, ⁷²Ge was used 138 for all runs except #N12-1, where only ⁷³Ge data were available. Given the heterogeneity of the 139 quenched metallic liquid and the non-equilibrium nature of the resulting quenched dendrites and 140 interstitial phases, analyses of different liquid points would often have considerable variability 141 from point to point. Multiple analyses points were taken in the liquid phase to determine the bulk 142 composition of the liquid, though the resulting combined errors were still quite large in some cases. 143 Errors were calculated as the standard deviation of the multiple analyses made for each 144 compositional phase, and Table 1 provides the compositional results. 145

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RESULTS AND DISCUSSION:

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149 **Partitioning Behavior into Troilite**

Figure 2 shows the partitioning results for 22 elements from each of the nine experiments that resulted in partition coefficients, D, that were statistically significant within 2σ , using the data

tabulated on Table 1. The data in Fig. 2 are ordered by increasing partition coefficient in the solid 153 metal-liquid metal system. While the nine experiments were run at temperatures ranging from 800-154 925°C and produced Ni contents in the solid metal that varied from 15-53 wt%, all nine 155 experiments produced consistent and indistinguishable results, as shown in Fig. 2. Additionally, 156 these nine experiments include five which were run at 850°C with durations varying from 1-7 days 157 to evaluate the achievement of equilibrium. From this consistency, we conclude that the runs 158 produced highly repeatable compositional results and that any effects from the range of 159 temperatures or Ni contents produced in the phases are not significant in influencing the 160 partitioning behavior in this system. 161

Consequently, we decided to utilize all of our experimental data to calculate partition 162 coefficients for the system. Table 2 provides the partition coefficients values determined as the 163 average of the D values in each run weighted by the standard deviation of each determination, with 164 the error determined as the standard error of the mean. Some partition coefficients were not 165 determined within 2σ statistical significance in any individual runs alone, but by utilizing the data 166 from all nine experiments, we were able to place limits on the partition coefficients for these 167 elements. In particular, this approach was applied to: Re and Ir for the solid metal-liquid metal 168 partition coefficients; Sb, Re, Os, Ir, Pt, Pb, and Bi for the troilite-solid metal partition coefficients; 169 and Ga, As, Sb, Re, Os, Pt, Pb, and Bi for the troilite-liquid metal partition coefficients. In these 170 cases, we first identified runs for which it was possible to detect the elements in the pertinent 171 phases and for which there was more than one measurement per phase, so that a standard deviation 172 could be obtained for the abundances in those phases. If these criteria were met, we listed these 173 abundances and errors in Table 1, even if the errors were large and the 2σ values exceeded the 174 abundance value measured. Using these values, the weighted average of the D values and the 175 standard error of the mean was calculated, as was done for the statistically significant D values 176 determined from individual runs. For elements with very large D(solid metal-liquid metal) and 177 D(solid metal-troilite) values, the standard error itself was not statistically significant because the 178 measured abundances from run to run in the troilite and liquid metal were almost always close to 179 180 the detection limit, which caused wide variability in the resulting partitioning values. In these cases, the lower bound was chosen to be the lowest measured D value out of all runs for that 181 element. For Pb and Bi, elements which had low abundances in the solid metal and troilite phases, 182 we used the standard error for both the lower and upper bounds, since the lowest calculated 183 coefficient was already much less than 1. Table 2 summarizes our best calculated values or limits 184 for the partition coefficients in this system, and these weighted average partition coefficients are 185 also plotted on Fig. 2. 186

Examining the partitioning results on Fig. 2, there are some expected trends. The elements plotted on the leftmost side of Fig. 2, Bi, Pb, Ag, Cu, and Zn, exhibit chalcophile behavior in the solid metal-liquid metal system, partitioning more strongly into the liquid metal as the S content of the liquid metal increases (Chabot et al., 2017). In the solid metal-troilite system (Fig. 2b), these same elements display an affinity for troilite, with D(solid metal-troilite) values that are less than or close to one. This affinity for troilite is consistent with their chalcophile nature.

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Figure 2. Partition coefficients determined from our Fe-Ni-S system experiments, plotted in order of increasing D values in the solid metal-liquid metal system. (a) Solid metal-liquid metal partition coefficients, (b) solid metal-troilite partition coefficients, (c) troilite-liquid metal partition coefficients. All partition coefficients are shown with 2σ error bars. Results from single experiments are shown in grey symbols, and the weighted average partitioning values determined from utilizing all nine experiments and listed in Table 2 are plotted as black circles.

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The elements plotted on the rightmost side of Fig. 2 are the highly siderophile elements of Rh, Ru, Pt, Os, Re, and Ir. In the Fe-Ni-S solid metal-liquid metal system, these elements exhibit a very strong affinity for partitioning into the solid metal rather than the S-bearing metallic liquid, and as the S content of the metallic liquid increases, so do their D(solid metal-liquid metal) values (Chabot et al., 2017). For the S-rich liquid present in our experiments, their solid metal-liquid metal partition coefficients range from ~80 to over ~3,000, as shown in Fig. 2a. As one would expect, these same highly siderophile elements display a strong affinity for solid metal rather than troilite, as shown in Fig. 2b where they have even higher partition coefficients, with values ranging from ~1,000 to 30,000. Likewise, As, Ge, Ga, and W exhibit siderophile behavior in the solid metal-liquid metal system (Fig. 2a) and show similar siderophile behavior in the solid metal-troilite system (Fig. 2b), strongly preferring the solid metal phase to the troilite phase.

The elements plotted in the middle of Fig. 2, spanning Sb through Au, exhibit the biggest 215 differences in their partitioning behaviors when comparing the solid metal-liquid metal (Fig. 2a) 216 and solid metal-troilite (Fig. 2b) values. The elements of Sb, Sn, Pd, and Au have substantially 217 higher partition coefficients in the solid metal-troilite system, ranging between 450 to 1,200, than 218 in the solid metal-liquid metal system, where the D values range between 2 to 8. These elements 219 demonstrate that even though they have moderately siderophile behavior in the system with a S-220 rich liquid and solid metal, they exhibit highly incompatible behavior for partitioning into troilite 221 in the solid metal-troilite system. 222

In contrast, among the siderophile elements, Mo exhibits unusual behavior since it has a D(solid 223 metal-troilite) value of about one (Fig. 2b). Thus, Mo would be more enriched in troilite compared 224 to other siderophile elements, and consequently, Mo could serve as a chemical signature in iron 225 meteorites where the metallic phases crystallized along with the crystallization of troilite. The solid 226 metal-troilite partition coefficients for Ni and Co are also notable among the siderophile elements, 227 having values of 24 and 10 respectively. While these partition coefficients still mean that 228 substantially more Ni and Co will partition into solid metal than into troilite, given the higher 229 concentrations of Ni and Co in iron meteorites than the other siderophile elements on Fig. 2, our 230 results indicate that measurable amounts of Ni and Co should partition into iron meteorite troilite 231 when it forms. 232

Interestingly, all of the 22 elements that were examined have D(troilite-liquid metal) values that are less than or equal to one, within error, as shown on Fig. 2c. Our experimental results show that there are no elements that strongly prefer troilite, but as the liquid metal crystallizes to solid metal and troilite, the option to remain in the liquid metal is removed. Thus, the final step in crystallization could result in distinct chemical signatures, in particular concentrating chalcophile elements into the last troilite to form.

Overall, our results show that the assumption made in recent iron meteorite crystallization 239 models (e.g., Ni et al., 2020; Chabot and Zhang, 2022; Hilton et al., 2022; Zhang et al., 2022; 240 2024) that elements do not partition into troilite in any significant manner is a very appropriate 241 assumption for many of the 22 elements we studied. The elements for which that assumption is 242 not valid are elements with chalcophile behavior in the Fe-Ni-S system, which are Bi, Pb, Ag, Cu, 243 and Zn in our experiments. While we do not have data for other chalcophile elements, such as Cr, 244 we expect that this conclusion would be applicable to other chalcophile elements as well. The 245 result that chalcophile elements partition into troilite is not surprising. The more noteworthy result 246 is that the assumption that the siderophile element Mo does not partition into troilite is shown to 247 not be valid with our results. This means that crystallization models that include the effects of the 248 formation of troilite should consider the solid metal-troilite partitioning value for Mo when 249 modeling this element rather than neglecting its partitioning into troilite. For Co and Ni, which 250 both prefer the solid metal by a factor of ten or more, including their partitioning into troilite in 251

the crystallization models will be a minor effect on the resulting metal composition, but would be worthwhile to predict the troilite compositions that would be produced.

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Comparison to Previous Experimental Studies

Our new experimental results can be compared to the few previously published determinations of D(solid metal-troilite) by Jones et al. (1993). Jones et al. (1993) determined solid metal-troilite partition coefficients for Ni, Mo, Pd, Ag and Pb, which we can compare to our new determinations, and also for Tl, which was not contained in our experiments. Figure 3 makes this comparison and shows that our new results are consistent with the previously determined values, within the large uncertainties given in the Jones et al. (1993) study. These limited data were a driving motivation for our current study, and our new results are consistent with these previously determined D values.



Figure 3. Solid metal-troilite partitioning results determined by Jones et al. (1993) are compared to our new experimentally determined values, showing strong consistency between our new results and the limited previously available determinations. Errors are for our experimentally determined values are 2σ ; Jones et al. (1993) provided a 1σ error for Ag, a range of values for Pb, and a lower limit for Pd.

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272 Many previous solid metal-liquid metal partitioning studies have been conducted in the Fe-Ni-S system, and these previous studies are tabulated in Chabot et al. (2017). Using these extensive 273 experimental results, Chabot et al. (2017) developed parameterization expressions to 274 mathematically calculate the resulting D(solid metal-liquid metal) value as a function of the S 275 content of the metallic liquid for 25 different elements. To compare our new determinations of 276 D(solid metal-liquid metal) given in Table 2 to previously determined values, we used the 277 parameterization of Chabot et al. (2017) to calculate the expected D(solid metal-liquid metal) value 278 for each element. The parameterization uses the S content of the experiment as an input parameter, 279 and the S content of our nine runs varied slightly, as seen in Table 1. To account for this, we used 280

the highest and the lowest S contents and their errors for the metallic liquid across all runs in Table 1 that contributed to the determination of the weighted average D values in Table 2 for each element. We then calculated the D value obtained from the parameterization at both of these S contents for each element. Table 3 gives the results of these parametrization calculations, and Fig. 4 plots the parameterization calculation results as a function of our measured weighted-average value of D(solid metal-liquid metal) given in Table 2.

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Figure 4. Solid metal-liquid metal partition coefficients (D) calculated from the parameterization of Chabot et al. (2017) are plotted as a function of the weighted average values determined from our experiments. The comparison shows strong agreement between the values calculated from the parameterization and those measured in the experiments, with the exception of Bi. The new parameterization we derive for Bi from this work is also shown, labeled as "Bi, reparameterized" on the graph.

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As seen in Fig. 4, our new experimental D(solid metal-liquid metal) values show good agreement with the values predicted from the parametrization of Chabot et al. (2017), providing further support for equilibrium behavior in the runs. A notable exception to the agreement seen on Fig. 4 is for Bi, where our measured value for the solid metal-liquid metal partition coefficient for Bi is roughly 1,000 times larger than calculated from the parameterization of Chabot et al. (2017). However, the Chabot et al. (2017) parameterization of Bi was based on only four experimental data points (Chabot et al., 2009; Chabot et al., 2017), all of which had S contents in the metallic
 liquid <20 wt%. As given in Table 1, we determined D(solid metal-liquid metal) for Bi at metallic
 liquid S contents of ~30 wt%, and these new determinations expand the range of S contents for
 which the solid metal-liquid metal partition coefficient for Bi has been determined.

Consequently, we used our new determinations of D(solid metal-liquid metal) for Bi and the previous determinations to derive a new parameterization for Bi, as shown in Fig. 5. We used the partition coefficient determined for Bi in the S-free Fe-Ni system, *Do*, of 0.012 ± 0.003 (Chabot et al., 2017). We then derived a best-fit line that went through that *Do* value and utilized the previously published and our new determinations of D(solid metal-liquid metal) for Bi. Our resulting revised parameterization, using the same form derived in Chabot et al. (2017), is:

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$$\ln(D(Bi)) = \ln(0.012) + 3.3 \ln(Fe \text{ Domains})$$
 Eq. 1

where *Fe Domains* is derived in Chabot et al. (2017) from the Fe-Ni-S system, with X_S being the molar fraction of S in the metallic liquid, and expressed as:

Eq. 2

Fe Domains = $(1 - 2X_S)/(1 - X_S)$

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Figure 5. Experimental determinations of D(solid metal-liquid metal) for Bi are plotted as a function of the calculated value for *Fe Domains* (Eq. 2) for each experimental data point. The new experimental results of this study, shown as triangle symbols, extend the data for Bi to higher liquid metal S contents, and hence a lower fraction of *Fe Domains*, than previous studies, providing the opportunity to revise the parameterization fit used for Bi.

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In the previous parameterization of Chabot et al. (2017), the value determined for Bi for β_S , the coefficient in Equation 1 that precedes the *Fe Domains* term, was 7.5 ±4.0 (2 σ). Our revised

parameterization shown in Fig. 4 yields a β_s value of 3.3 ±1.6 (2 σ) for Bi. However, the data 330 plotted in Fig. 5 display considerable scatter from the best-fit line, which could be an indication 331 that the parameterization of Chabot et al. (2017) based on Fe Domains is not well suited for 332 parameterizing elements with chalcophile behavior, as was suggested by Chabot et al. (2017) when 333 introducing the model. Nevertheless, we consider this revised solid metal-liquid metal 334 parameterization for Bi to be preferred over the previously published one since it better matches 335 the D values measured in our experiments with S-rich liquids, rather than suggesting partitioning 336 values that are 1,000 times too low. 337

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Comparison to Iron Meteorite Measurements

Measurements of the trace element composition of troilite in iron meteorites are limited, but in 342 Fig. 6 we show our experimental results compared to data reported in Hermann et al. (1971), Chen 343 and Wasserburg (1987; 1990), and Lunning et al. (2019), which are also tabulated in Table S1 of 344 the Supporting Information. As shown in Fig. 6, some of the iron meteorite measurements exhibit 345 orders of magnitude of scatter between measurements made on different meteorites but for the 346 same element, in particular from the early study of Hermann et al. (1971). This wide amount of 347 scatter within a single element could be due to chemical processes that occurred on iron meteorite 348 parent bodies after the initial formation of troilite that altered the troilite compositions so that they 349 no longer retain their original formation composition. Alternatively, the early measurements of 350 Hermann et al. (1971) might have lacked the sensitivity and precision to accurately determine low 351 concentrations of siderophile elements in iron meteorite troilite phases. The iron meteorite 352 measurements from Chen and Wasserburg (1987; 1990) for Pb, Pd, and Ag also show a wide range 353 354 of values for a given element, which supports post-formation modification of the chemical compositions of these phases in the iron meteorites. In contrast, the more recent study of Lunning 355 et al. (2019) shows good general agreement between our experimentally determined D(solid metal-356 troilite) values and iron meteorite measurements of neighboring solid metal and troilite for Cu, Co, 357 and Ni, as shown on Fig. 6. In particular, the measurable abundances of Ni and Co in the troilite 358 are consistent with our prediction and earlier discussion based on the partitioning behavior seen in 359 our experiments and the fact that Ni and Co are present in iron meteorites at higher concentrations 360 than other siderophile elements. 361

However, in general, high precision measurements of the trace element composition of troilite 362 in iron meteorites are lacking, especially for consistent measurements made for many elements at 363 the same time. The limited iron meteorite data available as shown in Fig. 6 highlights the need for 364 additional measurements of trace elemental abundances in troilite in iron meteorites. With 365 additional iron meteorite troilite measurements, agreement of D(solid metal-troilite) between iron 366 meteorites and our experimental results could be used to identify meteorites that are late-stage 367 products of fractional crystallization, formed near the Fe-Ni-S cotectic composition, or it could be 368 used to distinguish troilite that formed by trapped melt during crystallization. Alternatively, 369 disagreement between our experimental results and measurements made of solid metal and troilite 370 in iron meteorites could provide evidence that the troilite and/or metallic compositions have been 371 modified following their initial formation as crystallization products. Our experimental work 372

provides strong motivation to measure the trace element compositions of iron meteorites with troilite to gain insight into the late-stage crystallization and evolution of asteroidal cores.

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Figure 6. Solid metal-troilite partition coefficients determined in our work are plotted with 2-380 σ error bars and compared to measurements of iron meteorites between neighboring metal and 381 troilite phases. Meteorite data are from: Hermann et al. (1971), Chen and Wasserburg (1987; 382 1990), and Lunning et al. (2019). Error bars reported in Lunning et al. (2019) are $1-\sigma$. For those 383 items noted with a superscript 1 in the legend, in these studies the elemental abundances were 384 reported as a range of values, so the D(solid metal-troilite) values plotted from these studies are 385 also shown in the figure as range, with the marker denoting the middle of the range and the error 386 bars extending to the minimum and maximum points. 387

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389390 SUMMARY

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In summary, we have produced new experimental results that determined the partitioning behaviors of many elements in the Fe-Ni-S system with three coexisting phases of Fe-Ni solid metal, a S-rich liquid metal, and troilite. Our new experimental partitioning results are consistent with previous determinations of solid metal-liquid metal partitioning behavior, though our Bi results expand the previously covered range of liquid metal S contents and hence we develop a revised parameterization of D(Bi), as given in Eq. 1. Our new solid metal-troilite experimental results for 22 elements greatly expand the available dataset, from the determination for 6 elements previously by Jones et al. (1993). Key partitioning behavior results obtained from our experiments are:

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- Elements with chalcophile behavior in the Fe-Ni-S system, such as Bi, Pb, Ag, Cu, and Zn, have an affinity for partitioning into troilite.
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- The majority of elements with siderophile behavior in the Fe-Ni-S system are highly incompatible in troilite.
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• An exception is the element Mo, which has siderophile behavior in the solid metal-liquid metal system but also partitions into troilite as readily as it partitions into solid metal.

The siderophile elements of Co and Ni exhibit a factor of 10-20 times less affinity for troilite than for solid metal. However, given their higher concentrations in iron meteorites than other siderophile elements, this should result in measurable amounts of these elements in iron meteorite troilite, if the chemical composition of the troilite's formation is preserved.

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Overall, one of the driving motivations for this study was to evaluate the assumption being made 413 in iron meteorite crystallization models that consider trapped melt that the elements being modeled 414 can be considered to essentially have no partitioning into the troilite that forms. We find that this 415 assumption is valid for the large majority of siderophile elements modeled in iron meteorite studies 416 but that this assumption does not hold for chalcophile elements or for Mo. The elements of Co and 417 Ni are largely concentrated in the solid metal, but given their higher concentrations in iron 418 meteorites, their partitioning behavior indicates that measurable amounts of Ni and Co should be 419 present in iron meteorite troilite when it forms, and future crystallization models could include this 420 effect to make predictions for the troilite's composition. In this study, we have now provided the 421 needed solid metal-troilite partition coefficients so that iron meteorite crystallization models can 422 include these effects. 423

From conducting this study, it also brought to our attention the lack of trace element composition data for troilite in iron meteorites. Thus, we also find that making detailed compositional measurements of troilite in iron meteorite would be a valuable dataset, which could be compared to our experimental results and used to evaluate the conditions of the troilite formation and its chemical evolution subsequently in asteroidal cores.

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 <u>https://lib.jhuapl.edu/</u>. The experimental run products produced in this work are available in the
 Meteorite Lab at Johns Hopkins Applied Physics Lab.

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 493 494
 495 SUPPORTING INFORMATION
 496
 497 Table S1. Table S1 tabulates the previously published iron meteorite data that are plotted on
- 498 Fig. 6.