The parameterization of solid metal-liquid metal partitioning of siderophile elements

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Abstract–Many solar system processes involve a metallic liquid, and the composition of the metallic liquid, such as the liquid's concentrations of S, P, and C, will influence the partitioning of elements during such processes. We present a method for parameterizing solid metal-liquid metal partition coefficients for siderophile (metal-loving) elements as a function of the metallic liquid composition. Our parameterization method is based on an older theory of Jones and Malvin (1990), which stated that the metallic liquid is composed of metal and non-metal-bearing domains, and the domains are the dominant influence on the partitioning behavior. By revising the means by which the metal domains are calculated, our revised parameterization method is able to match experimental partitioning data from the Fe-Ni-S, Fe-Ni-P, Fe-Ni-S-P, and Fe-Ni-C systems. Mathematical expressions were derived for the solid metal-liquid metal partitioning of 13 siderophile elements. Elements that are chalcophile (S-loving), P-loving, or C-loving prefer the non-metal-bearing domains in the metallic liquid and, consequently, aren't fit by the parameterization method presented here. Possible applications for our parameterization method include modeling the crystallization of iron meteorites, planetary differentiation, and the solidification of Earth's inner core.

INTRODUCTION

Understanding the effects of metallic composition on partitioning behavior is important for understanding any process that involves a metallic liquid. Planetary examples of such processes include the crystallization of magmatic iron meteorites in asteroidal cores (e.g., Jones and Drake 1983; Haack and Scott 1993; Scott et al. 1996; Chabot and Drake 1999; Wasson 1999; Wasson and Richardson 2001), the separation of a metallic core from a silicate mantle during core formation (e.g., Righter et al. 1997; Righter and Drake 1999; Li and Agee 2001), and the crystallization of Earth's solid inner core from its liquid outer core (e.g., Brandon et al. 1999, 2003; Walker 2000). The composition of a metallic liquid can significantly affect the partitioning behaviors of elements. For example, some experimental solid metal-liquid metal partition coefficients (D), such as D(Ir), have been shown to increase by 3 orders of magnitude with increasing S content of the metallic liquid (Jones and Drake 1983). Along with S, the presence of other non-metals, such as P and C, has also been demonstrated to affect trace element partitioning behavior (e.g., Willis and Goldstein 1982). Thus, having a mathematical expression that parameterizes the partition coefficient as a function of the composition of the

metal is useful when applying the partitioning data to any physical processes.

Jones and Malvin (1990) developed a parameterization method that is based on the assumption that siderophile elements are excluded from non-metal-bearing domains in the metallic liquid. The Jones and Malvin (1990) method has had success at parameterizing element partitioning in the Fe-Ni-S, Fe-Ni-P, Fe-Ni-S-P, and Fe-Ni-C systems (Jones and Malvin 1990; Jones 1995; Lauer and Jones 1999). However, in multi-light element systems, the Jones and Malvin (1990) mathematical expression can become long and unwieldy. We have re-examined the theory of trace element partitioning in solid metal-liquid metal systems, and we present a revised parameterization method here. Our revised method builds on the model of Jones and Malvin (1990) but better handles partitioning in multi-light element systems. Preliminary results of this work were reported by Chabot and Jones (2003).

PREVIOUS PARAMETERIZATION

Jones and Malvin (1990) demonstrated that the partitioning between solid and liquid metal is dominantly influenced by the metallic liquid composition not the

temperature or properties of the solid metal. In the parameterization of Jones and Malvin (1990), the metallic liquid is modeled as being composed of non-metal-bearing "domains" and non-metal-free "domains." In the model, the term "domains" is used to conceptually represent the different compositional influences present in the metallic liquid and does not imply a rigorous chemical definition. The calculation of the domains in the parameterization depends on the exact speciation of the non-metal in the metallic liquid.

The large majority of experimental solid metal-liquid metal partitioning data is from the Fe-Ni-S system. The solid metal-liquid metal partition coefficient (D) for an element is defined as the concentration of that element in the solid metal divided by the concentration of that same element in the liquid metal. In the Fe-Ni-S system, by the Jones and Malvin (1990) method, D is expressed as:

$$\frac{1}{D} = \frac{(1 - 2\alpha_S X_S)^{(-\beta_S)}}{D_o} \tag{1}$$

where X_S is the mole fraction of S in the metallic liquid, D_o is D in the end member non-metal-free Fe-Ni system, α_S is a constant of 1.09 that is specific to partitioning in S-bearing systems, and β_S (the sign of which is negative for siderophile elements) is a constant specific to the element being parameterized. In the Jones and Malvin (1990) method, the values of D_o and β_S are determined by a linear fit to the experimental data. The factor of 2 comes from assuming that FeS is the predominant speciation of S in the metallic liquid (Sharma and Chang 1979). The metallic liquid is, thus, envisioned as being composed of FeS domains and S-free domains.

By the Jones and Malvin (1990) method, parameterization of partitioning in the Fe-Ni-P system is functionally similar to Equation 1:

$$\frac{1}{D} = \frac{(1 - 4\alpha_P X_P)^{(-\beta_P)}}{D_o} \tag{2}$$

with X_P as the mole fraction of P in the metallic liquid, α_P as a constant of 1.36 that is specific to partitioning in P-bearing systems, and β_P as a constant determined by the element being parameterized. The factor of 4 in Equation 2, as compared to the factor of 2 in Equation 1, arises from the different assumed speciation of P in the metallic liquid. Jones and Malvin (1990) used a speciation of Fe_3P, as compared to FeS, to parameterize partitioning in the Fe-Ni-P system. The metallic liquid in the Fe-Ni-P system is, thus, modeled as being composed of Fe_3P domains and P-free domains.

The factors of α_S and α_P were obtained by trial and error fitting in the Jones and Malvin (1990) work. Jones and Malvin (1990) noted that near the eutectic composition in the Fe-Ni-S and Fe-Ni-P systems, trace element partition coefficients often changed quickly with increasing non-metal content of the metallic liquid. To match the observed partitioning behavior, the factors of α_S and α_P were needed. The values of α_S and α_P were determined by Jones and Malvin (1990) to produce the best fits to the experimental data. Jones and Malvin (1990) noted that their best-fit values of 1.09 for α_S and 1.36 for α_P were close to the values needed to make the quantities of $2\alpha_S X_S$ and $4\alpha_P X_P$ unity at the eutectics of the Fe-S and Fe-P systems respectively, perhaps relating to the liquid activities of FeS and Fe_3P at their respective eutectics.

By the Jones and Malvin (1990) method, D_o in Equation 1 and Equation 2 should be the same: the partition coefficient in the non-metal-free Fe-Ni system. In contrast, β_S and β_P are different between the Fe-Ni-S and Fe-Ni-P systems, denoting different effects on the partitioning behavior from the presence of S or P in the metallic liquid. In the more complicated Fe-Ni-S-P system, the effects from both S and P need to be taken into account. Jones and Malvin (1990) developed the following expression for partitioning in the Fe-Ni-S-P system:

$$\frac{1}{D} = \frac{(1 - 2\alpha_S X_S - 4\alpha_P X_P)^{(-\beta_{SP})}}{D_o} \tag{3}$$

with

$$\beta_{SP} = \left[\frac{2X_S}{(2X_S + 4X_P)}\right]\beta_S + \left[\frac{4X_P}{(2X_S + 4X_P)}\right]\beta_P$$

As shown in Equation 3, with the Jones and Malvin (1990) method, partitioning behavior in the multi-light element system of Fe-Ni-S-P is expressed as a weighted average of the effects in the end member Fe-Ni-S and Fe-Ni-P systems. Therefore, to understand the partitioning behavior in the Fe-Ni-S-P system, one must first determine β_S and β_P in the Fe-Ni-S and Fe-Ni-P systems, respectively.

The original Jones and Malvin (1990) work did not specifically address partitioning in the Fe-Ni-C system. Jones (1995) and Lauer and Jones (1999) adapted the Jones and Malvin (1990) formulation to the Fe-Ni-C system with the following equation:

$$\frac{1}{D} = \frac{(1 - 4X_C)^{(-\beta_C)}}{D_o} \tag{4}$$

Similar to Equations 1 and 2, the variable X_C is the mole fraction of C in the metallic liquid, and β_C is a constant specific to the element being parameterized. The factor of 4 arises from assuming Fe_3C as the speciation of C in the metallic liquid. The lack of a factor of α_C in Equation 4 is due to the limited partitioning data available for the Fe-Ni-C system. With limited experimental data, the parameterization formula for partitioning in the Fe-Ni-C system is not as well refined or determined as in the Fe-Ni-S or Fe-Ni-P systems. By the Jones and Malvin (1990) method, the parameterization of partitioning in the Fe-Ni-S-C or Fe-Ni-P-

C systems would resemble Equation 3: a linear combination of partitioning in the end member systems. The expression would be correspondingly more complicated for the Fe-Ni-S-P-C system. In the Fe-Ni-S-P-C system, knowledge of the partitioning behavior in the Fe-Ni-S, Fe-Ni-P, and Fe-Ni-C systems would be required, and the resulting partitioning behavior would be expressed as a weighted average of the behavior from all 3 systems.

REVISED PARAMETERIZATION

Our new method is a revision of the theory presented in Jones and Malvin (1990). The composition of the metallic liquid is taken to be the dominant influence on the solid metal-liquid metal partitioning behavior, and the metallic liquid is envisioned to be composed of domains. For a siderophile, metal-loving element, the element being partitioned strongly prefers the light element-free "Fe domains" in the metallic liquid. Thus, we express the partition coefficient as a function of the concentration of these available "Fe domains:"

$$\frac{1}{D} = \frac{(\text{Fe domains})^{\beta}}{D_o} \qquad (5)$$

The form of Equation 5 is very similar to the Jones and Malvin (1990) method shown in Equations 1–4. The constant D_o is still D in the end member non-metal-free Fe-Ni system, and β is a constant specific to the element being parameterized, which is now positive in sign. The revision to the parameterization method comes in the calculation of the "Fe domains." We use the variable "Fe domains" to refer to the fraction of domains in the metallic liquid that are non-metal-free. In the Fe-Ni-S system, the Fe domains are calculated as:

$$\text{Fe domains} = \frac{(1 - 2X_S)}{(1 - X_S)} \qquad (6)$$

This calculation is based on using FeS as the speciation of S in the metallic liquid, which is the same as Jones and Malvin (1990). In the calculation, every S is paired with a free Fe, and the metallic liquid can be envisioned as being composed of Fe domains and FeS domains. Figure 1a shows experimental solid metal-liquid metal partitioning data for Ir in the Fe-Ni-S system (references given in the Appendix). As the S content of the metallic liquid increases, the siderophile element Ir partitions less into the liquid metal and 1/D(Ir) decreases by over 3 orders of magnitude. Figure 1b plots the calculated fraction of Fe domains in the metallic liquid against the S content of the metallic liquid. Similarly, as the S content of the metallic liquid increases, the fraction of non-metal-free Fe domains decreases. The trends in both Figs. 1a and 1b show a similar functional form, with change occurring more rapidly as the S content of the metallic liquid increases. The similar functional form suggests that the partition coefficient is a function of the Fe domains.
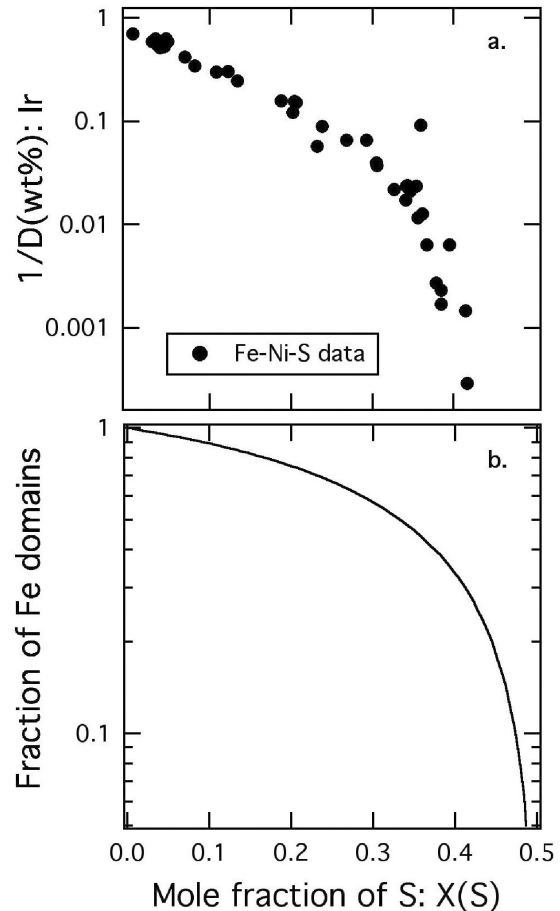

Fig. 1. a) As the S content of the metallic liquid increases, the siderophile (metal-loving) element Ir partitions less into the liquid metal and 1/D(Ir) decreases; b) similarly, as the S content of the metallic liquid increases, the fraction of Fe domains in the metallic liquid, as calculated by Equation 6, decreases. The data in (a) and the curve in (b) exhibit a similar functional form, suggesting that the choice of the calculated Fe domains to parameterize the siderophile experimental partition coefficients is a good one. References for the experimental data are given in the Appendix.

The theory of this parameterization method is based on the availability of Fe domains. To first order, therefore, S affects the partitioning behavior in a passive way by reducing the concentration of available Fe domains. Thus, the identity of the light element is not really important; but, understanding how the non-metal affects the availability of Fe domains is important.

The presence of any light element in the metallic liquid will decrease the fraction of Fe domains. However, to calculate the specific effect of a non-metal on the concentration of available Fe domains, one must know the speciation of the light element in the metallic liquid. Based on a thermodynamic evaluation of the Fe-S system, FeS is predicted to be the most abundant S species in the metallic liquid (Sharma and Chang 1979). To the best of our knowledge, such speciation calculations have not

been performed for the Fe-P and Fe-C systems, so we must rely on the stoichiometry of phosphide and carbide phases in these systems. In the Fe-P system, both Fe_2P and Fe_3P may coexist with a P-bearing metallic liquid. For the Fe-C system, graphite can coexist with a metallic liquid, and Fe_3C is not stable until sub-solidus conditions. The choices for the speciation of P and C in the metallic liquid were, thus, based on trial and error fitting of the parameterization to the available P- and C-bearing experimental data. For P and C, the use of Fe_2P and Fe_2C, respectively, as the species in the metallic liquid produced the best fits to the limited data. The C-bearing data are especially limited, as listed in the Appendix.

With the speciation assumed, the Fe domains in the Fe-Ni-S-P-C system can be calculated as:

$$Fe\ domains = \frac{(1 - 2X_S - 3X_P - 3X_C)}{(1 - X_S - 2X_P - 2X_C)} \tag{7}$$

The calculated Fe domains are used in Equation 5 to parameterize the partition coefficient. Combining Equation 5 and Equation 7, partitioning in the Fe-Ni-S-P-C system can be expressed as:

$$\frac{1}{D} = \frac{\left[\frac{(1 - 2X_S - 3X_P - 3X_C)}{(1 - X_S - 2X_P - 2X_C)}\right]^{\beta}}{D_o} \tag{8}$$

In contrast to the Jones and Malvin (1990) method, we find that only one β for each partitioning element is sufficient to fit the data well. Therefore, using our revised method, β is independent of the identity of the light alloying element. Having only one β simplifies the dealing of element partitioning in multi-light element systems. Also, the factors of α_S and α_P used by Jones and Malvin (1990) are no longer necessary in our revised method to fit the experimental partitioning data. Figure 2 compares the parameterization method of Jones and Malvin (1990) to our revised expression for Ir partitioning in the Fe-Ni-S and Fe-Ni-P systems. As shown in Fig. 2a, the parameterization of Jones and Malvin (1990) is able to fit the partitioning data in both the Fe-Ni-S and Fe-Ni-P systems but requires separate fits for each light element. Our revised parameterization method, shown in Fig. 2b, is able to fit the Ir data from the Fe-Ni-S and Fe-Ni-P systems with one expression: Equation 8.

Additionally, a subtle difference between our revised method and the work of Jones and Malvin (1990) is the form of the partition coefficient, D, used in the parameterization. Jones and Malvin (1990) used the molar partition coefficient, which is defined as the mole fraction of an element in the solid metal divided by the mole fraction of that same element in the liquid metal. However, for consistency, we have chosen to use what we will refer to as the "speciation partition coefficient." The theory of the parameterization method is that the metallic liquid is composed of domains. Consequently, for partitioning, we feel it appropriate not to use the mole fraction
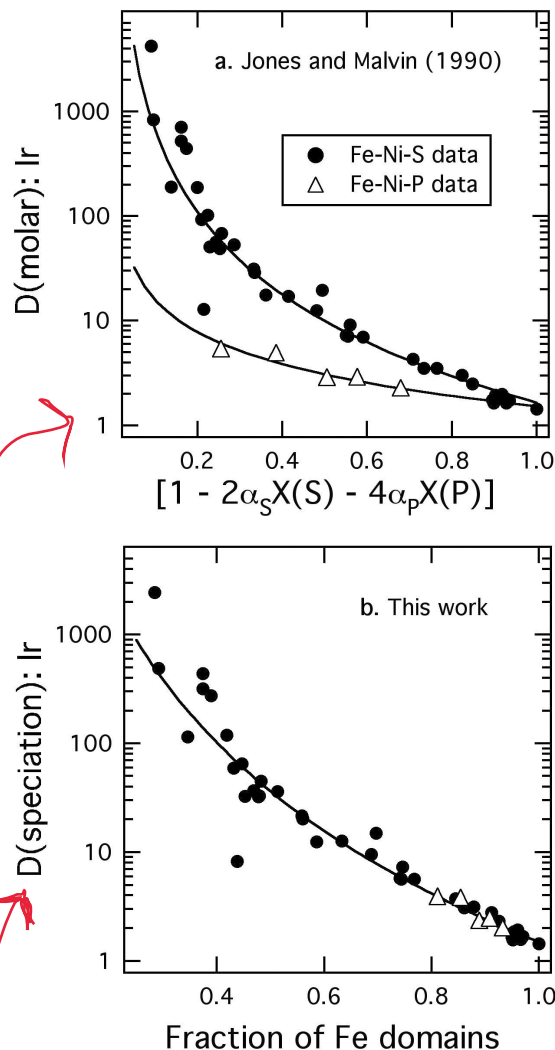

Fig. 2. Experimental partitioning data for Ir are shown for the Fe-Ni-S and Fe-Ni-P systems: a) when plotted against the parameterization terms of Jones and Malvin (1990), 2 separate fits are required to match the Ir data, one for the S-bearing and another for the P-bearing system; b) in contrast, when plotted as a function of the Fe domains, D(Ir) from both the Fe-Ni-S and Fe-Ni-P systems can be satisfactorily matched by a single fit. References for the experimental data are given in the Appendix.

of an element in the liquid metal but to use the fraction of that element relative to the metallic liquid domains. This requires a normalization factor for the metallic liquid to take into account the presence of domains. The speciation partition coefficient for an element (E) is calculated as:

$$D(E)(speciation) = \left[\frac{X_E(solid\ metal)}{X_E(liquid\ metal)}\right](1 - X_S - 2X_P - 2X_C)$$

$$= [D(E)molar](1 - X_S - 2X_P - 2X_C) \tag{9}$$

Experimentally determined partition coefficients are usually given as neither D(molar) nor D(speciation) but as

D(wt%), which is the wt% of an element in the solid metal divided by the wt% of that same element in the liquid metal. Based on our theory of partitioning in a liquid metal, D(speciation) is the partition coefficient of choice. However, in practice, having an expression for D(wt%) is quite useful since it eliminates the need to convert the partition coefficient from the form of the experimental data. Below, we show that both D(speciation) and D(wt%) can be parameterized by our revised method of Equation 8 to satisfactorily fit the experimental data, though separate parameterization constants, such as β, are required for the different forms of the partition coefficients.

PARAMETERIZING SIDEROPHILE ELEMENTS

Figure 3 plots experimental partitioning data for 12 siderophile elements commonly studied in iron meteorites. The vast majority of the data are from the Fe-Ni-S system. Other than for a few elements, such as Ge, partitioning data

in the Fe-Ni-P, Fe-Ni-S-P, or Fe-Ni-C systems are limited, and no data are available for other combinations of the Fe-Ni-S-P-C system. Data from the Fe-Ni-C system have the additional complication that the C contents of the metallic liquids were not measured in the run products but, rather, were estimated based on the experimental temperatures, analysis totals, and Fe-C phase diagram. The estimates of the C contents of the experimental run products, thus, have a large uncertainty. References for all experimental data are listed in the Appendix.

Fits to the experimental data using our revised parameterization method are also plotted in Fig. 3. Values for β and D_o were determined by fitting experimental data from the Fe-Ni-S system only, since the S-bearing data provide the largest data set of the different metallic systems. Previous fits as determined by Jones and Malvin (1990) for the Fe-Ni-S system are shown on Fig. 3 as dashed lines. Good agreement exists between our new fits and the previous work of Jones and Malvin (1990), which is not surprising since both
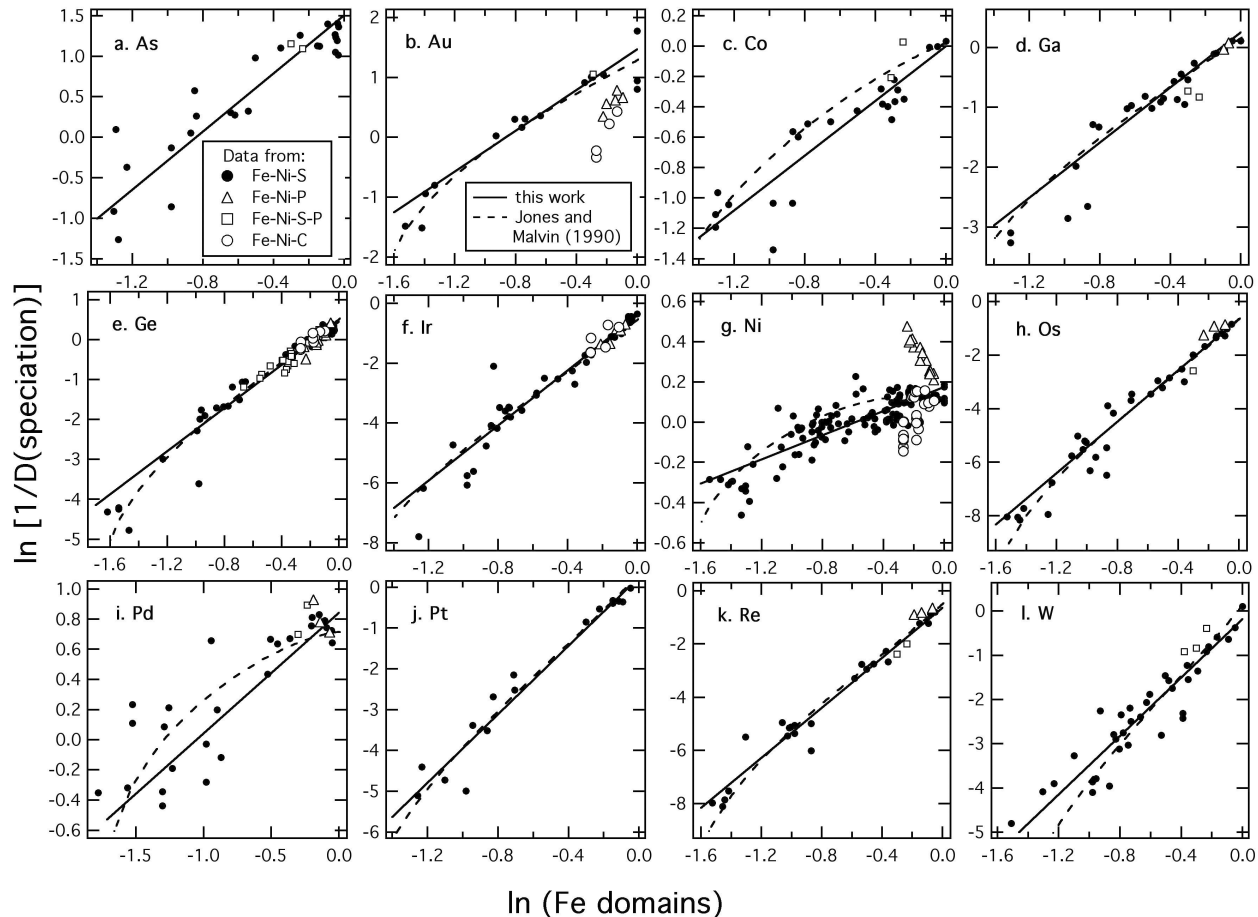

Fig. 3. Experimental partitioning data for (a) As, (b) Au, (c) Co, (d) Ga, (e) Ge, (f) Ir, (g) Ni, (h) Os, (i) Pd, (j) Pt, (k) Re, and (l) W from the Fe-Ni-S, Fe-Ni-P, Fe-Ni-S-P, and Fe-Ni-C systems are plotted against the Fe domains of the metallic liquid, which were calculated according to Equation 7. The fits from the parameterization method presented in this work are shown as solid lines and, with some exceptions discussed in the text, the experimental data are matched well by the fits. Previous fits from Jones and Malvin (1990) are also shown but are applicable to the Fe-Ni-S system only. References for the experimental data are given in the Appendix.

methods are fits to the experimental data. However, unlike our revised fits, the fits of Jones and Malvin (1990) on Fig. 3 are for the Fe-Ni-S system only, and separate fits are required for P or C-bearing data. In contrast, our revised parameterization method is able to match data in the Fe-Ni-S, Fe-Ni-P, Fe-Ni-S-P, and Fe-Ni-C systems with one fit (i.e., only one value of β). The experimental data in systems other than the Fe-Ni-S system are currently quite limited, and additional data from future studies will provide a more rigorous test of the applicability of our parameterization method to other light element-bearing systems. As shown in Fig. 2, the ability of a single fit to match the Fe-Ni-S and Fe-Ni-P data for D(Ir) is not simply due to the limited amount of data from the P-bearing system; using the same limited data, the Jones and Malvin (1990) parameterization method clearly requires separate fits for the Fe-Ni-S and Fe-Ni-P systems. Table 1 lists our fitted parameters of D_o and β for each element that is shown in Fig. 3.

The elements shown in Fig. 3 were added as trace elements in the partitioning experiments, with the exception of Ni, the concentration of which was often about 10 wt%. Despite Ni not being a trace element in the system, our parameterization method is able to fit D(Ni) as well as the trace siderophile elements in the Fe-Ni-S system. In general, the S-bearing data show an increase in scatter with increasing S content of the metallic liquid. The scatter arises from a combination of the accuracy with which high S content metallic liquids can be measured and the drastic effect a small change in S content can have on the partition coefficient at high S contents.

Issues and Inconsistencies

Even accepting the inherent scatter, a few exceptions exist where the data differ noticeably from our fit. As will be discussed in the next section, our parameterization method is only applicable for elements with partitioning behaviors that are dominated by their siderophile tendencies. We note that Ni, Au, and Pd, the elements discussed in detail below, have some of the lowest determined values of β and, consequently, some of the least siderophile natures for all of the elements in this study. Their partitioning behaviors, thus, may not be completely dominated by their siderophile tendencies, and additional terms in the parameterization, which are negligible for highly siderophile elements, may be needed to fully explain these less siderophile elements.

1. In the Fe-Ni-P system, Ni exhibits a different partitioning behavior than in the Fe-Ni-S system, as is evident in Fig. 3g. In iron meteorites, schreibersite ([Fe, Ni]$_3$P) has been reported to contain 10–45 wt% Ni, so evidence exists in natural systems for significant amounts of Ni to partition into P-rich phases even when Fe-Ni metal is available (Buchwald 1975). This tendency for Ni not to exhibit strictly siderophile

Table 1. Values for fitted parameters.

Element	D(speciation)		D(wt%)	
	D_O	β	D_O	β
As	0.22	1.8	0.22	2.2
Au	0.23	1.7	0.25	2.0
Co	1.0	0.9	1.0	1.2
Ga	0.78	2.3	0.78	2.6
Ge	0.64	2.7	0.66	3.0
Ir	1.5	4.6	1.5	4.9
Ni	0.84	0.3	0.86	0.6
Os	1.9	4.8	2.0	5.1
P	0.06	2.6	0.06	2.8
Pd	0.43	0.8	0.43	1.1
Pt	0.78	4.2	0.81	4.4
Re	1.9	4.7	2.0	5.0
W	1.2	3.3	1.2	3.6

We may treat presence of P as a qualitative variable, and then try to improve the fit, that is something to work on.

behavior in the presence of P may be responsible for the inability of our fit to match D(Ni) data in the Fe-Ni-P system. In contrast to schreibersite, Ni contents in cohenite (Fe, Ni)$_3$C and troilite (FeS) from iron meteorites range from only 0.7–2.3 wt% and 0.3–0.9 wt% respectively (Buchwald 1975). Thus, one would expect that Ni is behaving as a purely siderophile element in the Fe-Ni-C system and would exhibit partitioning behavior consistent with that in the Fe-Ni-S system. However, as shown in Fig. 3g, the partitioning of Ni in the Fe-Ni-S and Fe-Ni-C systems is not well matched by the same fit, and this discrepancy still requires an explanation.

The data for Fe-Ni-S is available from 1990, while the data for Fe-Ni-C is made available currently. So there is a chance that the experiments were conducted in different environments.

Part of the problem may be philosophical in nature. At least in the case of the Fe-Ni-P system, no actual variation in D(wt%) exists for Ni with varying P content of the metallic liquid. The variation in D(Ni) in Fig. 3g is therefore somewhat artificial. In Fig. 3g, D(Ni) decreases with increasing P content because of the calculation of D(speciation), which takes into account the fact that the total number of calculated domains decreases as the P content of the metallic liquid increases. However, since no variation in D(wt%) exists for Ni, one might reasonably ask if D(Ni) in the Fe-Ni-P system needs to be parameterized at all.

Also, Ni may represent a special case because D(Ni) is never far from unity, especially in terms of the speciation D(Ni). This means that Ni is equally at home in either Fe or non-metal domains. As we will show below, this lack of strong siderophile character violates both the spirit and letter of our model.

2. The partitioning behavior of Au in the Fe-Ni-P and Fe-Ni-C systems is also not matched by our best fit to D(Au) in the S-bearing experiments. This is surprising since, unlike Ni, no evidence exists for any deviation of Au from siderophile behavior. Additional experiments in P- and C-bearing systems could provide insight into the cause of the discrepancy.

3. Though the Pd-bearing data from the Fe-Ni-P system fall mostly within the scatter of the Fe-Ni-S experiments on Fig. 3i, the Fe-Ni-P runs define a trend that is different from the D(Pd) trend of the Fe-Ni-S data. The P-bearing trend for D(Pd) is only defined by 3 experimental data points and additional work could help to understand or resolve the inconsistency.

4. In some cases, the rate of change of our fits to the partition coefficients with increasing S content is not as rapid as the Jones and Malvin (1990) parameterization. This can be seen on Figs. 3e, 3h, 3j, and 3k and is also illustrated by comparing Figs. 2a and 2b. However, whether or not this is a real problem is currently unclear. First, the largest partition coefficients also have the greatest analytical uncertainty. Therefore, the revised parameterization fits the current data within error. Secondly, if we decide that this is a problem, we can still modify the model by reinstituting the use of α.

Regardless, the model currently works well enough that any α we use will have a numeric value close to unity. (Even the old α in the Fe-S system was only 1.09. Any new α will be considerably closer to unity.)

Weight% D values

The use of D(speciation) is consistent with the underlying theory of our parameterization method. However, as mentioned, having an expression for D(wt%) is often convenient since that is the quantity measured directly by solid metal-liquid metal partitioning experiments. Figure 4 plots the same experimental data shown in Fig. 3 but with the partition coefficient expressed as D(wt%) rather than D(speciation) (references for the experimental data are given in the Appendix). As is evident by comparing Figs. 3 and 4, both forms of the partition coefficient can yield equally good fits to the experimental data using our revised
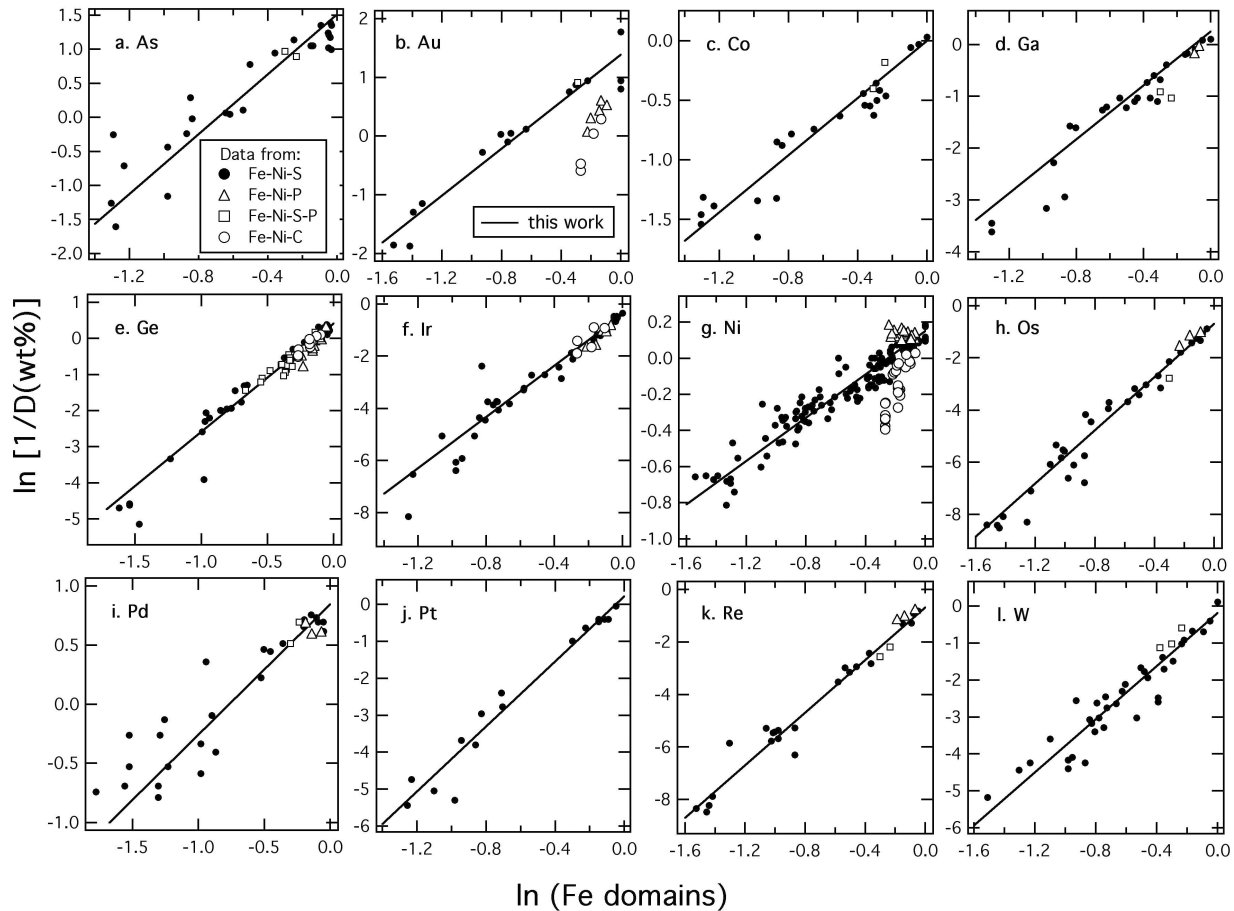

Fig. 4. Similar to Fig. 3, experimental partitioning data for (a) As, (b) Au, (c) Co, (d) Ga, (e) Ge, (f) Ir, (g) Ni, (h) Os, (i) Pd, (j) Pt, (k) Re, and (l) W from the Fe-Ni-S, Fe-Ni-P, Fe-Ni-S-P, and Fe-Ni-C systems are plotted against the Fe domains of the metallic liquid. This figure differs from Fig. 3 in its use of the weight ratio partition coefficient (D[wt%]) instead of the speciation D. Use of D(speciation) is consistent with the theory of the parameterization method, however, D(wt%) is often more convenient to use in models. Our parameterization method is able to satisfactorily match the experimental data when the partition coefficient is expressed as D(wt%). References for the experimental data are given in the Appendix.

parameterization method detailed in Equation 8. However, one must keep in mind that the fits in Fig. 3 and Fig. 4 require different fitted parameters for the different forms of the partition coefficients. Table 1 gives the values of β and D_o used for each element to produce the fitted lines shown in Figs. 3 and 4.

Phosphorus Partitioning

The partitioning of P in solid metal-liquid metal systems is an interesting example. In the P-bearing experiments, P is often not a trace element, and its concentration is one of the variables that influences the partitioning behavior, as shown in Equation 8. Figure 5 plots D(speciation) and D(wt%) for P against the calculated Fe domains of the metallic liquid, as was done for the other 12 elements in Figs. 3 and 4. For both forms of the partition coefficient, our parameterization method fits the experimental data well, and the values of β and D_o used in our parameterized fits are given in Table 1. The dependence of D(P) on P content is clearly small. In fact, since, by definition, P is not situated in Fe domains, that D(P) should be parameterized using the availability of such domains in the Fe-Ni-P system is not clear, even though, clearly, P should be thought of as residing in Fe domains in the Fe-Ni-S system.

NON-SIDEROPHILE ELEMENTS

Note that the parameterization method presented in this work is only for elements that exhibit siderophile, metal-loving behavior when partitioning in solid metal-liquid metal systems. In our parameterization, siderophile behavior is expressed as a function of the concentration of Fe domains. Siderophile elements strongly prefer the metallic Fe domains to the non-metal-bearing domains in the liquid and are, thus, a function of the availability of the Fe domains. In contrast, for elements that exhibit chalcophile, S-loving behavior, the availability of the S-bearing domains, not the Fe domains, is expected to be the dominant influence on the partitioning behavior. Similarly, for elements that are attracted to P or C, those light element-bearing domains will influence the partitioning behavior.

As an example, Fig. 6a plots the partition coefficient for the chalcophile element Cu in the Fe-Ni-S system against the S content of the metallic liquid. Unlike the siderophile elements in Figs. 3 and 4, as the S content of the metallic liquid increases, Cu, being S-loving, partitions more into the metallic liquid and 1/D(Cu) also increases. Experimental studies of Ag and Cr have shown similar chalcophile behavior (Ag, Cr, and Cu data compiled in Chabot et al. [2003]). Figure 6b shows the calculated FeS domains in an Fe-Ni-S liquid as a function of the S content of that metallic liquid. The D(Cu) data and the calculated FeS domains may have a similar functional form, suggesting that the availability of FeS
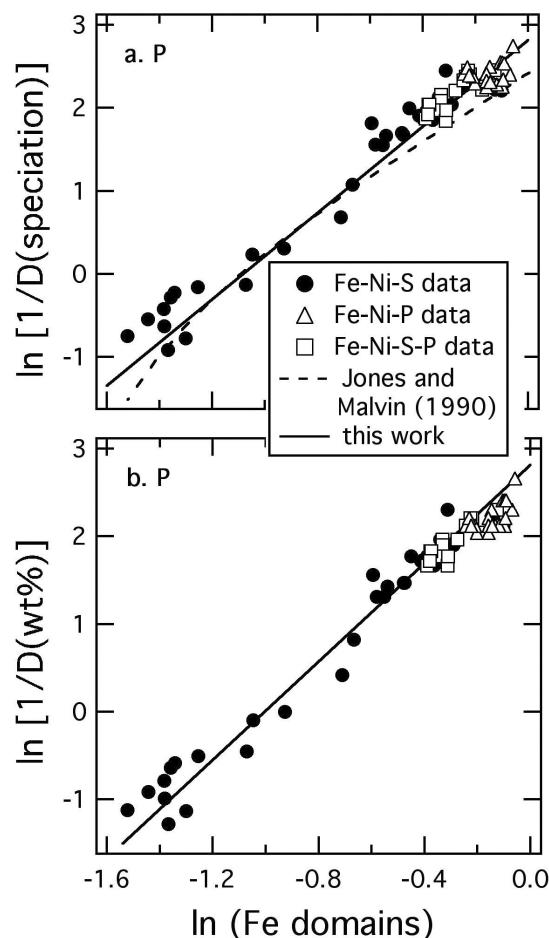

Fig. 5. The experimental (a) speciation and (b) weight partition coefficients for P are plotted against the calculated Fe domains. Unlike the elements shown in Figs. 3 or 4, in the case of P, the concentration of the partitioning element is used to calculate the fraction of available Fe domains. The P data are fit well by our parameterization for the Fe-Ni-S (<1 wt% P), Fe-Ni-P, and Fe-Ni-S-P systems. References for the experimental data are given in the Appendix.

domains in the metallic liquid is influencing the partitioning behavior of Cu, as would be expected by our parameterization theory for a chalcophile element.

In contrast to the parameterization method presented in this paper, Jones and Malvin (1990) applied their parameterization method to both siderophile and chalcophile elements. Figure 6a shows the Jones and Malvin (1990) method applied to the chalcophile data of Cu. The functional form of the Jones and Malvin (1990) parameterization in Fig. 6a is concave up, quite different from the concave down functional form of the fraction of FeS domains shown in Fig. 6b. Though we suggest that the D(Cu) data may be better fit by a functional form like that of the availability of FeS domains, unfortunately, the scatter in the D(Cu) data is too large to definitively distinguish between the 2 options.
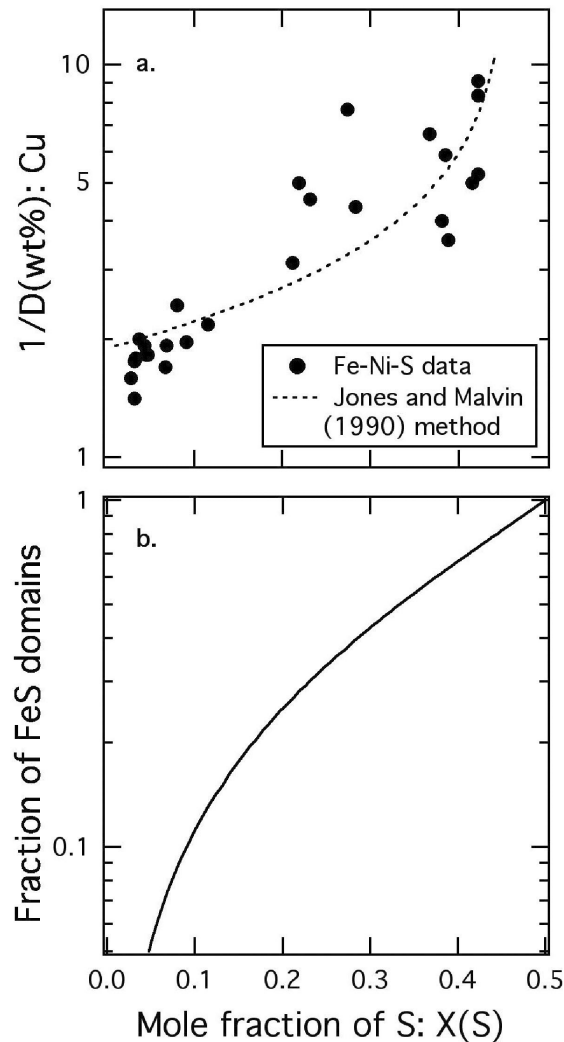
Fig. 6. a) Experimental data for the chalcophile (S-loving) element Cu show that as the S content of the metallic liquid increases, Cu partitions more into the liquid metal and 1/D also increases; b) similarly, as the S content of the metallic liquid increases, more S-bearing domains are available in the metallic liquid. A similar functional form between the chalcophile data of Cu and the calculated fraction of FeS domains would suggest that the partitioning of chalcophile elements could be expressed as a function of the FeS domains in the metallic liquid. In contrast, the parameterization method of Jones and Malvin (1990) has a very different functional form from that suggested by the fraction of available FeS domains. Unfortunately, the current D(Cu) data contain too much scatter to decisively distinguish which functional form provides the best match. The experimental data are from Hongsresawat et al. (2002) and Chabot et al. (2003).

Additional data for chalcophile elements have the potential to resolve the correct functional form.

As for chalcophile elements, we expect a similar dependency for P- or C-loving elements on the P or C-bearing domains, respectively. Lauer and Jones (1999) found W to exhibit "carbophilic" behavior in the Fe-Ni-C system. Thus,

in Figs. 3 and 4, the C-bearing data for W from Lauer and Jones (1999) are not plotted since we already knew that such data would be a function of the C-bearing domains, not the Fe domains, in the metallic liquid. Future experimental studies will be able to test our prediction regarding the dependencies of the partitioning behaviors of P- and C-loving elements.

In an earlier abstract, we presented a method for parameterizing the partitioning of chalcophile elements in the Fe-Ni-S system (Chabot and Jones 2002). The parameterization was similar in theory to that presented for siderophile elements in this work but included 2 terms in the mathematical formulation: one term for a dependency on the Fe domains, as presented here, and one term for a dependency on the FeS domains. We believe that both these terms are governing the behavior of chalcophile elements in the Fe-Ni-S system. However, we are uncertain as to how the 2 terms should be combined. The simple addition of the 2 terms, as used in our abstract (Chabot and Jones 2002), leads to an expression that does not reduce correctly in the special case where an element partitions into either type of domain in the metallic liquid equally. As discussed above, elements such as Ni fall into this category, and our ability to simultaneously explain D(Ni) in the Fe-Ni-S and Fe-Ni-P systems must surely suffer as a result. Thus, an accurate mathematical expression for the partitioning of non-siderophile elements in metallic systems requires further work.

CONCLUSIONS AND APPLICATIONS

Our parameterization method for the partitioning of siderophile elements in metallic systems is based on the theory of Jones and Malvin (1990) in which the metallic liquid is assumed to be composed of metal- and non-metal-bearing domains, the availability of which are the dominant influence on solid metal-liquid metal partitioning behavior. However, with our revised calculation of the fraction of available Fe domains in the metallic liquid, the need for the Jones and Malvin (1990) factor of α in the equations is virtually eliminated. Further, our revised method only demands 2 free variables, β and D_o, for each siderophile element to parameterize partitioning in the Fe-Ni-S-P-C system. In contrast, the previous method of Jones and Malvin (1990) required a separate value of β for each light element in each metallic system, and systems with multiple light elements were modeled as linear combinations of the values in the end member, single light element systems.

Many planetary processes involve a metallic liquid, and often, that metallic liquid is believed to contain multiple light elements. For example, magmatic iron meteorites are believed to have crystallized in the central metallic cores of asteroid-sized parent bodies (Scott 1972). The crystallization of magamatic iron meteorites is modeled as occurring in the Fe-Ni-S-P system, due in part to the observation of frequent

troilite (FeS) nodules and the presence of P in the metal of magmatic iron meteorites (e.g., Haack and Scott 1993; Scott et al. 1996; Chabot and Drake 1999). The possibility of liquid immiscibility in molten asteroidal cores is even debated due to the high concentrations of both S and P in the crystallizing magmatic iron meteorite system (Ulff-Møller 1998; Chabot and Drake 2000). Our parameterization of solid metal-liquid metal partition coefficients can be used to model the crystallization of magmatic iron meteorites in the Fe-Ni-S-P system even if liquid immiscibility occurs. Chabot et al. (2003) reported partition coefficients in the Fe-Ni-S-P system for 2 experiments (#E2 and #E9) that contained solid metal and immiscible P-rich and S-rich metallic liquids. Partition coefficients for both the solid metal-P-rich liquid metal and the solid metal-S-rich liquid metal are shown on Figs. 3 and 4 and fall on the fitted trends.

As another example, recent studies of planetary core formation propose an early, deep magma ocean on the Earth out of which molten metal segregated from molten silicate (Li and Agee 1996; Righter et al. 1997). The recent models include variables in their calculations to account for the influence of the S content and/or C content of the metallic liquid on the core formation process (Righter and Drake 1999; Li and Agee 2001; Chabot and Agee 2003). Righter and Drake (1999) and Li and Agee (2001) base their choice of expressions for S and/or C on the parameterization of Jones and Malvin (1990). Our revised parameterization method is better suited than the work of Jones and Malvin (1990) to deal with the partitioning of a metallic liquid in the complex Fe-Ni-S-C system.

A final example of a planetary process involving a metallic liquid that possibly contains multiple light elements is the solidification of Earth's solid inner core from its liquid outer core. The liquid outer core is known from seismic studies to be composed of about 10% of an element lighter than Fe-Ni (Birch 1964), with popular choices being S, C, O, Si, and H and combinations of those elements (e.g., review by Hillgren et al. [2001]). Recent Os isotopic studies have advocated that material from the Earth's liquid outer core is being incorporated into the mantle (e.g., Walker et al. 1995; 1997; Brandon et al. 1998, 1999, 2003; Meibom and Frei 2002). The studies further suggest that the inner and outer core have the ability to fractionate Pt, Re, and Os from each other during crystallization of the solid inner core. Currently, these studies often use iron meteorites as compositional analogues, but our parameterizations could be useful in modeling the crystallization of Earth's solid inner core, especially if multiple light elements are present in the system. Admittedly, the experiments parameterized by our study were conducted at 1 atm, and we do not know currently if such experiments are applicable at the high pressure conditions within the Earth's core. Initial experimental work suggests that no significant change occurs in solid metal-liquid metal partitioning behavior between 1 atm and 100 kbars (Jones and Walker 1991; Walker 2000), though 100 kbars is still significantly lower than the megabar pressures experienced within the Earth's core.

Additionally, unlike Equations 1 and 2 of Jones and Malvin (1990), our parameterization expressions do not become undefined at the eutectic composition in the Fe-Ni-S or Fe-Ni-P system. The elimination of the constant of α in the Jones and Malvin (1990) equations and the revised calculation of the Fe domains in the metallic liquid are responsible for this difference. Consequently, our parameterizations can now be applied to processes involving metallic liquids with eutectic compositions, which was not possible using the Jones and Malvin (1990) expressions.

Our revised parameterization method also has predictive power. For example, once one verifies that an element exhibits siderophile behavior in both the Fe-Ni-S and Fe-Ni-P systems, performing experiments with every combination of S and P to understand the partitioning behavior of that element in the Fe-Ni-S-P system may be unnecessary. Our parameterization method predicts that the partitioning behavior will be a function of the available Fe domains, regardless of the identity of the non-metal. Additional data for the partitioning of siderophile elements in metallic systems with multiple non-metals can be used to further test the parameterization method presented in this work.

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APPENDIX: REFERENCES FOR EXPERIMENTAL DATA

References for experimental partitioning data in the Fe-Ni-S, Fe-Ni-P, Fe-Ni-S-P, and Fe-Ni-C systems are given in Tables A1–A3. Experiments from Fleet and Stone (1991), which contained Pd and Ni, were not used in the determinations of the parameterizations due to the much larger scatter in the Fleet and Stone (1991) data set as compared to all other experimental studies. The numbers given in the tables of this appendix represent the number of experimental data points per element used from each reference.

Table A1. References for Fe-Ni-S data.

Reference	As	Au	Co	Ga	Ge	Ir	Ni	Os	P	Pd	Pt	Re	W
Bild and Drake (1978)	–	1	1	–	–	–	4	–	–	–	–	–	–
Chabot and Drake (1997)	–	–	–	–	–	–	–	–	–	11	–	–	–
Chabot and Drake (2000)	–	–	–	–	–	–	–	–	10	–	–	–	–
Chabot et al. (2003)	21	–	11	9	11	26	42	25	7	11	14	16	26
Fleet et al. (1999)	–	2	–	–	–	2	4	9	–	2	2	7	–
Hillgren (1993)	–	–	8	6	–	–	23	–	3	–	–	–	5
Hongsresawat et al. (2002)	–	–	–	–	–	–	10	–	–	–	–	–	–
Jones et al. (1993)	–	1	–	–	–	–	–	–	–	1	–	–	–
Jones and Drake (1983)	–	7	–	3	16	7	27	–	4	–	–	–	–
Jones and Malvin (1990)	–	5	3	–	2	3	15	–	8	–	–	–	–
Liu and Fleet (2001)	6	–	–	6	6	–	–	–	–	–	–	–	4
Malvin et al. (1986)	–	–	–	–	–	–	–	–	31	–	–	–	–
Narayan and Goldstein (1982)	–	–	–	–	–	–	–	–	5	–	–	–	–
Willis and Goldstein (1982)	–	–	–	–	2	2	8	–	6	–	–	–	–

Table A2. References for Fe-Ni-P and Fe-Ni-S-P data.

Reference	As	Au	Co	Ga	Ge	Ir	Ni	Os	P	Pd	Re	W
Chabot and Drake (2000)	–	–	–	–	–	–	–	3	5	3	3	–
Chabot et al. (2003)	2	–	2	2	–	–	–	1	2	2	2	2
Jones and Malvin (1990)	–	1	–	–	1	1	3	–	5	–	–	1
Malvin et al. (1986)	–	3	–	–	23	2	6	–	16	–	–	–
Narayan and Goldstein (1982)	–	–	–	–	5	–	1	–	5	–	–	–
Willis and Goldstein (1982)	–	2	–	2	–	2	6	–	6	–	–	–

Table A3. References for Fe-Ni-C data.

Reference	Au	Ge	Ir	Ni
Jones and Goodrich (1989)	3	4	3	10
Lauer and Jones (1999)	–	–	–	7
Willis and Goldstein (1982)	1	5	3	11