

Subsolidus Metal – Olivine Trace Element Partitioning. E. Hill¹, G. R. Huss², K. Domanik¹, and M. J. Drake¹.
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Introduction: Trace-element partitioning between metal and olivine ((Mg, Fe)₂SiO₄) is a fundamental process in the planetary sciences. It occurs at the mantle – core interface of planetary bodies and in asteroids with metallic cores and is likely to have influenced the composition of siderites and mesosiderite meteorites. Metal – olivine distributions of minor and trace elements have applications ranging from the determination of the composition of the lunar and terrestrial cores (e.g., [1]), oxygen barometry (e.g., [2]) and are particularly relevant to discerning the origin and cooling history of the pallasite meteorites, a mixture of FeNi-alloy and olivine.

Experimental determination of metal – olivine partition coefficients ($D^{\text{met/ol}}$) has been limited to Fe-alloy-melt – olivine crystallization experiments at temperatures (T) above the melting point of the metal alloy and in which the silicate portion is at subliquidus T. Extrapolation to lower T is required to study of the origins, compositions, and cooling rates of mesosiderites and pallasites. However, because we do not know the values of the partial molar enthalpies of natural minerals, the best we can do is to extrapolate approximations of the partition coefficients using the enthalpies of the pure end members. To date, only two direct measurements of metal/olivine Ds at pressure (P) of interest, both for Ni, appear in the literature [3]. In view of this dearth of data, it is obvious that more metal / olivine trace element partitioning values for elements of interest, at relevant T and P, are required.

Here we present a method for obtaining trace element partition coefficient at subsolidus temperatures. By performing metal – olivine diffusion experiments at low T and 1 bar, we have been able to measure diffusion rates and calculate trace element partition coefficients relevant to the study of the evolution of planets, asteroids and meteorites.

Methods: Experimental charges were composed of a mixture of Fe, Ni and Co metal powders and synthetic forsterite crystals (Mg₂SiO₄). Chromium and Mn are present in trace amounts. The use of natural olivines, crystallized under more oxidizing conditions than those of our experiments, resulted in the exsolution of transition metals into beads forming a snow-field effect in the crystals. As a result, it was impossible to use natural olivines to determine the diffusion rates of the cations of interest. The use of synthetic, pure forsterite in diffusion and partitioning experiments has been shown as a suitable substitute for natural olivines and avoids the exsolution problem [2, 4].

Experimental charges were suspended in the hot spot of a vertical quench furnace and run at 1 bar and

1823 K, 1573 K or 1173 K. Reducing conditions were maintained at 1 log unit below the iron – wüstite buffer ($\Delta fO_2 = IW -1$) by controlling H₂ – CO₂ gas mixes. Our highest experimental temperature, 1823 K, is above the melting point of alloy but below that of forsterite and is aimed at reproducing the insertion of a molten alloy into an olivine body; a reasonable first step in the formation of mesosiderites. The 1573 K and 1173 K experiments were run at 1823 K for an hour, to allow for melting and homogenization of the metal alloy, before the temperature was lowered to that desired for the experiment. Despite the reasonably high T of our experiments, the relatively slow diffusion of cations through the forsterite resulted in runs of as long as 1532 hours.

Analyses of the major-element composition of experimental charges were performed using a Cameca SX50 electron microprobe at the LPL. Trace element concentrations were analyzed by Secondary Ion Mass Spectrometry at the University of Hawai'i.

Results and discussion: The three sets of experiments produced diffusion profiles in olivines from which it has been possible to calculate diffusion rates for Cr, Mn, Fe, Co and Ni, and metal – olivine trace element partition coefficients for Si, Mg, Cr, Mn, Co and Ni (Table 1). Trace element partitioning values are presented as the distribution coefficient ($\log KD = (\log M^{\text{m}}Fe^{\text{ol}}/M^{\text{ol}}Fe^{\text{m}})$) where M is the cation of interest, 'ol'=olivine and 'm'=metal) a form that takes account of the influence exerted by fO_2 on partitioning.

Table 1. Metal/forsterite distribution coefficients (KD) and diffusion rates in forsterite.

	1823 K	1573 K	1173 K
	log KD	log KD	log KD
Si	-7.19 (12)	-4.96 (20)	-3.78 (13)
Mg	-9.08 (10)	-8.50 (30)	-5.98 (31)
Cr	-1.88 (14)	-2.76 (40)	-3.01 (12)
Mn	-3.15 (16)	-3.60 (10)	-4.33 (37)
Co	1.17 (10)	1.01 (17)	1.05 (26)
Ni	2.26 (8)	2.16 (20)	1.38 (11)
Diffusion Coefficients (cm ² /s)			
Cr	1.02 x 10 ⁻¹¹	4.30 x 10 ⁻¹³	4.26 x 10 ⁻¹⁴
Mn	6.04 x 10 ⁻¹²	5.26 x 10 ⁻¹³	3.08 x 10 ⁻¹⁴
Fe	1.76 x 10 ⁻¹¹	2.57 x 10 ⁻¹²	7.31 x 10 ⁻¹⁴
Co	1.23 x 10 ⁻¹⁰	2.18 x 10 ⁻¹²	9.26 x 10 ⁻¹⁴
Ni	8.43 x 10 ⁻¹²	2.09 x 10 ⁻¹²	4.06 x 10 ⁻¹⁴

Numbers in parentheses represent $\pm 2\sigma$ of least significant digits.

Diffusion rates were obtained by fitting measured concentration profiles using an equation of the form $(C - C_1)/(C_0 - C_1) = \text{erf}X/(2(Dt))^{1/2}$ [where D=diffusion coefficient] for a semi-infinite medium with constant con-

centration C_0 and constant surface concentration C_l (Fig. 1). This is a very good approximation to our system as the concentration of the diffusing species is several orders of magnitude higher in the source than in the medium it diffuses into.

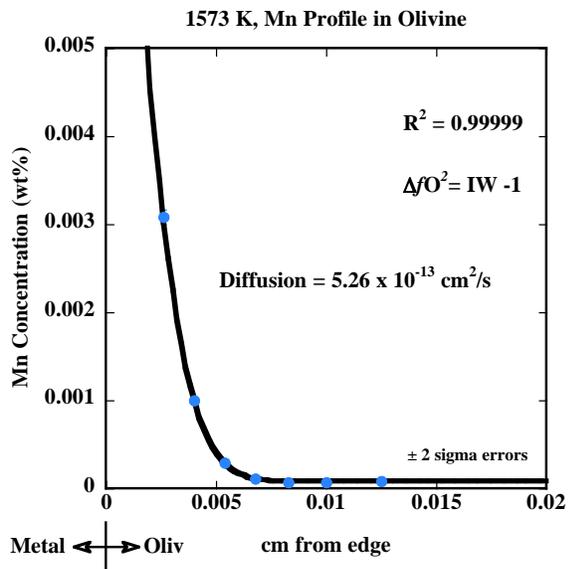


Figure 1: Manganese-concentration diffusion profile in forsterite crystal. Concentration increases markedly toward the forsterite – metal interface. The fit to the profile meets the y-axis at the surface constant concentration thus allowing for the calculation of the relevant distribution coefficient.

Manganese, Cr, Fe, Ni and Co are present in the metal alloy and diffuse into the forsterite. Silicon and Mg partition from the olivine to the metal. As is expected, diffusion coefficients for all elements decrease with decreasing T. The orthorhombic structure of olivine means it is anisotropic, and therefore diffusion rates for this mineral are commonly adjusted for crystallographic orientation. The diffusion rates presented here are not yet adjusted, however, the values have merit as approximations to an average diffusion rate under the conditions specified. Such an approach allows for fast interpretation of trends if not for fully quantitative evaluations. The validity of the rates is shown by their broad agreement with published values for Cr (e.g., [5]) and Ni (e.g., [6]).

Trace element partitioning patterns reveal Ni and Co display siderophile behavior while Cr and Mn show a higher affinity for the olivine. With the exception of values for Si and Mg, $\log KD^{\text{met/ol}}$ decrease as a function of T and fO_2 . With decreasing T and fO_2 , $\log KD_{\text{Si}}$ and $\log KD_{\text{Mg}}$ increase, although, they remain strongly lithophile (Table 1, Fig. 2).

It is presently unclear why $\log KD_{\text{Si, Mg}}$ increase with decreasing T and further study of the experimental charges is required. Despite efforts to remove surface contamination, it is possible that measured Si and Mg concentrations are contaminated by Si and Mg

present in the carbon coating, thus the $\log KD$ values presented here may represent upper limits. Another possibility, is that at the two highest T, Si and Mg are exsolving from the metal during quench and are preferentially precipitating at the forsterite – metal interface thus producing an artificial low concentration. Such behavior has previously been observed for Si in metal-melt / silicate-melt experiments at higher pressures (e.g., [7]). The linearity of the trends, however, argues for a real effect.

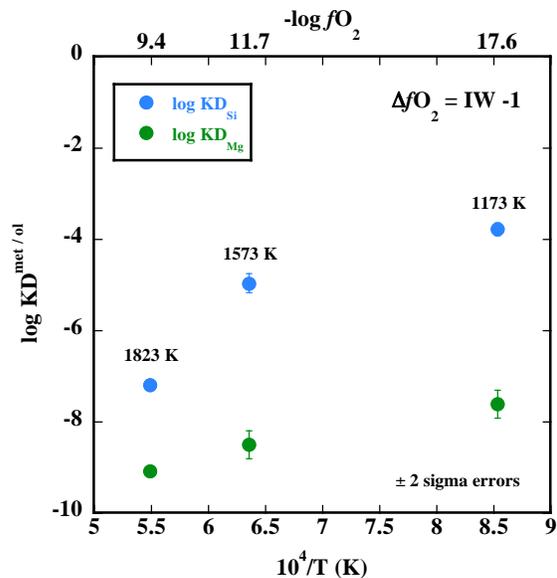


Figure 2: Plot of $\log KD^{\text{met/ol}}$ versus T for Si and Mg. Log KD values for Si and Mg increase with decreasing T with the largest increase experienced by Si. Regardless of the increase, Si and Mg remain very incompatible in the metal.

Conclusions: Metal – olivine subsolidus diffusion experiments provide diffusion rates suitable for the study of cooling rates of mesosiderites. Mathematical fits to trace-element diffusion profiles, found in silicate phases, provide the surface constant concentration thus allowing the calculation of equilibrium distribution coefficients at subsolidus temperatures.

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