

Cation Distribution Between Forsterite and Metal Alloy at High Temperatures: Implications for the cooling rates of Pallasites. E. Hill¹, K. Domanik¹ and M. J. Drake¹, ¹Lunar and Planetary Laboratory, University of Arizona, 1629 E University Blvd, Tucson, AZ 85721. (eddy@lpl.arizona.edu)

Abstract: We report metal/olivine partition coefficients for Ni as functions of temperature, composition and fO_2 . Such partition coefficients are essential to interpreting zoning profiles in pallasitic olivines in terms of cooling rates.

Introduction: Pallasites are intimate mixtures of olivine and metal, thought to be samples of the core-mantle boundaries of disrupted asteroids or larger planetesimals. As these phases attempted to re-equilibrate, during the slow cooling experienced deep within the parent bodies, zoning profiles developed in olivine and metal. Tomiyama and Huss [1] have obtained zoning profiles, in olivine, for a series of elements including Cr, Ca, and Co. Applying these zoning profiles to a one dimensional spherical cooling model, they obtain cooling rates four orders of magnitude faster than metallographic cooling rates [2].

Calculations based on zoning profiles in pallasites assume a constant metal/olivine partition coefficient (D) boundary condition between metal and olivine. This assumption cannot be correct. D is dependent on variables such as temperature (T), pressure (P), crystal and melt compositions (X), and fO_2 . As P is believed to have remained constant throughout the cooling history of the pallasites, it will not have an effect on the variability of D values. Temperature, the composition of the FeNi alloy in contact with the forsterite, and the fO_2 of the system may all have varied over time, however, and metal/olivine Ds encompassing these changes are required to establish reliable, evolving boundary conditions.

To date, only two direct measurements of metal/olivine Ds at P of interest, both for Ni, appear in the literature [3]. In view of this dearth of data, we are performing experiments to determine the metal/olivine partition coefficient of a range of elements including transition elements, REE, and HFSE. Our first efforts have been focused on Ni and Co, elements whose concentrations we expect to be able to measure, with a level of confidence, in both metal and silicate by electron microprobe analysis. Measurement of the other proposed elements in these same experiments will require the use of SIMS in order to resolve the low concentrations encountered in metal, silicate, or both.

We report here on progress to date and provide preliminary values for D_{Ni} at 1823 K and 1773 K.

Experimental and Analytical Methods: Experiments are being performed at decreasing temperatures and under three fO_2 conditions i.e., IW -0.5, IW -1 and IW -2. To account for variability in FeNi composition

in pallasites, we use two different starting metal mixes (High – $Fe_{78}Ni_{14}Co_8$ and Low – $Fe_{92}Ni_4Co_4$). Our highest experimental temperature, 1823 K, is above the melting point of alloy but below that of forsterite and is aimed at reproducing the very first conditions of pallasite formation. The lower temperature experiment reported was run at 1823 K for an hour, to allow for melting and homogenization of the metal alloy, before the temperature was lowered to 1773 K. Each experimental run consists of two capsules (one for each metal alloy) suspended in the hot spot of a vertical quench furnace with the relevant fO_2 conditions controlled by H_2 - CO_2 gas mixes. Despite the high temperature of our experiments, the relatively slow diffusion of Ni and Co through the forsterite has resulted in run durations of as much as 235 hours. Runs of this duration are required to provide an equilibrated volume of olivine sufficient for analysis beyond the area affected by secondary fluorescence and by excitation of the neighbouring metal body (Figures 1 and 2).

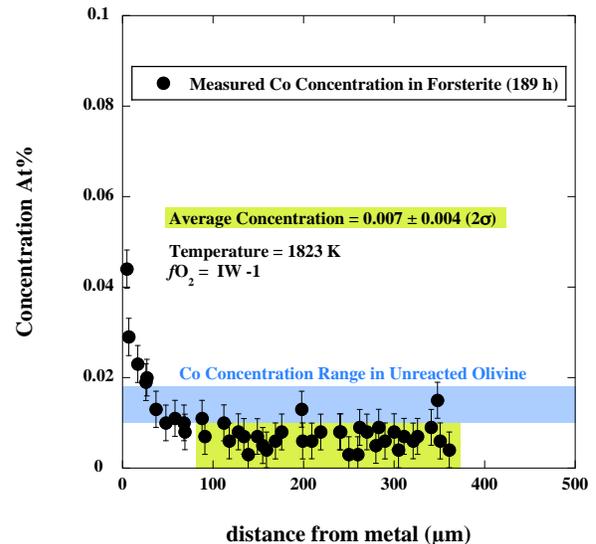


Figure 1: Measured Co concentration in forsterite after 189 hours. The zoning profile from 0-50 μm is the effect of secondary fluorescence, which we eliminate from our calculations. The average concentration presented is for those values encapsulated in the blue box. These values are chosen as they are beyond the effect of fluorescence and because they differ from the original composition of the olivine before the experiment (red box).

Analysis of experimental charges and products were performed using a Cameca SX50 electron microprobe at the LPL. Analytical conditions were 15 kV and 40 nA (Fe) -100 nA (Ni and Co) for metals with peak counting times of 20 s and 40 s respectively. Olivines were analysed using an accelerating potential of

15 kV and beam currents of 40 nA (for major elements) and 290 nA (for Ni and Co). Peak counting times were 20 s and 120 s respectively. Under these conditions, detection limits for Ni and Co were approximately 20 ppm. Analyses of the Marjalahti and Springwater olivines, known to contain 30 and 50 ppm of Ni respectively, were used as controls.

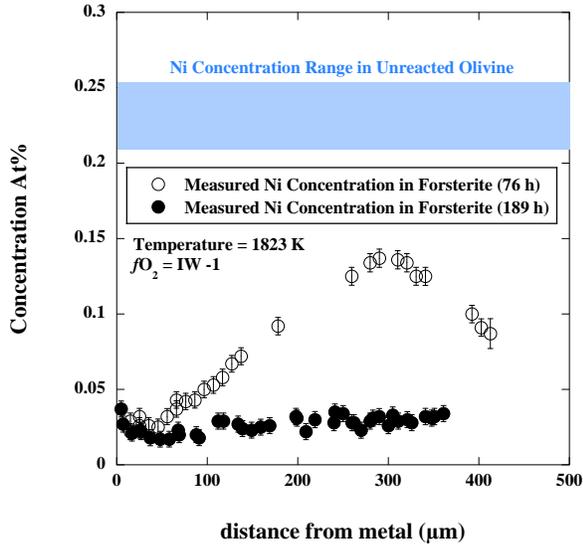


Figure 2: Measured Ni concentration in forsterite after 76 and 189 hours. Evident in the 76 h run is a rise in concentration towards original olivine levels followed by a decrease as analyses cross the center of the crystal and approach the opposite edge. Values for the 189 h run are closer to being homogenous across the crystal. A slight rise in values away from the edge, however, means that full equilibration was not achieved throughout the crystal. The effects of Ni excitation in the adjoining metal can be observed for the first 30–40 μm .

Results and Discussion: Experimental run conditions and $\ln D_{\text{Ni}}$ values are listed in Table 1. Concentrations of Co in the olivines are much lower than had been expected (10s of ppm) and close to the detection limit. As a consequence, values have large associated uncertainties and we have opted to not report them here pending SIMS analyses. Ni concentrations, near the edge of olivines, are an order of magnitude higher than Co's, however, the uncertainty on the counting statistics is typically $\geq 10\%$ of X_{Ni} resulting in relatively large propagated errors for $\ln D_{\text{Ni}}$.

Table 1. Experiment run conditions and results.

Temp (K)	FeNiCo Comp	Duration (h)	$f\text{O}_2$ buffer	$\ln D_{\text{Ni}}$	2σ
1823	High	235	IW -0.5	6.4	1.1
1823	High	189	IW -1	6.6	1.0
1823	High	76	IW -2	6.7	1.6
1823	Low	235	IW -0.5	5.8	1.6
1823	Low	189	IW -1	5.6	0.8
1823	Low	76	IW -2	5.2	1.4
1773	High	235	IW -1	6.9	1.5
1773	Low	235	IW -1	5.7	0.8

Our present data do not allow the effects of temperature on the distribution of Ni between metal and olivine to be determined. It is possible, however, to make some first observations regarding the effects of composition and $f\text{O}_2$. An attempt to separate the compositional effects by comparison of $X_{\text{Fe}}/X_{\text{Ni}}$ in metal and olivine results in no apparent compositional trend (cf. [4]). A clearer relationship can be found between the concentration of Ni in olivines and oxygen fugacity (Figure 3).

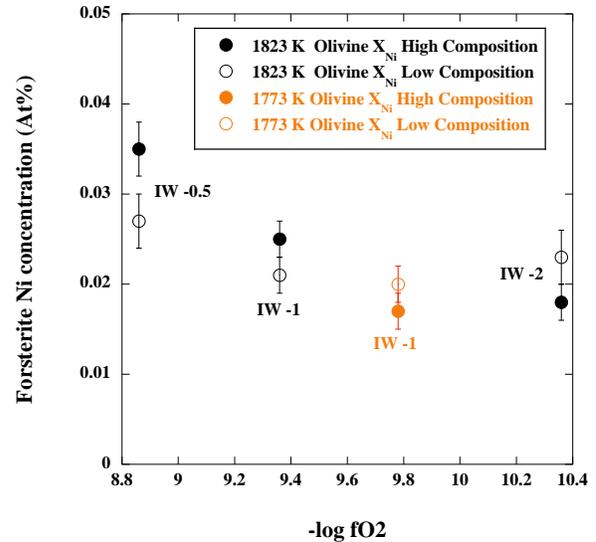


Figure 3: A clear correlation can be observed between the concentration of Ni in forsterite and the $f\text{O}_2$ of the system. For runs at 1823 K, an increase in X_{Ni} occurs with increasing $f\text{O}_2$.

Concluding Remarks: Further experiments over a wide range of temperatures will serve to determine the effect of temperature on partitioning of trace elements between forsterite and a metal alloy. The current data set indicates no statistically significant dependence on composition and hence, changes in Fe/Ni ratio in the metal during cooling should not affect metal/olivine Ni partitioning. The sole apparent control on the concentration of Ni in olivine is the oxygen fugacity of the system. As such $f\text{O}_2$ will influence $\ln D_{\text{Ni}}$.

Values of $\ln D_{\text{Ni}}$ presented here are preliminary. Analysis of our experimental products by SIMS will serve to refine these values and to provide useable Co concentrations.

References: [1] Tomiyama and Huss (2006) *LPSC XXXVII* (2132) **40**, A156. [2] Buseck and Goldstein (1969) *Geol. Soc. Amer. Bull.* **80**, 2141-2158. [3] Ehlers, Grove, Sisson, Recca and Zervas (1992) *Geochim. Cosmochim. Acta* **56**, 3733-3743. [4] Holzheid A., and Grove T.L. (2005) *Chem. Geol.* **221**, 207-224.