DIFFUSION OF AU, PD, PT AND IR IN FE-NI METAL AT LOW TEMPERATURES. J. D. Price, D. J. Cherniak, and E. B. Watson, Department of Earth & Environmental Sciences, Rensselaer Polytechnic Institute, 110 8th St., JSC 1W19 Troy, NY 12180, pricej@rpi.edu.

Introduction: A range of siderophile elements occurs in trace but measurable abundances in meteorites containing Fe-Ni metals. Understanding diffusion behavior of these elements in Fe-Ni alloys may be useful in enhancing and refining the metallographic method of cooling rate estimation for kamacite/taenite exsolution (e.g. [1-3]). Recent studies have determined diffusivities for many siderophile elements [2, 4-7]. However, these studies were largely conducted at temperatures and pressures higher than those conditions most relevant for exsolution. We present new data for the diffusion of the siderophile elements Au, Pd, Pt and Ir at temperatures between 585-900ºC and pressures less than 130 Pa, which may be more directly applied in addressing these problems without down-temperature extrapolation.

Experimental Technique: Fe-Ni metal rods were synthesized from homogenized mixtures of Fe and Ni powders contained in an MgO capsule at 1400 ± 50 ºC under 1 GPa isostatic pressure. Three alloy compositions were synthesized, having 5%, 10%, and 20% Ni by weight. The prepared rods were sectioned into wafers roughly 1 mm thick and 2.5 mm in diameter. One side of each wafer was ground and polished to a mirror finish free from scratches greater than 100 nm. The surface was then coated with a thin film of the diffusant. Au-Pd (60%Au-40%Pd) films were deposited by sputtering, and Pt and Ir films by vacuum evaporation of high-purity powders. Coated wafers were sealed in silica glass capsules evacuated to <130 Pa and heated in vertical tube furnaces for times ranging from 5 to 30 minutes. Following diffusion anneals, capsules were removed from furnaces and quenched by immersing in cold water.

RBS analysis and data fitting: Wafers were removed from their capsules and immediately analyzed with Rutherford backscattering spectrometry (RBS), using ^{4}He+ incident beams of 2 to 3.5 MeV energy. Spectra were converted to concentration profiles employing procedures similar to those described in previous work (e.g. [8, 9]). The resultant profiles were fit to determine the diffusion coefficient (D). In determining the appropriate model with which to fit the data, it is essential to consider the initial and boundary conditions imposed by the experimental configuration. For experiments on diffusion of siderophile elements in Fe, [2] proposed the use of a thin-film source solution. However, in the case of thicker deposited layers of diffusant, solutions for a source of finite thickness or even a semi-infinite source

(a complementary error function) may be more suitable. In all of these cases, it is assumed that the diffusant not remaining at the surface diffuses into the material, with no loss of diffusant to the surrounding environment. However, we note loss of the diffusant to the surrounding atmosphere and onto the inner surface of the sealed silica capsule during our experiments, which necessitates an alternate model to account for this evaporative loss. Consequently, we model the data with a solution from [10] for diffusion with surface adsorption/desorption where $C(x=0) = C_o - kt$, with constant k. This results in the expression

$$C = C_o erfc\left(\frac{x}{\sqrt{4Dt}}\right) - kt\left[\left(1 + \frac{x^2}{2Dt}\right)erfc\left(\frac{x}{\sqrt{4Dt}}\right) - \frac{x}{\sqrt{\pi Dt}}\exp\left(\frac{-x^2}{4Dt}\right)\right]$$

Diffusivities were determined from this expression by fitting the data with a non-linear fitting routine, using both Levenberg-Marquardt [11] and grid-search [12] algorithms. Profiles were fit for the initial surface concentration (C_o), the surface loss factor (k) and the diffusivity (D). The uncertainties in concentration and depth from each data point (mainly derived from counting statistics in the former and detector resolution in the latter) were used to evaluate the uncertainties in the diffusivities determined from the fits to the model. The expression above provides better fits to the data than either a thin-film, finite source, or infinite-source models; however, it should be noted that fits of the data to these other models yielded similar diffusivities, suggesting relatively little sensitivity to the choice of model for typical diffusion profiles in this study.

Results: Our diffusion coefficients (D) are plotted in Figure 1 and provide a preliminary look at diffusion for 585-900 ºC. These Arrhenius plots reveal several trends. Over this temperature range, Pd is slightly faster than Au, and both appear to diffuse faster than Pt and Ir. For Au, we obtain the following Arrhenius relations for 5%, 10% and 20% Ni:

$$D_{Au5\%} = 2.5\,^{+7.4}_{-3.1}\times 10^{-12}\exp(-117\pm 12/RT)$$

$$D_{Au10\%} = 1.5\,^{+5.7}_{-1.9}\times 10^{-8}\exp(-188\pm 14/RT)$$

$$D_{Au20\%} = 4.1\times 10^{-9}\,^{+1.6\times10^{-6}}_{-4.1\times10^{-9}}\exp(-177\pm 50/RT)$$

For Pd, the following Arrhenius relations are determined:

$$D_{Pd5\%} = 1.6\,^{+6.1}_{-1.9}\times 10^{-12}\exp(-107\pm 13/RT)$$

$$D_{Pd10\%} = 1.4\,^{+18}_{-1.5}\times 10^{-9}\exp(-166\pm 23/RT)$$

$$D_{Pd20\%} = 5.3\times 10^{-11}\,^{+5.1\times10^{-7}}_{-5.3\times10^{-11}}\exp(-145\pm 72/RT)$$

where D and D_o are in $m^2 s^{-1}$, E_a is in kJ mol^{-1}, and T is in K.

Although the diffusion of Pd appears slightly faster, Au and Pd have similar activation energies for diffusion in a given alloy composition. The behavior of Ir and Pt is less constrained because there are fewer data, but diffusivities of Ir seem to be slightly slower than Au or Pd. Pt diffusion data has only been determined for two different temperatures in 10%Ni, but appears to have an activation energy similar to those for Pd.

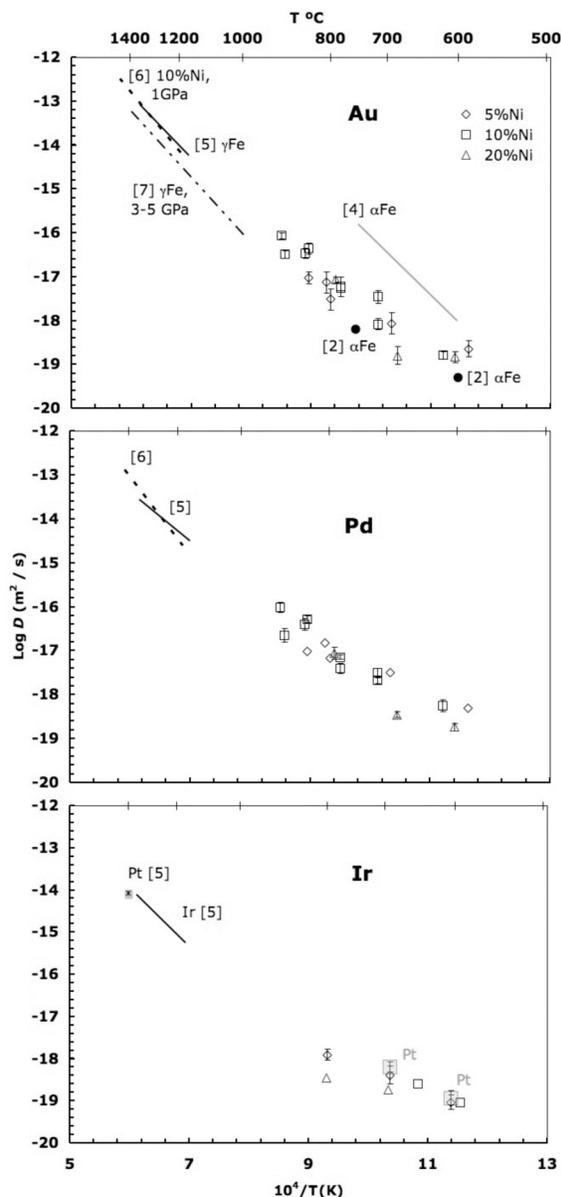Most previous efforts determined diffusivities at

Figure 1. Arrhenius plots of the Au, Pd, Ir (with Pt) diffusion data from this study and those reported on relevant systems by other workers. Symbols for new data correspond to wt.% Ni in Fe-Ni metal alloy.

high temperatures and for trace elements in pure Fe, with the exceptions of the Au diffusion studies under low temperature – low pressure conditions by Watson [2] and Oikawa [4], and measurements of siderophile element diffusion in FeNi alloys at 1GPa by Watson and Watson [6]. Although our data suggest a dependence on Ni content, the effect is slight in this compositional range. Our data agree with the low-temperature values for Au from [2], but have substantially lower activation energies than those of [4]. Our data also exhibit lower activation energies than those determined previously from high temperature experiments; this may be in part attributed to limitations on down-temperature extrapolation and in constraining activation energies derived from sampling a narrow range in 1/T. Diffusivities may also be affected by pressure (as shown in [2], although these effects will likely be small for moderate pressures), or differences between the α and γ phases. However, our data do appear to be broadly consistent with the findings of [6] and [7].

Conclusions: Diffusion of Au, Pd, Ir, and Pt in FeNi metal has been measured for 585-900°C by depositing a thin layer of diffusant on the sample surface and annealing in silica capsules sealed under vacuum; resulting diffusion profiles were measured by RBS. The diffusivities of these four elements are largely similar. Au and Pd are only slightly affected by changes in the Ni concentration, while Ir appears more sensitive to alloy composition, although more data are required to substantiate this. Our diffusivities differ from those that would be obtained through downward extrapolation of high-temperature data, confirming the need for data over the range of 1/T that is applicable to the cooling history of Fe meteorites.

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