Diffusion of trace elements in FeNi metal: Application to zoned metal grains in chondrites

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Abstract—We have measured diffusion coefficients for P, Cr, Co, Ni, Cu, Ga, Ge, Ru, Pd, Ir, and Au in Fe metal from 1150 to 1400°C and at 1 bar and 10 kbar. Diffusion couples were prepared from high-purity Fe metal and metal from the IIA iron meteorite Coahuila (single crystal kamacite) or the pallasite Springwater (polycrystalline kamacite) and held at run conditions for 3.5 to 123 h. Diffusion profiles were measured using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) or the electron microprobe. Many elements were measured from the same experimental runs so interelemental comparisons are improved over previous studies. Some literature diffusion coefficients (D) for Ni and Co in taenite can be up to a factor of 3 higher for Ni than Co, yet our results show no difference (e.g., $D_{Ni}$ and $D_{Co} < 2.2 \times 10^{-15}$ m$^2$/s at 1150°C). Thus, diffusion of Ni and Co in single crystal taenite will not measurably fractionate the Ni/Co ratio. On the other hand, the large difference in $D_{Ni}$ and $D_{Ir}$ ($D_{Ir}$ is $\sim 5$ times lower) and the similarity of $D_{Ni}$ and $D_{Ru}$ at all temperatures investigated indicates that Ni/Ir and Ni/Ru ratios in zoned metal grains will be useful discriminators of processes controlled by diffusion vs. volatility. In zoned metal grains in primitive chondrites, deviations of the Ni/Ru and Ni/Ir ratios from a condensation curve are opposite to a diffusion-controlled process, but consistent with a volatility-controlled process. The new multielement diffusion coefficients will also be useful in evaluating a variety of other processes in planetary science. Copyright © 2005 Elsevier Ltd

1. INTRODUCTION

A thorough knowledge of diffusion of siderophile elements in planetary metals has many applications in cosmochemistry, redox processes, kamacite/taenite cooling rates, and the origin of zoned metal grains in chondrites. Hypotheses involving diffusional processes are difficult to evaluate for many elements due to lack of diffusion data for appropriate metal compositions, degrees of metal crystallinity, or relevant conditions for chondritic meteorites. Furthermore, what data exist can have a significant amount of variation between studies, making interelemental comparisons uncertain (Fig. 1).

We have measured diffusion coefficients for Cr, Co, Ni, Ga, Ge, Ru, Pd, Ir, and Au in Fe metal: IIA iron meteorite metal couples from 1150 to 1400°C, at both 1 bar and 10 kbar. We have also measured diffusion coefficients for P, As, and Pt at a single temperature in several runs. These new measurements offer two advantages. First, the low concentrations of most siderophile elements in the meteoritic metal allow determination of diffusion coefficients at concentration levels appropriate for natural systems (Ni and Co are relatively high, but still at natural levels, ~6.0 wt% and ~0.5 wt%, respectively). Second, the results will provide an internally consistent data set in that diffusion coefficients for all elements were determined from the very same experiments, thus reflecting more realistic relative differences. The results are used to evaluate the role of diffusion in controlling the zoning in metal grains in metal-rich chondrites, and to illustrate the potential for diffusion to control the distribution and mobility of Cr, Ni, and Ir in planetary metals.

2. EXPERIMENTAL

Diffusion couples were prepared from high-purity Fe metal rod (Alfa Aesar 99.995% Fe, initially polycrystalline, and oriented with 110 plane coincident with diameter of rod) and metal from the IIA iron meteorite Coahuila (initially single crystal kamacite) or the pallasite Springwater (initially containing a micro-Widmanstätten pattern and kamacite outlining olivine). Starting materials were chosen to closely approximate natural Fe-Ni metals because diffusion coefficients are compositionally dependent, and the Fe-Ni alloys are the compositions of interest to cosmochemistry. Compositions of starting materials are given in Table 1. Metal lengths were lathed into rods and cut into 3 mm lengths (Fig. 2). The circular faces of these rods were polished and then the coupled rods were encapsulated with MgO. For 1 bar runs, the couples were first hot pressed for annealing for 1 h at 10 kbar (in a piston cylinder apparatus) and at the same temperature as the target temperature for the run. The annealing was done to ensure physical contact between the two halves of the couple. One might question whether plastic strain occurred at these higher pressures during the anneal and caused increased diffusion rates due to the introduction of dislocations. However, this is not relevant in this case for the following reasons: (1) the relatively long run times of the 1 bar experiments—all >84 h—compared to the 1 h anneal time; (2) hydrostatic pressure does not cause permanent strain unless it is greater than the yield strength (Poirier, 1985), which did not occur in this case; and (3) plastic strain has potentially strong effects on anisotropic metals but the metals here are isotropic (Poirier, 1985; Davidson et al., 1965). For the 10 kb runs, no hot pressing step was necessary. The MgO-sheathed metal couples (Fig. 2) were then placed either in a piston cylinder apparatus (10 kb) or alumina crucible within an evacuated silica tube (1 bar) in a vertical furnace and held at run temperature (with the duration depending upon the temperature; Table 2). In both experimental configurations, Fe is in contact with alumina. Therefore, oxygen fugacity in the experiments was fixed near the IW buffer by equilibria between metal and alumina: $Fe + Al_2O_3 + 1/2 O_2 = FeAl_2O_4$ (e.g., Atlas and Sumida, 1958).

Run products were then mounted in epoxy, cut perpendicular to the interface, and polished. In some cases, the crystallinity of samples was
examined by etching a polished surface or by X-ray diffraction. In this way, the grain size could be determined, and the issue of whether diffusion occurred through single crystals or a polycrystalline matrix could be evaluated. Both the Fe rod and the kamacite had changed structure to taenite under the run conditions. X-ray diffraction patterns of run products reveal both polycrystallinity and loss of 110 orientation in the pure Fe half of the couple. In experiment 6, a diffusion couple run at 10 kb, 1400°C and one of the shortest runs in this study (19 h), the grain size near the couple interface was large (150 –300 μm), as defined by clear grain boundaries in the etched products. In longer runs of run products reveal both polycrystallinity and loss of 110 orientation in the pure Fe half of the couple. In experiment 6, a diffusion couple run at 10 kb, 1400°C and one of the shortest runs in this study (19 h), the grain size near the couple interface was large (150–300 μm), as defined by clear grain boundaries in the etched products. In longer runs

![Comparison of published diffusion data for Ni, Co, and Cu in γ Fe](image)

Fig. 1. Summary of diffusion data for Ni, Co, and Cu in γ Fe. The order of magnitude range of the data reflects the effects of various factors such as grain size and crystallinity (single crystal or polycrystalline), metal composition (purity), experimental technique (thin film, nuclear, or diffusion couple), and analytical technique (electron microprobe, or other X-ray techniques). Ni data sources are Hirano et al. (1961): single crystal, thin layer residual activity method; Badia and Vignes (1969): polycrystalline, diffusion couple and thin layer autoradiography; and Mehrer (1995): polycrystalline, thin layer residual activity. Co data sources are Henry et al. (1975): polycrystalline, residual activity method; and Badia and Vignes (1969): polycrystalline, diffusion couple and thin layer autoradiography. Cu data sources are Mehrer (1995): polycrystalline, diffusion couple and EMPA; Rothman et al. (1968), single crystal, thin layer sectioning and counting; Salje and Feller-Kniepeimer (1977): single crystal, thin layer and EMP A; and Majima and Mitani (1978): polycrystalline, thin layer residual activity method. The end points of temperature ranges covered in these studies are capped with a symbol. 

<table>
<thead>
<tr>
<th>Element</th>
<th>Coahuila II A iron</th>
<th>Springwater pallasite*</th>
<th>Fe metal^</th>
<th>QUE 94411 core^</th>
<th>QUE 94411 rim^</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>2800</td>
<td>–</td>
<td>1.3</td>
<td>1200</td>
<td>3100</td>
</tr>
<tr>
<td>Cr</td>
<td>40</td>
<td>–</td>
<td>1.9</td>
<td>1500</td>
<td>2100</td>
</tr>
<tr>
<td>Co</td>
<td>4590</td>
<td>5950</td>
<td>8.3</td>
<td>4600</td>
<td>3200</td>
</tr>
<tr>
<td>Ni</td>
<td>55100</td>
<td>126000</td>
<td>2.9</td>
<td>59000</td>
<td>122000</td>
</tr>
<tr>
<td>Cu</td>
<td>140</td>
<td>153</td>
<td>1.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ga</td>
<td>57.6</td>
<td>19.2</td>
<td>0.37</td>
<td>&lt;4</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Ge</td>
<td>178</td>
<td>32.4</td>
<td>1.7</td>
<td>&lt;4</td>
<td>&lt;4</td>
</tr>
<tr>
<td>As</td>
<td>–</td>
<td>27.8</td>
<td>0.08</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ru</td>
<td>23.4</td>
<td>0.82</td>
<td>&lt;0.005</td>
<td>3.7</td>
<td>12.4</td>
</tr>
<tr>
<td>Pd</td>
<td>1.81</td>
<td>6.25</td>
<td>&lt;0.01</td>
<td>3.3</td>
<td>3.8</td>
</tr>
<tr>
<td>Ir</td>
<td>18.17</td>
<td>61.9</td>
<td>&lt;0.01</td>
<td>2.8</td>
<td>6.9</td>
</tr>
<tr>
<td>Pt</td>
<td>51.77</td>
<td>1.58</td>
<td>&lt;0.01</td>
<td>4.9</td>
<td>11.7</td>
</tr>
<tr>
<td>Au</td>
<td>0.76</td>
<td>2.78</td>
<td>&lt;0.05</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>C</td>
<td>100</td>
<td>n.a.</td>
<td>0.0015</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>S</td>
<td>20</td>
<td>n.a.</td>
<td>3.5</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

* from Campbell et al. (2001) and Herzog et al. (2000); *Davis (1977).
^ provided by Alfa Aesar; C and S data for Coahuila from compilation of Buchwald et al. (1975).
such as experiments 19 or 20 (84 h), grain boundaries are not evident, indicating that the annealing process has coarsened grain size even further. Diffusion profiles were thus acquired across single crystal interfaces. Additionally, when grain boundaries are crossed in a diffusion profile, there is typically a small peak within the profile (e.g., Dean and Goldstein, 1986; for phosphorus). We did not observe any such peaks in our profiles.

### 3. ANALYTICAL

Polished sections of the run products were examined using scanning electron microscopy (SEM). No phosphide rhabdites, sulfides, or chromites were observed in the run products. Small MgO grains from the sample assembly occasionally occurred along the diffusion interface and were identified using the SEM and avoided, because they could affect the diffusion process across the interface. In most cases the low, natural concentrations of siderophile elements were lower than the detection limits of electron microprobe analysis (~100 ppm). Diffusion profiles were measured using an electron microprobe for major elements (Ni, Co, P), and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for trace elements (Fig. 3).

Iron, Ni, Co, and P were analyzed with a CAMECA SX-50 electron microprobe at the University of Arizona, using an accelerating voltage of 15 kV and beam current of 20 nA. Standards include Fe, Ni, Co, and GaP and KOVAR metal (FeNiCo alloy). PAP $\delta$-rho-$z$ corrections were used in the data reduction (Pouchou and Pichoir, 1991).

Diffusion profiles for trace elements were measured using LA-ICP-MS. A CETAC LSX-200 laser ablation peripheral (Nd:YAG 266 nm) was used for solid sample introduction into a magnetic sector ICP-MS, the Finnigan Element, at the University of Chicago. Isotopes monitored were $^{59}$Co, $^{60}$Ni, $^{61}$Cu, $^{67}$Ga, $^{74}$Ge, $^{75}$As, $^{102}$Ru, $^{105}$Pd, $^{193}$Ir, $^{195}$Pt, and $^{197}$Au. The laser spot size was 15 $\mu$m, and profiles were obtained using a scan rate of 5 $\mu$m/s. Mass sweeps were completed every ~0.75 s, and data points represent an average over several mass sweeps.

Instrumental sensitivity correction factors for each isotope were determined by measuring signal intensity from metal standards that have known concentrations of the elements of interest; these included the IVB iron meteorite Hoba, the IIA iron meteorite Filomena, and the NIST standard reference materials 1158 and 1263a (Campbell et al., 2001; Campbell et al., 2002). Averages of at least five measurements from each standard were used in the calibrations. The corrected intensities were converted to elemental abundances by normalization to $^{56}$Fe + $^{58}$Fe + $^{59}$Fe = 100 wt%. Precision of the LA-ICP-MS measurements of platinum group elements was typically +/-11% (1σ), based on repeat measurements of the Hoba standard. Counting statistics contributed a significant proportion (typically ~40%) to the variance. The suitability of the grain size and other aspects of iron meteorites for use as standards as well as the precision and accuracy of analyses of a variety of trace elements in natural metals have been discussed earlier (Campbell and Humayun, 1999; Campbell et al., 2002).

### 4. RESULTS

Diffusion profiles for these experiments are defined both by electron microprobe analyses of Ni, Co, or P, and by LA-ICP-MS analyses of trace metals such as Ru. The profiles obtained had constant composition at each end of the diffusion interface (Fig. 3), and the diffusion coefficients were derived...
Table 2. Summary of experimental run conditions and diffusion coefficients (m²/s).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Pressure</th>
<th>Temperature (°C)</th>
<th>Duration (hrs)</th>
<th>Couple</th>
<th>Coahuila</th>
<th>Springwater</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>1 bar</td>
<td>1150</td>
<td>123</td>
<td>20</td>
<td>Coahuila</td>
<td>Coahuila</td>
</tr>
<tr>
<td>19</td>
<td>1 bar</td>
<td>1200</td>
<td>84</td>
<td>17</td>
<td>Coahuila</td>
<td>Coahuila</td>
</tr>
<tr>
<td>20</td>
<td>1 bar</td>
<td>1255</td>
<td>84</td>
<td>19</td>
<td>Coahuila</td>
<td>Springwater</td>
</tr>
<tr>
<td>15</td>
<td>1 bar</td>
<td>1300</td>
<td>84</td>
<td>4</td>
<td>Coahuila</td>
<td>Coahuila</td>
</tr>
<tr>
<td>11</td>
<td>10 kbar</td>
<td>1350</td>
<td>3.5</td>
<td>6</td>
<td>Coahuila</td>
<td>Coahuila</td>
</tr>
<tr>
<td>10</td>
<td>10 kbar</td>
<td>1400</td>
<td>90</td>
<td>11</td>
<td>Coahuila</td>
<td>Coahuila</td>
</tr>
<tr>
<td>14</td>
<td>10 kbar</td>
<td>1400</td>
<td>19</td>
<td>14</td>
<td>Coahuila</td>
<td>Coahuila</td>
</tr>
<tr>
<td>12</td>
<td>10 kbar</td>
<td>1200</td>
<td>76</td>
<td>10</td>
<td>Coahuila</td>
<td>Coahuila</td>
</tr>
<tr>
<td>13</td>
<td>10 kbar</td>
<td>1250</td>
<td>72</td>
<td>11</td>
<td>Coahuila</td>
<td>Coahuila</td>
</tr>
<tr>
<td>16</td>
<td>10 kbar</td>
<td>1200</td>
<td>12</td>
<td>14</td>
<td>Coahuila</td>
<td>Coahuila</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Experiment</th>
<th>Pressure</th>
<th>Temperature (°C)</th>
<th>Duration (hrs)</th>
<th>Concentration (C0, C1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>18</td>
<td>1 bar</td>
<td>1150</td>
<td>123</td>
<td>20.80(1.30)E-14</td>
</tr>
<tr>
<td>Cr</td>
<td>18</td>
<td>1 bar</td>
<td>1150</td>
<td>123</td>
<td>2.19(0.25)E-14</td>
</tr>
<tr>
<td>Co</td>
<td>18</td>
<td>1 bar</td>
<td>1150</td>
<td>123</td>
<td>2.19(0.25)E-14</td>
</tr>
<tr>
<td>Ni</td>
<td>18</td>
<td>1 bar</td>
<td>1150</td>
<td>123</td>
<td>2.19(0.25)E-14</td>
</tr>
<tr>
<td>Cu</td>
<td>18</td>
<td>1 bar</td>
<td>1150</td>
<td>123</td>
<td>2.19(0.25)E-14</td>
</tr>
<tr>
<td>As</td>
<td>18</td>
<td>1 bar</td>
<td>1150</td>
<td>123</td>
<td>2.19(0.25)E-14</td>
</tr>
<tr>
<td>Ru</td>
<td>18</td>
<td>1 bar</td>
<td>1150</td>
<td>123</td>
<td>2.19(0.25)E-14</td>
</tr>
<tr>
<td>Pd</td>
<td>18</td>
<td>1 bar</td>
<td>1150</td>
<td>123</td>
<td>2.19(0.25)E-14</td>
</tr>
<tr>
<td>Ir</td>
<td>18</td>
<td>1 bar</td>
<td>1150</td>
<td>123</td>
<td>2.19(0.25)E-14</td>
</tr>
<tr>
<td>Pt</td>
<td>18</td>
<td>1 bar</td>
<td>1150</td>
<td>123</td>
<td>2.19(0.25)E-14</td>
</tr>
<tr>
<td>Au</td>
<td>18</td>
<td>1 bar</td>
<td>1150</td>
<td>123</td>
<td>2.19(0.25)E-14</td>
</tr>
</tbody>
</table>

1σ error is shown in parentheses and is based on linear fits as in Figure 4.

### 4.1. Interdiffusion: Ni and Co

Because one side of the diffusion couples is pure Fe metal and the Coahuila metal contains relatively high concentrations of Ni and Co, there might be compositional effects on the diffusion of these elements. Because the difference in composition is small (0 vs. 6 wt% for Ni and 0 vs. 0.5 wt% for Co), the effect is likely to be small but the magnitude of the effect is nonetheless of interest for comparison to other studies. To illustrate the magnitude of the compositional effect for Ni and Co, Boltzmann-Matano analysis was carried out on run 18, a diffusion couple run at 10 kb, 1150°C, and 123 h. Using the Boltzmann solution of Fick's second law:

\[
C(x,t) = C_0 \left(1 - \text{erf}\left(\frac{x}{\sqrt{4Dt}}\right)\right)
\]

where \(C_0\) and \(C_1\) are the concentrations at the interface (or midplane) \(x = 0\), therefore, was found as

\[
C_1 = C_0 \left(1 + \frac{1}{2} \text{erf}\left(-\frac{x}{\sqrt{4Dt}}\right)\right)
\]

The discussion that follows will be split into two parts. The first part involves a discussion of all other elements, which are treated as a case of interdiffusion. The second part involves the compositional dependence of the diffusion coefficient (of element i) is governed by Fick's Second Law, assuming diffusion in a semi-infinite medium (Fig. 4). The inverse of the complementary error function, \(\text{erfc}^{-1}\), was determined using a generalized power series solution from the application Mathematica (Wolfram Research, Inc. Champaign, IL). The position of the Matano interface (or midplane), \(x = 0\), was calculated using the Boltzmann-Matano solution of Fick's second law:

\[
D = \frac{1}{2} \int_0^x C(\mu) \right d\mu
\]

where \(C(x)\) is the concentration at a given \(x\), and \(C_1\) is the concentration at \(x > 0\). The inverse of the complementary error function, \(\text{erfc}^{-1}\), was determined using a generalized power series solution from the application Mathematica (Wolfram Research, Inc. Champaign, IL). The position of the Matano interface (or midplane), \(x = 0\), was calculated using the Boltzmann-Matano solution of Fick's second law:

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D = \frac{1}{2} \int_0^x C(\mu) \right d\mu
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D = \frac{1}{2} \int_0^x C(\mu) \right d\mu
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D = \frac{1}{2} \int_0^x C(\mu) \right d\mu
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D = \frac{1}{2} \int_0^x C(\mu) \right d\mu
\]

where \(C(x)\) is the concentration at a given \(x\), and \(C_1\) is the concentration at \(x > 0\). The inverse of the complementary error function, \(\text{erfc}^{-1}\), was determined using a generalized power series solution from the application Mathematica (Wolfram Research, Inc. Champaign, IL). The position of the Matano interface (or midplane), \(x = 0\), was calculated using the Boltzmann-Matano solution of Fick's second law:

\[
D = \frac{1}{2} \int_0^x C(\mu) \right d\mu
\]
The diffusion coefficient was calculated for three different compositions (Fig. 5). The positive dependence of $D(Ni)$ on the Ni content of the FeNi alloy is expected, based on previous work such as Goldstein et al. (1965). The minor effect here, over a small compositional range, is noted. Because the focus of this study is on relative differences in $D$, this minor effect over a small compositional range will be ignored.

4.2. Tracer Impurity Diffusion

Based on the previous assessment, the small Ni compositional gradient will have only a minimal effect on the diffusion coefficient for Ni. The effect of the Ni gradient on the diffusion of all other low concentration elements will be insignificant as well. Furthermore, because the composition of the couples is fixed for the experiments, the diffusion of all other elements can be treated as tracer impurity diffusion. Because the com-

![Fig. 3. Profiles of Ni (electron microprobe) and Ru (LA-ICP-MS) across the interface of experiment 15 and Ga (LA-ICP-MS) across experiment 18. Dashed lines are fits to the diffusion profiles using diffusion coefficients derived from Eqn. 2 (see text). $C_i$ and $C_0$ are calculated as averages of the points on the "plateau" on each side of the profile. Vertical dashed lines are the Matano interface (defined in text).](image-url)
position of the couples is fixed, this study can focus on relative differences in diffusion coefficients and lead to important distinctions in diffusion behavior between elements.

A summary of all diffusion coefficients determined in this study is presented in Table 2 and Figure 6, and split into the 1 bar and 10 kb experiments. There are four general groups of...
elements based on their relative diffusion coefficients. Phosphorus exhibits the highest diffusion coefficient (Fig. 6B), whereas Cr, Cu, Ga, Ge, and Au have lower values. Nickel, Co, Pd, and Ru all have intermediate values, while Ir has the lowest values, approximately a factor of 5 lower than Ni. These very general groupings will be useful when simultaneously examining zoning patterns of all of these elements in meteoritic metal. The dependence of diffusion coefficients upon temperature can be fit to an Arrhenius equation, $D = D_0 \exp(\Delta H/RT)$, where $D_0$ is the preexponential factor, $\Delta H$ is the activation enthalpy, and $R$ is the gas constant, 8.3144 J/mol K. A plot of logD vs. 1/T yields a slope that corresponds to $\Delta H$ and an intercept that corresponds to $D_0$ (Table 3).

At both 1 bar and 10 kb, the elemental groupings and relative diffusivities are similar, and there are a few additional data for As and Pt, indicating that these two elements are rapid and intermediate diffusers, respectively (Fig. 6). Although it is difficult to make a direct comparison because of different metal compositions (12.6% Ni in Springwater vs. 5.5% Ni in Coahuila; Table 1) and crystallinity, $D_{Pd}$ is similar in magnitude to $D_{Ni}$ and $D_{Pt}$, whereas $D_{As}$ is higher than $D_{Cu}$ and $D_{Ge}$ and is probably similar to $D_{P}$.
5. DISCUSSION

5.1. Comparison to Previous Work

The relative importance of diffusion in metals is illustrated by comparing diffusion data for Co in olivine (Morioka, 1980) and akermanite (Morioka and Nagasawa, 1991) to D(Co) in FeNi metal from this study (Table 2). Cobalt diffusion in taenite (from this study) is 100 times more rapid than Co diffusion in either olivine or akermanite (at a given temperature). Thus, diffusion of siderophile elements in metals will be relatively rapid in mixed metal-silicate systems.

5.2. Nickel

Comparison can also be made to literature data for selected elements (Fig. 7). For instance, Goldstein et al. (1965) measured Ni diffusion coefficients in FeNi alloys and found that diffusion coefficients for Ni vary with Ni content; diffusion coefficients for Ni in Fe_{90}Ni_{10} metal are approximately a factor of 15 lower than those in Fe_{30}Ni_{70} metal. Our results for low Ni metal agree in general with this earlier work (Fig. 7A); however, there is a significant difference in slope, or activation energy. A main contributing factor to the differences (in slope or \( H \)) between this work and Goldstein et al. (1965) is the influence of phosphorus. Studies by Heyward and Goldstein (1973) and Dean and Goldstein (1986) have shown that diffusion of Ni in the ternary Fe-Ni-P system is faster than in the binary Fe-Ni, even with P contents as small as 0.25 wt%. The

<table>
<thead>
<tr>
<th>Element</th>
<th>( D_0 ) (m²/s)</th>
<th>Error</th>
<th>( H ) (kJ/mole)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>( 1.22 \times 10^{-4} )</td>
<td>1.5 \times 10^{-5}</td>
<td>-287</td>
<td>50</td>
</tr>
<tr>
<td>Co</td>
<td>( 7.19 \times 10^{-7} )</td>
<td>2.3 \times 10^{-8}</td>
<td>-231</td>
<td>40</td>
</tr>
<tr>
<td>Ni</td>
<td>( 2.25 \times 10^{-6} )</td>
<td>1.1 \times 10^{-7}</td>
<td>-245</td>
<td>35</td>
</tr>
<tr>
<td>Cu</td>
<td>( 7.11 \times 10^{-8} )</td>
<td>1.5 \times 10^{-9}</td>
<td>-185</td>
<td>35</td>
</tr>
<tr>
<td>Ga</td>
<td>( 5.92 \times 10^{-6} )</td>
<td>1.3 \times 10^{-7}</td>
<td>-240</td>
<td>48</td>
</tr>
<tr>
<td>Ge</td>
<td>( 1.12 \times 10^{-5} )</td>
<td>0.6 \times 10^{-6}</td>
<td>-246</td>
<td>66</td>
</tr>
<tr>
<td>Ru</td>
<td>( 3.92 \times 10^{-6} )</td>
<td>1.2 \times 10^{-7}</td>
<td>-258</td>
<td>28</td>
</tr>
<tr>
<td>Pd</td>
<td>( 5.24 \times 10^{-9} )</td>
<td>1.5 \times 10^{-10}</td>
<td>-170</td>
<td>53</td>
</tr>
<tr>
<td>Ir</td>
<td>( 7.45 \times 10^{-10} )</td>
<td>2.5 \times 10^{-11}</td>
<td>-168</td>
<td>44</td>
</tr>
<tr>
<td>Au</td>
<td>( 2.48 \times 10^{-5} )</td>
<td>1.0 \times 10^{-6}</td>
<td>-263</td>
<td>31</td>
</tr>
</tbody>
</table>

Error cited is based on 90% confidence limits for the calculated coefficients.

![Fig. 7](image-url)
lower activation energy has been attributed to the effect of Group Va metals such as P, As, and Sb that increase vacancy density, and therefore enhance diffusivity (Dean and Goldstein, 1986). Dean and Goldstein (1986) argued that P-bearing Fe-Ni metal would promote diffusion of many elements since the P acts to decrease the vacancy formation energies and thus increase the vacancy concentration. Since our couples have a small amount of P, the differences in activation energy (or slope) are likely due to P concentrations rather than Fe/Ni ratios.

5.3. Chromium, Cobalt, Palladium, and Ruthenium

Comparison of D(Cr), D(Co), D(Pd), and D(Ru) from the literature (e.g., compilation of Mehrer, 1995) illustrates the dangers of assembling data from various sources and techniques to interpret relative elemental variations in natural samples. For instance, literature values for D(Cr) and D(Fe) show large differences at a given temperature, yet our results show only a modest difference of ~4 (Fig. 7B). Furthermore, literature data for Ru and Pd would suggest similar diffusion coefficients at 1150°C (Fig. 7C). However, our results show a clear and significant difference in their diffusion coefficients at temperatures <1250°C (Fig. 7C). The shallower slope of D(Pd) vs. 1/T for our results compared to literature studies could also be due to the effect of phosphorus (Dean and Goldstein, 1986), as discussed above for D(Ni). Finally, measurements of D(Ru) in Ni-rich metal were made by Blum et al. (1989). Our results for D(Ru) across similar temperatures are nearly identical (Fig. 7C), suggesting that Ni content has only a small effect on D(Ru) in the FeNi system.

5.4. Copper, Gold and Iridium

Comparison of D(Cu) to results of Watson and Watson (2003) indicates agreement at temperatures of overlap between the two studies. However, D(Pd) and D(Au) are lower by nearly an order of magnitude at all temperatures investigated in our study (Fig. 7D). Most of this difference is likely due to two effects. First the Ni content in our metal (5–6 wt%) is slightly lower compared to that in their study (10 wt%). Second, much of the disparity could be due to differences in the concentrations of diffusing element. In contrast to the natural abundances employed in the present study, Watson and Watson (2003) used 1 to 2 wt% levels of siderophile elements in their diffusion couples. Higher doping levels are known in other systems to increase diffusivity (e.g., Ni in Goldstein et al., 1965). Finally, D(Ir) from our studies and previously reported D(Os) coefficients (Watson and Watson, 2001) show a similarly low relative value to D(Ni), indicating that Ir and Os have relatively low-diffusion coefficients, as might be expected given other similarities in their chemical properties (e.g., Shirey and Walker, 1997).

In summary, the absolute differences in D(Ru), D(Pd), D(Au), D(Fe), and D(Cr) between the various studies and our work are most likely due to differences in metal composition and tracer impurity concentrations, but defect density and crystallinity could also play a role. Measuring multiple elements in a single run improves interelement comparisons and is one of the strengths of our approach and dataset.

5.5. Comparison to Stokes-Einstein Equation Estimates

The Stokes-Einstein equation is sometimes used to estimate diffusion coefficients in the absence of data. The Stokes-Einstein equation predicts that the diffusivity of i through medium j (\(D_{ij}\)) is inversely proportional to the atomic radius of the diffusing species, \(R_i\) according to: \(D_{ij} \mu_j / kT = 1/6 \pi \eta R_i\) (where \(\mu_j\) is viscosity, \(\kappa\) is Boltzmann constant, and \(T\) is temperature; Bird et al., 1960). However, our diffusion data show that this approach is not rigorous and would lead to erroneous values of \(D\). Although there is an inverse correlation evident in a subset of elements such as Cr, Cu, Ge, Ru, Pd, and Ir, there are some glaring exceptions such as Ga and Au, all of which have high D’s but also large atomic radii (Fig. 8).

Comparison of diffusion coefficient and melting point temperature of the pure metal shows some correlation, as expected from diffusion theory (e.g., Shewmon, 1963). Although there are some trends with melting point, there are some notable exceptions such as Cr and Ga. In summary, Figure 8 shows that there are no systematic trends of \(D\) with atomic radius, crystal structure, or melting point, demonstrating the advantage of measuring diffusion coefficients over theoretical predictions.

5.6. Effect of Pressure

Our series of experiments at 10 kbar can be compared with our 1 bar data to make an assessment of the effect of pressure (Fig. 9). There is approximately one order of magnitude decrease in D(Ni) between 1 bar and 10 kbar. This decrease is in accord with results of Goldstein et al. (1965), who showed a slightly larger decrease for D(Ni) in metal of composition Fe90Ni10 at 40 kbar (Fig. 9A). Similarly, the values for D(Ga), D(Co), D(Ru), and D(Ir) are a factor of 3 to 10 higher at 1 bar than at 10 kbar, depending on the temperature of comparison (Table 2 and Fig. 9B). This is consistent with the results of Watson et al. (2003), who also showed a decrease in D(Pd) and D(Au) from 1 bar to pressures up to 200 kbar.

6. ORIGIN OF ZONED METAL GRAINS IN CHONDRITES

Zoned metal grains have been found in several different chondrite groups, including CH chondrites and the Bencubbin-like group (e.g., Hammada al Hamra (HH) 237 and Queen Alexandra Range (QUE) 94411). The metal grains are zoned in major elements such as Fe, Ni, Co, and P (Weisberg et al., 1995; Meibom et al., 1999; Campbell et al., 2001) as well as trace elements such as Mo, Cr, and the highly siderophile elements (HSE; Ru, Ir, Os, Rh, Pd, Pt, Re, and Au) (Campbell et al., 2001). Refractory elements are enriched in the cores and depleted in the rims, and volatile elements such as Cr and P have a reversed zoning pattern with high concentrations at the rims. Several different origins of these striking grains have been proposed. Initial models proposed an origin by fractional condensation from solar nebular gas (e.g., Newsom and Drake, 1979; Meibom et al., 1999; Weisberg and Prinz, 1999; Petaev et al., 2000; Meibom et al., 2001; Petaev et al., 2003). A second hypothesis, proposed by Campbell et al. (2001), is that the condensation of metal from a cooling gas would have to be in the presence of a gas saturated with refractory elements. Otherwise, the gas would be depleted early in refractory siderophile elements given their higher condensation temperatures,
leading to superenriched cores and depleted rims. A third hypothesis was proposed by Campbell et al. (2001) and followed on from the second scenario—early condensing metal grains have refractory siderophile element enriched cores and Fe-rich rims and were later reequilibrated by diffusional processes. Diffusion coefficients determined in this study can be used to place limits on the timescales of these hypotheses, especially since the diffusion behavior of the elements studied falls into several broad groups: fast (Cr, Cu, Au, and P), intermediate (Ni, Co, Ru, and Pd), and slow (Ir) diffusers.

Because Au, Cr, Cu, and P commonly have flat or reverse profiles in grains that are otherwise zoned in Ni, Co, Ru, Rh, Os, and Ir (Campbell et al., 2001; Campbell and Humayun, 2004), and these elements have higher diffusion coefficients than the latter (this study), these two groups of elements may provide information about the cooling rates and time required to preserve zoning in some grains but not others.

Diffusion coefficients reported by previous workers for Ni and Co in taenite are up to an order of magnitude different (Fig. 1), yet they are always identical in experiments from this study. Some of the variation may be due to differences in crystallinity and grain size, experimental technique, or metal composition.
Some diffusion data reported in the literature is for polycrystalline metal, and any estimates of diffusion length scales utilizing such data will be overestimated. For example, the literature diffusion coefficients for Ni and Co in taenite utilized by Meibom et al. (2001) are a factor of 3 higher for Ni than Co, yet our results show little difference (e.g., $D_{\text{Ni}}$ and $D_{\text{Co}}$ are nearly identical, within a factor of 1.3 to 1.9) at all temperatures investigated indicating that Ni/Ru ratios will also not strongly fractionate during diffusional reequilibration (Fig. 10). Thus, diffusion of Ni, Co, and Ru in taenite will not strongly fractionate Ni/Co or Ni/Ru ratios (Fig. 10).

On the other hand, the large difference in $D_{\text{Ni}}$ and $D_{\text{Ir}}$ ($D_{\text{Ir}}$ is $\sim$5 times lower) at all temperatures investigated indicates that Ni/Ir ratios in zoned metal grains may be useful discriminators of whether diffusion has occurred (Fig. 10). Because $D_{\text{Ni}}$ is greater than $D_{\text{Ir}}$, any diffusive reequilibration of metal con-

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densed from a solar nebular gas would produce a zoning pattern with relatively Ni-poor and Ir-rich metal (i.e., lower Ni/Ir ratios than initial).

Many CR, CH, and CB chondrites contain unzoned as well as zoned metal grains, and if diffusional reequilibration is involved in producing the unzoned grains, limits can be placed on the timescale of this process by considering the new diffusion data. Estimates of the timescale for diffusive reequilibration can be made using a simple model for diffusion in a sphere (Crank, 1975). As a sphere with a concentration gradient from surface to center undergoes diffusive reequilibration, $Dt/a^2$ (where $t$ is time and $a$ is radius) approaches 0.4 as the concentration profile is flattened or erased (Crank, 1975). By monitoring this value ($Dt/a^2$) during a cooling path, we can estimate how long a zoned metal grain can exist under specific conditions, or how much time would be required to flatten a metal grain profile with an initially HSE-rich core. Using the new diffusion coefficients for Cr, Ni, and Ir, representing fast, intermediate, and slow diffusing elements in this study, the time required to eliminate a primary zoning pattern (from either hypothesis 1, 2, or 3 from above) during cooling of a taenite grain can be calculated. Assuming a 150 μm radius grain, with an initial temperature of 1373 K and a cooling rate of 0.011 + 0.022$\Delta T$ K/h (based on the model of Petaev et al., 2003), and using the temperature dependence of 1 bar diffusion coefficients determined in this study (Tables 2 and 3), Cr, Ni, and Ir profiles will be flattened by diffusion in 75, 105, and >115 d, respectively. For this calculation, $Dt/a^2$ is calculated at each step of the cooling path, and the times correspond to 50 steps ($\Delta T = 2°C$), 72 steps ($\Delta T = 10°C$), and >80 steps ($\Delta T = 20°C$), respectively. The value for Ir represents a lower limit because Ir diffuses so slowly; it is unlikely that Ir zoning patterns would be erased unless cooling was extremely slow. Two of the other fast diffusers, Ga and Au, both equilibrate faster than Cr on timescales of 25 to 40 d.

This demonstrates that whatever process was responsible for preserving the zoning patterns measured in QUE 94411 metal grains could have involved slow cooling for a short period time of time (<100 d at ~0.01 K/h) before a rapid temperature drop to preserve zoning in Ir and Ni. This is consistent with the calculations of Meibom et al. (2001), in which it is shown that metal grains of this size can grow in 84 h or less. On the other hand, the production of unzoned metal grains documented in some meteorites (e.g., PCA91467 and ALH85085; Campbell and Humayun, 2004) by a diffusion-controlled process would require >120 d along a slow cooling path to ensure no zoning of slow-diffusing elements such as Ir or Os.

7. FUTURE AND CONCLUSIONS

Zoning and composition of metal grains in chondrites can be caused by a number of different factors, such as growth rates, diffusion, reequilibration with a gas, gas/dust ratios, and nebular pressures. The simple modeling in this contribution illustrates the important role defined by diffusional processes, but the zoned metal grains should be evaluated using a more detailed model that combines metal grain nucleation, condensation, growth, diffusion, and cooling histories similar to that of Petaev et al. (2003). In addition, generalized expressions relating temperature, pressure, and metal composition for diffusion coefficients would have a very widespread and useful application to many problems in meteoritics. However, too many gaps in the present experimental coverage of such parameters preclude the derivation of such expressions. Nonetheless, it is clear that these new data have placed constraints on the required timescales of diffusional equilibration and reequilibration in producing zoned metal grains.

These new data will also be useful in evaluating a variety of processes in metal-bearing planetary materials such as isotopes and chronometry, redox processes, and kamacite/taenite based cooling rates. For instance, metal occurs in planetary materials
in a variety of textures and grain sizes, such as small inclusions in chondrules (Grossman and Wasson, 1985), zoned metal grains (70 – 200 μm; Weisberg et al., 1995), lamellae in iron meteorites (Buchwald, 1975), metal chondrules (1 – 3 mm) in Bencubbin (Weisberg et al., 1990), metal nodules in aubrites (cm sized; Casanova et al., 1993), metal veins in acapulcoites (McCoy et al., 1996), and metal-rich clasts in mesosiderites (up to 3 cm; Mittlefehldt et al., 1998). The time required for diffusional reequilibration of metals in such materials can vary from less than a year (small grains) to hundreds of years (cm-sized metal clasts), at temperatures <1100°C, and up to millions of years for subsolidus equilibration (octahedrites).

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