DIFFUSION OF SIDEROPHILE ELEMENTS IN Fe METAL: APPLICATION TO ZONED METAL GRAINS IN CHONDRITES.

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Introduction

The distribution of highly siderophile elements in planetary materials is controlled mainly by metal. Diffusion processes can control the distribution or re-distribution of these elements within metals, yet there is little systematic or appropriate diffusion data that can be used to interpret HSE concentrations in such metals. Because our understanding of isotope chronometry, redox processes, kamacite/taenite-based cooling rates, and metal grain zoning would be enhanced with diffusion data, we have measured diffusion coefficients for Ni, Co, Ga, Ge, Ru, Pd, Ir and Au in Fe metal from 1200 to 1400 °C and 1 bar and 10 kbar. These new data on refractory and volatile siderophile elements are used to evaluate the role of diffusional processes in controlling zoning patterns in metal-rich chondrites.

Experimental

Diffusion couples were prepared from high purity (99.995%; Alfa Aesar) Fe metal rod and metal from the IIA iron meteorite Coahuila or the pallasite Springwater. Faces of the metal rod and meteorite were polished, coupled and then sheathed in MgO. Metal couples for the 1 bar runs were annealed for one hour at 10 kbar and final run temperature. The metal couple plug was then placed in an alumina crucible within an evacuated silica tube, and held at run temperature (at 1 bar) for 24 to 150 hours, depending upon the temperature. Run products were then mounted in epoxy, cut perpendicular to the couple interface, polished and analysed using either electron microprobe or laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

Knowledge of sample crystallinity is important in diffusion studies, as grain boundary diffusion can occur and it enhances diffusion rates. Springwater pallasite metal plugs are initially polycrystalline, whereas the Coahuila and pure Fe metal are initially single crystals. However, at run conditions, these metals are transformed into coarse-grained polycrystalline taenite. For several runs, the crystallinity of a sample was examined by etching a polished surface with HF; in this way the grain boundaries were identified and grain size could be compared to the length of a typical diffusion profile (150 to 300 μm). The grain size in these cases was larger than the length of a diffusion profile and diffusion profiles were acquired across single crystal interfaces.

Analytical

Diffusion profiles were measured using an electron microprobe for major elements (Ni, Co, P), and LA-ICP-MS for trace elements [1]. Iron, Ni, Co and P were analyzed with a CAMECA SX50 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. PAP $\phi-\rho-Z$ corrections were used in the data reduction. 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 ThermoFinnigan Element, at the University of Chicago. Isotopes monitored were ^{59}Co, ^{60}Ni, ^{63}Cu, ^{69}Ga, ^{74}Ge, ^{101}Ru, ^{105}Pd, ^{193}Ir, and ^{197}Au. The laser spot size was 15 microns, and profiles were obtained using a scan rate of 5 microns per second. Mass sweeps were completed every approximately 0.75 seconds, 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 (see [1] and discussion in [2,3]). The corrected intensities were converted to elemental abundances by normalization to [Fe] + [Co] + [Ni] = 100 wt%. Precision of the LA-ICP-MS measurements of PGE's was typically +/- 11 % (1 sigma), based on repeat measurements of the Hoba standard. Counting statistics contributed a significant proportion to the variance, typically 7%.

Application to zoned metal grains

Zoned metal grains have been found in many different chondrite groups, including CH chondrites, the Bencubbinite group, HH 237, QUE 94411 and LEW 85332. The metal grains are

zoned in major elements such as Fe, Ni, Co and P [4-6] as well as trace elements such as Ru, Ir, Os, Rh and Pt [2]. Several different origins of these striking grains have been proposed, including: a) equilibrium fractional condensation from solar nebular gas [4], b) reduction of Fe during chondrule formation [7], c) non-equilibrium fractional condensation [2, 8], d) diffusion between HSE-rich cores and HSE depleted rims [2], and hybrid models of condensation and diffusion [8].

Application of our new diffusion data shows that diffusion is unlikely to have played a significant role in establishing the zoning in the metal grains.

Ni and Co: Although nearly solar Ni/Co ratios in zoned metal grains have been used to argue for a primitive condensation origin for these grains [4, 9], significant deviations from solar Ni/Co values indicate operation of a process in addition to equilibrium condensation from a solar gas. Some investigators (e.g., [6]) have argued that diffusion may be responsible. Diffusion coefficients for Ni in polycrystalline taenite [10] are up to 50x higher than those for single crystal taenite [this study], presumably due to grain boundary diffusion. Much of the diffusion data from the literature is for polycrystalline metal, indicating that estimates of diffusion lengthscales utilizing literature diffusion data will overestimate diffusion lengthscales by a factor of at least 10, and probably much more. Furthermore, the literature diffusion coefficients [10] are a factor of 3 higher for Ni than Co (in taenite), yet our results show little difference at any given temperature (e.g., D_{Ni} and D_{Co} ~ 1.1×10^{-14} m^2/s at 1300 °C). Thus, diffusion of Ni and Co in a zoned metal grain will not fractionate the Ni/Co ratio, and deviations from a solar Ni/Co ratio must either be primary, or the result of another process.

Ni, Ru and Ir: The similarity of D_{Ni} and D_{Ru} at all temperatures investigated indicates that the Ni/Ru ratio will not be fractionated by diffusion either. On the other hand, the large difference in D_{Ni} and D_{Ir} (D_{Ir} is ~5x lower; Figure 1) indicates that Ni/Ir ratios could be fractionated during diffusional re-equilibration. However, no such fractionation is observed in zoned metal grains. In fact, diffusional re-equilibration should produce lower than solar Ni/Ir ratios in the metals, but Ni/Ir measured by [2] are higher than solar. The zoning profiles of Ru and Ir observed by [2] show a slight depletion in the refractory elements at the high Ni end, which cannot be explained by diffusional trans-

port since Ir diffuses at very different rates relative to Ru and Ni.

The diffusion coefficients obtained in the present study are widely applicable to siderophile element distribution in meteoritic metal.
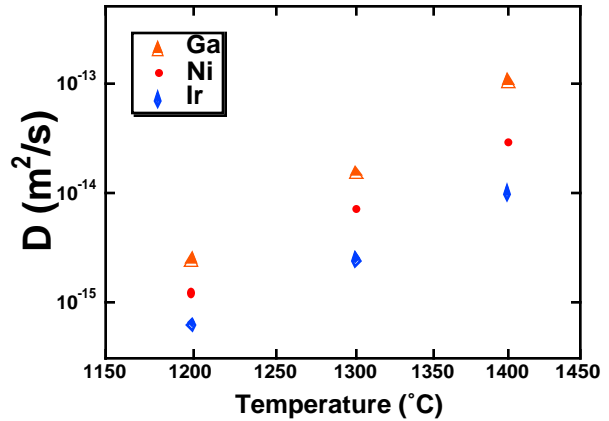

Figure 1: Diffusion coefficients for Ga, Ni and Ir in Fe metal, measured at 1200, 1300 and 1400 ºC and 10 kbar.

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