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Experimentally Determined Subsolidus Metal-Olivine Element Partitioning with Applications to Pallasites

Patrick H. Donohue^{a,*}, Eddy Hill^b, and Gary R. Huss^a

^aHawai'i Institute of Geophysics and Planetology, University of Hawai'i at Mānoa, 1680 East-West Road, POST 602, Honolulu, Hawai'i 96822, USA

^bLunar and Planetary Laboratory, University of Arizona, Tucson, Arizona 85721, USA

Abstract

Pallasite meteorites, which consist primarily of olivine and metal, may be remnants of disrupted core-mantle boundaries of differentiated asteroids or planetesimals. The early thermal histories of pallasites are potentially recorded by minor- and trace-element zonation in olivine. However, constraining this history requires knowledge of element behavior under the conditions of pallasite formation, which is lacking for many of the main elements of interest (e.g., Co, Cr, Mn). In this study, we experimentally determined metal/olivine partition coefficients for Fe, Ni, Co, Cr, and Mn in a pallasite analogue at subsolidus temperatures. Metal/olivine partition coefficients (K_M) increase in the order $K_{Mn} < K_{Cr} < 1 < K_{Fe} < K_{Co} < K_{Ni}$, with five orders of magnitude separating K_{Mn} from K_{Ni} . Transition metals also become more siderophile with increasing experimental temperature (900 to 1550°C). The experiments incidentally produced diffusion profiles in olivine for these elements; Our results suggest they diffuse through olivine at similar rates. Core compositions of pallasite olivines are consistent with high-temperature equilibration with FeNi-metal. Olivine zonation toward crystal rims varies significantly for the investigated transition metals. We suggest rim zonation results from partial re-equilibration during late stage crystallization of minor phases (e.g., chromite, phosphates). This re-equilibration occurred over short timescales relative to overall pallasite cooling, likely tied to initial cooling rates on the order of 100–300°C/Myr.

Keywords

experiments; metal-silicate partitioning; siderophile elements; SIMS

*Corresponding author. phd2@hawaii.edu.

Additional Information—The authors declare no competing financial interest.

Dedication: This study was initiated based on a conversation between Mike Drake and Gary Huss at a Gordon Conference in 2005. Drake knew that data on partitioning between metal and olivine was lacking and he wanted to fill this void. He and his Postdoc, Eddy Hill, designed and carried out the experimental work. Huss made the SIMS measurements. The project was nearing completion when Drake passed away in September 2011. We dedicate this paper to Mike Drake for originating this work and carrying out the experiments.

1. Introduction

Pallasite meteorites are, primarily, mixtures of high-Mg olivine and Fe-Ni metal. These stony-iron meteorites may have originated in core-mantle boundaries of now disrupted asteroids or planetesimals (Mason, 1962; Anders, 1964; Buseck and Goldstein, 1969). An origin in core-mantle boundaries is supported by textural and chemical evidence of slow cooling recorded in the Widmanstätten structures in Fe-Ni metal (intergrown taenite and kamacite lamellae). These patterns form at low-temperature (~550 to 300°C) and there is a recognized relationship between taenite-kamacite Ni diffusion profiles and cooling rate. Widmanstätten patterns in pallasites are calculated to form at cooling rates on the order of ~1–10 °C/Myr (Short and Goldstein, 1967; Buseck and Goldstein, 1969; Wood, 1979; Wasson and Choi, 2003). Above the temperatures at which these patterns form, there are few constraints on the thermal evolution of pallasites; for this, a thorough understanding of olivine may be key.

Olivine in pallasites exhibits chemical gradients in some elements (Fig. 1) that are generally assumed to result from diffusion at higher temperatures (above 800°C) during slow cooling as the system tries to reach equilibrium (Leitch et al., 1979; Miyamoto, 1997; Hsu, 2003; Tomiyama and Huss, 2005; Boesenberg et al., 2012). Some sort of disturbance or change in the olivine environment would be required to initiate the observed profiles. This disturbance could be a natural consequence of olivine transport into molten metal or metal injection into an olivine cumulate. Yet, while some minor elements are depleted at olivine margins (e.g., Cr, Co, Ni, Ca), others exhibit relatively flat profiles (e.g., Fe, Mn) or may increase toward rims (e.g., Mn, P) (Fig 1). Previous attempts to model zoning profiles by diffusion produced disparate cooling rates of 2000°C/Myr to >>10,000 °C/Myr (Buseck and Goldstein, 1969; Miyamoto, 1997; Hsu, 2003; Tomiyama and Huss, 2006). These rates are several orders of magnitude faster than those determined for the metallographic cooling rates discussed above. Such large differences in inferred cooling rates appear incompatible with a single stage model for formation of pallasites (i.e., simple mixing of olivine and metal). In addition, modeling of elements with different zonation profiles yields cooling rates that vary by up to two orders of magnitude (Hsu, 2003; Tomiyama and Huss, 2006). There is a clear disconnect between cooling rates obtained by metallographic *versus* zoning-profile-diffusion models that requires additional consideration of the changing chemical and thermal factors (i.e., boundary conditions) of an olivine-metal mixture.

Boundary conditions of diffusion in pallasites are dependent on the partitioning of elements between olivine and adjacent metal. Partition coefficients, in turn, may change over time, as they are variably dependent on temperature, pressure, crystal and melt compositions, and oxygen fugacity. Therefore, geochemical models require a clear understanding of partitioning over a range of environmental conditions. Mineralogy and mineral chemistry of siderophile elements place fO_2 in pallasites below the iron-wüstite (IW) buffer, likely around IW-1 (Dauphas et al., 2015). Ito and Ganguly (2006) determined there was little effect of fO_2 on Cr diffusion between IW and IW+2. The behavior of transition metals determined at higher fO_2 may not apply to pallasites due to varying partitioning behavior at different valence states (Jollands et al., 2016). Generally, metal-olivine trace-element partition coefficients (K) and diffusivities are determined in silicate-melt systems; Ehlers et al. (1992)

calculated $K_{Ni}^{met/ol}$ of 647 ± 73 (IW-0.4) and 1899 ± 298 (IW-2) in 1 atm, at $\sim 1300^\circ\text{C}$. However, cation behavior between metal and olivine in silicate-melt systems may not be directly applicable to the low-SiO₂ system compositions of pallasites (Petry et al., 2004; Zhukova et al., 2014). In addition, as the system cools, nucleation of new phases (e.g., phosphate, chromite) alters the interstitial composition. There are thus few studies of cation behavior for olivines in metal-rich systems that would help to constrain the thermal history of pallasites.

In this study, we determined metal–olivine element partitioning behaviors of Fe, Ni, Co, Cr, and Mn at temperatures and oxygen fugacity conditions analogous to pallasites. As an unintended byproduct, these experiments yielded compositional gradients that are treated as diffusion profiles. The partition coefficients that we found show that pallasites did not partition the elements exclusively between metal and olivine during single stage cooling. However, we find that chemical gradients in pallasites are consistent with partial re-equilibration at cooling rates on the order of $\sim 200^\circ\text{C}/\text{Myr}$. The reduced gap between cooling rates derived from olivine and metallographic relationships is consistent with a simple power-law decrease of cooling rate with time, which can be accommodated by insulation of pallasite precursors after mixing.

2. Methods

2.1 Starting Materials and Experimental Techniques

Pallasite analogues were created to match the predominantly forsteritic olivine (Mg_2SiO_4) and FeNi-metal composition of natural samples. Experiments were conducted at the Lunar and Planetary Laboratory (University of Arizona) between 2007 and 2010. Synthetic forsterite crystals ($\text{Mg}\# = 99.98$) were created at the University of Arizona. To account for compositional variability of pallasite metal, we used four metal alloys: Fe (Fe_{100}), Fe-Ni ($\text{Fe}_{86}\text{Ni}_{14}$), Fe-Co ($\text{Fe}_{92}\text{Co}_8$), and Fe-Ni-Co ($\text{Fe}_{78}\text{Ni}_{14}\text{Co}_8$). Pure metals (Fe, Co, and/or Ni) were mixed by grinding in an agate mortar in ethanol until dry. Manganese and Cr are present in trace amounts in the Fe powder.

Fragments of forsterite were mixed with metal alloys in MgO crucibles, and multiple charges for a given sequence were suspended in a single vertical-tube, gas-mixing furnace at 1 bar pressure. For our purposes, the 1 bar pressure used would be indistinguishable from the ~ 1 kbar pressure at the center of the largest planetesimals (Anders, 1964). Reducing conditions were maintained below the iron–wüstite buffer (at $f\text{O}_2 = \text{IW-1}$) using a H_2 - CO_2 gas mixture. Capsules (one for each metal alloy) were inserted into the hotspot of a single furnace at 1550°C and held at that temperature for one hour. This melted the metal, as the liquidus was $\sim 1480^\circ\text{C}$, $\sim 1500^\circ\text{C}$, and $\sim 1525^\circ\text{C}$ for the FeNiCo, FeNi, and FeCo alloys, respectively (Guillermot, 1989). The maximum temperature was below the forsterite solidus, simulating injection of olivine into metal-rich environment or vice versa. Peak temperatures of pallasites likely did not exceed ~ 1600 – 1700°C (Boesenberg et al., 2012). Temperature was monitored by thermocouples and controlled to better than $\pm 20^\circ\text{C}$. The temperature was subsequently lowered to the temperature of interest at a rate of 3°C min^{-1} , or maintained at 1550°C for high temperature runs. Experiment durations were initially extrapolated from the experiments of Petry et al. (2004), then dictated by the slow diffusion rate of elements into

olivine. The 900°C, 1300°C, and 1550°C experiments lasted for 1532, 570, and 354 hours, respectively. Sample charges were mounted in 502 Araldite epoxy, sectioned, and polished for petrographic and chemical analysis. Preliminary experiments using natural forsteritic olivine (Fig. 2a) resulted in the exsolution of metal at the experimental redox conditions. This exsolution formed beads and stringers up to 1 µm in diameter. To prevent formation of exsolution, the use of synthetic, pure forsterite in place of natural olivines in partitioning experiments has been shown to be viable (e.g., Ito et al., 1999).

Olivine and metal compositional profiles (Fig. 2b) were determined using electron microprobe analysis (EMPA) and secondary ion mass spectrometry (SIMS). The exposed surfaces of analyzed olivine grains ranged in length from 0.07 to 0.75 mm (Fig. 2b). The use of pure forsterite as starting material meant that all elements (except Si and Mg) diffused into the olivine from the metal, producing positive diffusion profiles in olivine. Dissolution of olivine crystals was not significant, but several charges precipitated discontinuous blebs of magnesiowüstite at the olivine-metal boundary. Magnesiowüstite likely precipitated because of the use of Mg-crucibles.

2.2 Analytical Setup

Samples were cut, polished, and carbon coated for characterization by EMPA, scanning electron microscopy (SEM), and SIMS analysis. Major- and minor-element compositions of starting olivine and run products were determined using a Cameca SX50 electron microprobe at the Lunar and Planetary Lab at the University of Arizona. A 1 µm beam size was used with 15 kV accelerating voltage and 20 to 40 nA beam current. Oxygen was calculated by stoichiometry. An acceptable analysis had analytical totals between 98.5 and 101.5 wt.% and a structural formula close to the ideal of M_2SiO_4 normalized to 4 oxygen units. Calibration was performed using repeat analyses of well-characterized standards at the beginning of each day. These standards were: Si, Mg: Forsterite; Mn: Rhodonite (rhod-791); Fe: Fayalite; Ni, Co, W: synthetic materials. An in-house synthetic steel standard (SN99-9) was used for Fe and Ni analyses in metal. Typical uncertainties for olivine standards, based on counting statistics, were < 1% of amount present for Si and Mg, < 2% for Fe, 5–10% for Ni, and 10–20% for Mn and Co. Nickel, Mn, and Co were often too low in experimental products to reliably measure by EMPA.

Trace-element compositions of experimental materials and run products were measured by SIMS using the Cameca ims 1280 ion microprobe at the W. Keck Cosmochemistry Lab at the University of Hawai'i (UH). An O^- beam was used to create positive ions for measurement. We measured ^{24}Mg , ^{30}Si , ^{52}Cr , ^{55}Mn , ^{57}Fe , ^{59}Co , and ^{60}Ni in mono-collection mode at a mass resolution (m/m) of ~7500, sufficient to separate molecular interferences. Before each measurement, the spot was pre-sputtered for 2 to 5 minutes using a 15–25 µm raster and a 1 to 4 nA beam to eliminate surface contaminants. Then the beam current was reduced to 0.25–0.5 nA (5–10 µm diameter) and the raster was reduced to ~5 µm for measurements. Typical measurement spots were 7–10 µm in diameter (Fig. 2), and 30 cycles were obtained for each spot. A field aperture corresponding to 25–37.5 µm on the sample was used, and the secondary-ion beam was automatically centered in the field

aperture. Magnetic-field centering and energy scans (to account for minor sample charging) were carried out at the beginning and in the middle of each measurement.

SIMS Olivine measurements were standardized to San Carlos olivine. The composition of our San Carlos olivine standard was, in weight percent, MgO, 48.74; SiO₂ 41.19; CaO, 0.069; Cr₂O₃, 0.027, MnO, 0.136; FeO, 9.64; CoO, 0.018; and NiO, 0.35. Magnesium was used for normalization. Multiple analyses of San Carlos olivine were performed at the beginning and/or end of analytical sessions. SIMS measurements of metal were standardized with respect to a series of metal standards, including three standards from NIST and four from the Collection of European Certified Reference Materials (EURONORM – CRM). The standards were NBS 868, NIST 1766, NIST 1173, BAM 181, BAM 182, BAM 194, and BAM 194; these cover a compositional range of Fe (40.5–99.9 wt.%), Cr (0.024–2.6 wt.%), and Mn (0.052–1.19 wt.%). Average sensitivity factors determined from this suite of standards were used for calibration and Fe was used for normalization. Data reported for Mn and Cr in metal are from SIMS; data for Fe, Ni, and Co are from EMPA.

Olivine crystals were imaged by secondary electron (SEI) and backscatter electron (BSE) techniques on a JEOL 5900 LV SEM at UH prior to and subsequent to SIMS analysis. The SEM was also equipped with a Nordlys energy dispersive X-Ray Detector and an Oxford Instruments HKL Channel 5 electron backscatter diffraction (EBSD) detector, which was used to determine olivine crystallographic orientation. FeNiCo charges were prepared for EBSD analysis by light polishing to remove the carbon coat, followed by ultra-fine polishing using colloidal silica on a VibroMet™ vibrating polisher. For EBSD measurements, the SEM was operated at low vacuum (11 Pa) with 20 kV accelerating voltage and 5 nA beam current and 70° tilted stage (Brugger and Hammer, 2015). Five to ten point analyses were conducted on each sample to ensure that single crystals were analyzed.

The experimental charges displayed compositional gradients in olivines between rims and unreacted cores. It was necessary to extrapolate measured profiles to the crystal rim in order to accurately determine the interface concentration. An incidental consequence of starting experiments with pure forsterite crystals was to create diffusion-controlled composition gradients. The experimental setup involves a large volume of metal phase relative to olivine. Thus, metal composition should remain relatively constant during the experiments and the metal acts as a concentration buffer. With these conditions, the system can be treated as one-dimension diffusion in a semi-infinite medium. When diffusion D (cm² s⁻¹) is independent of concentration, Fick's Law can be solved by implementing the complementary error function (*erfc*):

$$\text{erfc}\left(\frac{c - c_0}{c_i - c_0}\right) = \frac{x}{2\sqrt{Dt}}, \quad \text{Eqn. 1}$$

where C is the concentration (ppm) at distance x (cm) from the interface, C_0 is the farfield composition in olivine, C_i is the interface concentration, and time t is the experimental duration (seconds). A non-linear least-squares solution was used to solve for C_i and D simultaneously (c.f., Qian et al., 2010). Analytical uncertainties (2σ) of concentration data

were used in the weighted regression, whereas we assumed no uncertainty in point locations. Partition coefficients ($K_M^{met/ol}$) were then calculated as the ratio of the concentration of M (Fe, Ni, Co, Cr, and Mn, in mol. %) in metal to the concentration of M in olivine at the interface. To verify we obtained reasonable C_i values, we also calculated C_i from linear, power law, or exponential fit equations, depending on profile shape.

3. Results

3.1 Olivine and metal elemental compositions

Two or more compositional profiles were obtained on post-run olivine crystals (complete profiles are available in Supplementary Tables S1 and S3). Representative olivine compositions, obtained from individual analyses between 10 and 30 μm from olivine rims, are given in Table 1. The central portions of olivines from the 900° and 1300° series remained above Mg# 99.5, with rim compositions as low as 96.5. The majority of 1550°C series olivine experienced minor core modification (products had Mg# of 95 to ~100). Trace-element-abundance zonation profiles, from rims to unreacted olivine interiors, increased in length from ~10–30 μm in 900° runs, to ~30–40 μm in 1300° series runs. The farfield concentrations are similar in the 900° and 1300° series, and the 1550° core compositions are elevated. Given these factors, the gradients are assumed to be diffusion profiles, with the olivine-metal interface compositions in equilibrium with metal and magnesiowüstite. The increase in profile lengths from 900°C to 1550°C olivines is consistent with a faster diffusion at higher temperatures.

Post-run metal compositions (Table 1; all analyses are available in Supplementary Tables S2 and S4) were not the same as the starting compositions due to evaporation of Fe, Co, and Ni at different rates. The effect is more pronounced at higher temperatures. The Fe contents of the 900°C charges were ~1% lower than the starting compositions, while those of the 1300°C charges were lower by 6–8% and in the 1550°C experiments by 15–22%, with corresponding increases in Co and Ni concentration. The increases in Co and Ni are not a result of system contamination, as there is negligible Ni (<0.06 wt.%) in any FeCo run products, and similarly negligible Co in FeNi run products. The decrease in Fe in metal means Fick's law is not explicitly met in these charges. However, this problem has been noted previously and results in minimal bias in the calculation of C_i and partition coefficients (Kegler et al., 2008; Righter et al., 2011).

3.2 Metal-olivine partitioning behavior

Partition coefficients increase by an order of magnitude from Fe to Co and again from Co to Ni (Table 2). Partitioning is variable between runs of different temperatures and alloy compositions. Because the experiments were run at constant $f\text{O}_2$, pressure, and with known starting olivine composition, the apparent differences must result from a combination of different temperatures and alloy composition. The metal liquidus was between 1480 and 1525°C in all alloys (Nishizawa and Ishida, 1984; Guillermet, 1989; Swartzendruber et al., 1991), and thus the 1550°C runs reveal olivine-metal_{liquid} partitioning. The activity of Co and Ni in metal alloys are different at liquidus temperatures compared to subsolidus, which affects partitioning. The Fe activity likely remains approximately ideal (i.e. $a_{\text{Fe}} = 1$) for the

temperature range investigated (c.f., Fraser and Rammensee, 1982). Additionally, Fraser and Rammensee (1982) determined Henry's Law is followed for Ni in metal up to ~20 wt.%.

Alloy composition affects partitioning behavior. To account for variable Fe content in our experiments, we calculated olivine-metal equilibrium coefficients (KD) using the equation:

$$KD^{M-Fe} = K_M^{met/ol} \times X_{ol}^{Fe} / X_{met}^{Fe} \quad \text{Eqn. 2}$$

where X is the concentration (wt.%) of Fe in the olivine and metal. The equilibrium coefficients are presented in Table 3. Where Fe has a strong effect on partitioning (e.g., for Ni), alloys with different partition coefficients yield similar equilibrium coefficients. The average KDs generally increase with temperature, although it is not always resolvable given the large uncertainties. By accounting for Fe-in-metal effects on partitioning, and maintaining constant fO_2 , we can investigate how temperature and alloy composition affects partitioning. The high-temperature experiments exceeded the metal liquidus for all alloys. The 900°C and 1300°C experiments, by contrast, were at subsolidus temperatures for both olivine and alloy. At most compositions investigated here, solid alloys are stable in face centered cubic (FCC) structure. At 900°C, the FeCo system is stable in body centered cubic (BCC) structure, but this does not appear to have affected equilibrium partitioning.

3.3 Treatment of compositional gradients as diffusion profiles

A byproduct of the experimental setup was the creation of composition profiles controlled by diffusion. This was an unintended consequence, and the experiments were not set up to constrain many components of typical diffusivity experiments (e.g., pre-experiment axis orientation, multiple time series, and reversal experiments). However, there are few similar studies in the literature, and, as these results may be instructive, we report diffusivities calculated from Eqn. 1 (Table 4).

Diffusivities are expected to follow an Arrhenius relationship, in which they increase with increasing temperature in a predictable fashion if other conditions remain constant (e.g., buffer concentration and fO_2). This Arrhenius relationship defines a straight line of $\log D$ versus $1/T$ such that:

$$\log D_M = \log D_0 - E_a / 2.303RT, \quad \text{Eqn. 3}$$

where D_M is the diffusion coefficient of element M , D_0 is the pre-exponential factor ($\text{cm}^2 \text{s}^{-1}$), R is the gas constant, E_a is the activation energy (kJ mol^{-1}), and temperature T is in K. A weighted best-fit line yields a slope equivalent to E_a and an intercept at D_0 . Arrhenius parameters derived from each series were averaged to create a best-values set of parameters (Table 5). Our experimental data are not linear for all elements (Fig. 3). While some scatter may result from the aforementioned shortfalls of the experimental setup, it is also likely a result of changing metal activity at the solidus boundary. The metal matrix in our experiments is liquid during the 1550°C series, and solid at the 900°C and 1300°C series. Fraser and Rammensee (1982) also noted a change in relative activities for solid-liquid

transitions of some Fe/Ni and Fe/Co alloys. Overall, these results suggest similar diffusivities for Cr, Mn, Fe, Ni, and Co in olivine. Diffusivities of Ni and Co are intermediate between those from Zhukova et al. (2014) and Petry et al. (2004) for 1300°C and 1550°C, and yield comparatively higher diffusivities at 900°C (Fig. 3).

4. Discussion

4.1 Comparison with previous experimental work

This study is, to our knowledge, the first report of metal/olivine partition coefficients for Fe, Cr, Mn, Co, and Ni simultaneously at subsolidus temperatures. Where olivine-metal partition coefficients are reported in the literature, they are typically determined for silica-rich systems. The most similar relevant study is that of Ehlers et al. (1992), who determined $K_{Ni}^{met/ol}$ at low fO_2 with a starting composition of an ordinary chondrite analog. Their $K_{Ni}^{met/ol}$ of 1900 ± 300 (1350°C, IW-2) is within error of our results at 1300°C (Table 2). However, partition coefficients are a function of melt composition. Using Eqn. 2, we recalculated Ehler's partition coefficient to account for Fe activity, yielding KD^{Ni-Fe} of 117, which is higher than our KD^{Ni-Fe} at 1300°C (Table 3). At X_{ol}^{Fe}/X_{met}^{Fe} ratios similar to our 1300°C experiments (~ 0.02 – 0.03), this KD^{Ni-Fe} would yield $K_{Ni}^{met/ol}$ of 3800 to 4700. The partition coefficients reported in Table 2 may be lower because of the higher fO_2 or lower SiO_2 of our experiments (e.g., Spandler and O'Neill, 2010).

Spandler and O'Neill (2010) noted Mn, Co, Fe, and Ni are expected to diffuse at similar rates at 1300°C, whereas Cr is slower, due primarily to cation ordering and diffusion pathways. Jollands et al. (2016) determined Mn, Co, and Ni have similar diffusivities in olivine between 1300°C and 1550°C. Here, the similar length of zonation profiles for elements in a given sample also suggest similar diffusivities of transition metals. Calculated diffusivities for Ni are within an order of magnitude of those from Petry et al. (2004). However, at 900°C, our results indicate faster diffusivities than would be extrapolated from most previous studies by 2–3 orders of magnitude (Fig. 3). These previous studies are also primarily from high αSiO_2 experiments. A full investigation of these differences in diffusion mechanics are beyond the scope of this study. Of significance to this study, we emphasize that Mn, Co, Ni, Cr, and Fe were measured simultaneously in olivine profiles, and our results support similar diffusivities for these elements in this system (see Section 4.3 for further discussion of the importance of relative diffusion rates).

4.2 Re-assessment of olivine-metal equilibrium

The partition coefficient parameters determined in this study allow reassessment of the extent and nature of metal-olivine equilibrium in pallasites. We evaluated five main-group pallasites (Brenham, Albin, Imilac, Glorieta Mountain, and Springwater) and the Eagle Station pallasite where literature olivine and metal compositions for Fe, Cr, Mn, Co, and Ni were available. Data selection is critical, and relatively few studies have reported relevant compositional data for all the elements investigated here. Of particular interest are reports of olivine core and rim compositions (Hsu, 2003; Tomiyama and Huss, 2006; McKibbin et al., 2013). The ion probe olivine study by Hsu et al. (2003) contained multiple profiles for Cr,

Mn, and Ni for each pallasite. Tomiyama et al. (2006) reported olivine core and rim Cr compositions for Albin, Esquel, Imilac, Springwater, and Eagle Station. McKibbin et al. (2013) investigated a Brenham olivine grain and reported all elements of interest. Additional single point or average olivine analyses come from a variety of studies (Buseck and Goldstein, 1969; Leitch et al., 1979; Lugmair and Shukolyukov, 1998; Wasson et al., 1999; Lucas, 2011; Boesenberg et al., 2012; Herzog et al., 2015; Greenwood et al., 2015). The only gap in the olivine element record is for Glorieta Mountain, for which no Co data are published. The high-Co and high-Ni values for Brenham were reported from ICP-OES analysis (Herzog et al., 2015), and may have incidentally incorporated some metal in analyses.

Metal data comes from a more limited selection (Mason, 1963; Wasson et al., 1999; Wasson and Choi, 2003; Papanastassiou, 2012), and we did not find any reports of Mn in metal for Springwater, Brenham, or Imilac. Further, Cr in Springwater and Imilac from Wasson and Choi (2003) are subject to large uncertainties due to the possibility that their samples may have included tiny chromite grains. Here, we use the lowest reported Cr values from duplicate analyses (Table 2 of Wasson and Choi, 2003) for Imilac (12 ppm) and Springwater (14 ppm), which are similar to typical Cr concentrations in pallasite metal (~12 ppm, average of several main group pallasites from Herzog et al. 2015).

Compositions of olivine in equilibrium with metal (indicated as gradients in Fig. 4) were calculated from metal compositions and *KDs* (Table 3) for each pallasite of interest at 900°C, 1300°C, and 1550°C. If chemical profiles observed in pallasite olivines result from partial to complete equilibration with metal, then the extent and temperature of equilibration can be determined by comparing pallasite olivine compositions with equilibrium olivine compositions. Corrections for Fe variability were unique for each pallasite due to differences in olivine and metal compositions. We also assumed that olivine was more Mg-rich during the initial mixing stage, so that partition coefficients at 1550°C were calculated using an olivine Fe of 5 wt.% (Mg# 94). This increases metal/olivine partition coefficients (i.e., element behavior is more siderophile), lowering the calculated equilibrium olivine compositions. The bulk metal composition is assumed to remain relatively constant in these models, which may not hold true for trace elements in natural systems.

Olivine that remains in equilibrium with metal during cooling should be comparable to calculated equilibrium compositions (Fig. 4). For example, the core Cr composition of Brenham olivine are in equilibrium with metal at 1550°C, whereas Albin and at least one Imilac grain are in equilibrium at lower temperatures. In general, Cr in olivine cores appears to have equilibrated with metal at high temperatures (~1200°C). However, ubiquitous decreases in Cr, Co, and Ni abundance in olivine rims contradicts the expected behavior if olivine were to remain in equilibrium with metal during cooling. We attribute these decreases to late stage appearances of other phases (e.g., chromite for Cr and Co, schreibersite for Ni) in pallasites. Partial equilibration between chromite, olivine rims, and metal would occur at temperatures lower than for core equilibrium (~1000°C). The rim Cr abundance of olivine in Albin was consistently ~30 ppm, whereas for Eagle Station the rim Cr range is 20–65 ppm. This may reflect arrested equilibration in Eagle Station. Examination of Mn results (Fig. 4b) suggests that Glorieta Mountain and Albin were in

equilibrium with metal at ~1300°C and ~1550°C, respectively. Calculated equilibrium olivine Mn concentrations for Eagle Station are too high for observed olivine core compositions. Eagle Station is not a main group pallasite and has a unique metal composition, but we cannot rule out that the high Mn may be due to issues with representative sampling of Mn in metal. Of note, the total Mn range across all pallasite olivine is relatively limited (~1100 to ~3600 ppm). If other pallasites have Mn in metal concentrations similar to Glorieta Mountain and Albin, then they would all be in olivine-metal equilibrium at similar temperatures. Most Ni, and some Co compositions may indicate equilibration between metal and olivine cores at high temperatures. However, the fit is better for Co, and most Ni compositions are generally too low in pallasite olivine to record equilibration with the observed metal composition at the experimental temperatures.

4.3 Closure temperature and cooling rates

Low-temperature (below ~600°C) cooling rates are well-constrained by kamacite-taenite profiles to be on the order of ~1°C/Myr (e.g., Buseck and Goldstein, 1969; Yang et al., 2010). Cooling rates are poorly defined at temperatures above ~600°C because there are few phases recording this stage of cooling. Significant effort has been poured into the use of olivine as a pallasite cooling-rate recorder by investigating compositional zonation at grain boundaries. Based on the assumption that these compositional profiles are diffusion profiles, several authors have calculated high-temperature cooling rates. Miyamoto (1997) treated the composition profiles as Fe-Mg interdiffusion profiles and calculated cooling rates of ~20–200°C/yr. Ito and Ganguly (2006), in a similar treatment, found these same diffusion profiles could result from lower cooling rates of 2000°C/Myr. Note the orders of magnitude difference in cooling rates. However, these cooling rates were calculated for static conditions of an olivine-metal environment, and the calculated profiles did not match the observed profiles particularly well. In reality, the temperature change would have affected partitioning and diffusion rates, and any new phases that formed by subsolidus recrystallization would have affected metal compositions. In addition, it was recently demonstrated that environments with low silica activity, as in a metal-dominated matrix, would reduce diffusion rates of transition metals in olivine (Zhukova et al., 2014; Jollands et al., 2016). Thus, some previously utilized diffusion rates may be inapplicable to pallasite environments. These issues are addressed in the discussion below.

The driving force for diffusion of an element is its chemical potential, which is in part a function of temperature. Diffusion is faster at higher temperature and slower at lower temperature. Closure temperature (T_C) is a *characteristic* temperature representing the approximate temperature above which diffusion occurs in a theoretical crystal and below which diffusion is negligible. We calculated T_C for pallasite olivine diffusion profiles using the classic Dodson (1973) formulation and Arrhenius parameters from our study (Table 5):

$$T_C = \frac{E_a}{R} \ln \left(- \frac{A}{RT_c^2 D_0} a^2 E_a \frac{dT}{dt} \right), \quad \text{Eqn. 4}$$

where E_a is activation energy, R is the gas constant, D_0 is the pre-exponential factor, A is a geometric constant (55 for spherical geometry), a is grain-size characteristic radius, and

dT/dt is the cooling rate. One can also define a “time of retention” as the time required at a given cooling rate for a system to reach T_C . Time of retention and T_C are determined iteratively for a range of cooling rates and potential grain sizes (Fig. 5). The calculations for Fig. 5 assume peak temperatures of 1100°C at the start of diffusion after the change in metal composition (Ito and Ganguly, 2006). The similar Arrhenius parameters (E_a and D_0) for Cr, Mn, Co, Fe, and Ni (Table 5) yield similar T_C values, with T_C ranging from ~400°C to ~700°C, depending on the cooling rate. The T_C values at the low end of this range are below the temperature of kamacite nucleation in taenite. Wasson et al. (1999) found that the chromite-olivine geothermometer gives closure temperatures for these minerals of ~600°C in Brenham and Albin. If these closure temperatures are analogous, the model illustrated in Fig. 5 would imply cooling rates of ~200°C/Myr.

Closure temperatures derived from diffusion parameters from other studies can be quite different. Ito and Ganguly (2006) suggested T_C for the ^{53}Mn - ^{53}Cr isotope system was ~985–1000°C for cooling rates of ~20–40°C/Myr (off the top of Fig. 5a), but they utilized slower Cr diffusion rates. The diffusion parameters of Zhukova et al. (2014), which are also slower than those from our study, would yield similar closure temperatures to Ito and Ganguly (2006) at similar cooling rates. Despite these higher T_C , the time of retention (Fig. 5b) would only decrease by approximately half (e.g., at 100°C/Myr, the closure time would be ~2 Myr instead of ~5 Myr). The cooling rates (>100°C/Myr) and timescales (~1–5 Myr) on Fig. 5b would be consistent with similar limits for mafic intrusions (Brenan et al., 2005), which are feasibly analogous to mixing of metal and olivine in pallasites (i.e., high temperature mixing of solids and partial melt, followed by insulated slow cooling). The cooling rates of 200°C/Myr discussed earlier are slower than were calculated by Ito and Ganguly (2006) (~2000°C/Myr), but indicate cooling rates on the scale of degrees per million years are more realistic than the fastest rates of degrees per year as calculated by Miyamoto (1997). Slower cooling rates of 100–300°C/Myr also support a thermal history of gradual cooling in a parent body as modeled by Ito and Ganguly (2006) and McKibbin et al. (2016).

The new diffusivity parameters can also be used to place some constraints on the timescales required to form and preserve compositional profiles measured in pallasite olivine. An approximation of the length of diffusion is given by the characteristic length (C_L), where $C_L = (D_M \times t)^{-1/2}$ (Crank, 1975). Temperatures of ~900°C held for two million years yield C_L of 1–2 cm; this would disturb the ^{53}Mn - ^{53}Cr system in large grains, as interpreted by McKibbin et al. (2016). These authors also determined radiogenic ^{53}Cr incorporation in olivine occurred after ^{53}Mn was extinct, requiring several million years at elevated temperatures. For large olivine grains (~1 cm), cooling from 1300°C to the T_C (Fig. 5a) would take 6.5 Myr at rates of 100°C/Myr; An order of magnitude faster or slower cooling rate yields order of magnitude shorter or longer timescales, respectively. Given the limitations of the diffusion data, the timescales from our study may only yield order of magnitude confidence for timescale and cooling rate calculations. However, it is apparent that faster cooling rates (>1000°C/Myr) would not allow sufficient time for element exchange. Based on T_C and diffusivity parameters, we find high temperature cooling rates of 100–300°C/Myr reasonably explain pallasite olivine geochemical development. Our cooling rate requirements are also in good agreement with initial cooling rates of ~100–200°C/Myr

estimated by McKibbin et al. (2016). Subsequent zonation would then form over a short period of time relative to the 5–10 Myr of overall cooling (Ito and Ganguly, 2006), and at higher temperatures than for metallographic textural development.

4.4 Causes of compositional zoning in pallasite olivine

Multiple hypotheses have been put forward to generate pallasite parent bodies (Fig. 6; c.f., recent review by Boesenberg et al., 2012). Most start with a differentiated parent body (Stage I of Fig. 6). As differentiation of the parent body reached completion, the olivine and metal would be in approximate chemical equilibrium, with homogeneous trace-element profiles and abundances in olivine and metal controlled by equilibrium distribution coefficients. Several suggested mechanisms set mixing of olivine and metal at the core-mantle boundary (Stage IIb of Fig. 6). For example, Boesenberg et al. (2012) suggest that convection in the molten outer core could entrain overlying olivine, mixing it into the metal. McKibbin et al. (2013) suggested accumulation of olivine as it settles from the molten silicate could initiate mixing of metal and olivine.

In the Stage III model (Fig. 6), the solidifying mixture of metal and olivine reacts and new mineral phases nucleate. Boesenberg et al. (2012) attributed minor and trace element concentration gradients in olivine to diffusion at low-temperature (<1300°C). There was insufficient time for the system to reach a new equilibrium, leaving concentration gradients in the olivine. Alternatively, a catastrophic origin for pallasites (Stage IIa of Fig. 6) would involve disruption of the parent body, also changing the equilibrium partitioning among phases. Concentration profiles in the olivines would be generated during re-accretion, with rapid cooling (likely in the degrees per year range) during the early stages, freezing in the profiles. In both models, the cooling rate eventually slows to the range inferred from metallographic cooling rates (Scott and Taylor, 1990; Yang et al., 2010).

Previous work has focused on modeling cooling rates of olivine diffusion profiles of individual elements (e.g., Cr) or element-element pairs (e.g., Fe-Mg interdiffusion). The result has been disparate calculated cooling rates and cooling times (e.g., Miyamoto, 1997; Tomiyama and Huss, 2005; Ito and Ganguly, 2006). In particular, relatively flat Mn and Fe profiles appeared to indicate longer diffusion timescales or faster diffusion compared to zoned Cr and Ni profiles. In this study, supported by recent work (Spandler and O'Neill, 2010; Jollands et al., 2016), olivine diffusivities in low-SiO₂-activity systems appear similar for Cr, Mn, Fe, Ni, and Co. We suggest that the observed chemical profiles in pallasite olivines result from changing boundary conditions rather than, for example, secondary catastrophic disruptions to the system.

These changes can be modeled as relative concentrations in liquid metal (Fig. 7a) and hypothetical olivine (Fig. 7b). In this scenario, a homogeneous olivine is injected into metal during a mixing event (e.g., Fig. 6). During olivine-metal mixing (Fig. 7, Stage II), olivine partially re-equilibrates with pallasite metal. Metal is a persistent sink for Ni and Co, and olivine core and rim compositions (Hsu, 2003) are consistent with progressive equilibration above 1300°C (e.g., Fig. 1). Recrystallization by olivine-metal subsolidus reactions to form minor phases (Stage III) results in zonation profiles of olivine rim compositions as in Hsu

(2003). These initial compositional profiles would be gradually flattened by subsequent low-temperature diffusion, to varying effect.

Minor phases preferentially deplete the system in specific elements during crystallization. Partial re-equilibration of metal with chromite, FeCr_2O_4 , or schreibersite, $(\text{Fe,Ni})_3\text{P}$, would change the boundary conditions for Cr and Ni, respectively, by lowering their concentration in metal and olivine. Indeed, partition coefficients suggest olivine cores reflect equilibrium with a metal melt with a higher Cr abundance than currently observed in FeNi-metal. The Cr abundance decreases by 50–70% between cores and rims of olivine zoning profiles (Hsu, 2003). This translates to a <100 ppm decrease in Cr-in-metal that is easily produced by subsolidus crystallization of minor chromite (<1 modal %); Chromite is a ubiquitous phase present in trace amounts in main-group pallasites (e.g., 0.3 vol% in Esquel; Ulff-Møller et al., 1998; Wasson and Choi, 2003). Wasson et al. (1999) also suggested solid-state diffusion of Cr in metal was fast enough for chromite to pull Cr from metal. In contrast, Mn is generally not zoned in olivine (Fig. 1), despite being more compatible in olivine compared to metal. The only phase besides olivine that might take up Mn in appreciable quantities is stanfieldite, a minor phosphate found in only a small number of pallasites, and which typically has < 0.05 wt.% MnO (Buseck and Holdsworth, 1977). However, increasing late-stage Mn uptake by olivine does occur in a few pallasites where thin (< 500 μm) overgrowths of high-Mn phosphoran olivine overgrowths form on olivine rims (Boesenberg et al., 2012; McKibbin et al., 2016). Macroscale heterogeneities arising from isolation of late-stage melt packets would have higher Si activity and, likely, higher $f\text{O}_2$ to drive these changes (Boesenberg et al., 2012; Zhukova et al., 2014). Late-stage appearance of secondary minerals, especially phosphates, would also impact the distribution of Ca and P, which are relatively more compatible in phosphates than in metal or olivine.

As discussed here, high-temperature cooling rates derived from olivine compositional profiles (~100–300°C/Myr) are two orders of magnitude higher than has been determined from low-temperature metallographic relationships (~1°C/Myr); this difference is consistent with an asymptotically decreasing cooling rate with time (cf., Ito and Ganguly, 2006). The gradual decrease could be accommodated by insulation of pallasite precursors after mixing. The cooling rates could also be consistent with some versions of the catastrophic disruption model if the insulating layer formed relatively rapidly. In either model, after the disruption of the pallasite parent body (Fig. 6, Stage II), slow cooling allowed for high-temperature equilibration between olivine and metal, which overprinted initial olivine compositions. Thus, if initial cooling rates were in fact significantly faster (degrees per year) than rates determined here, they are not recorded by the compositional profiles. In either case, temperatures likely cooled to ~1000°C within ~5 Myr, coinciding with the appearance of new phases and thus changing equilibrium conditions. Partial equilibration between olivine, metal-dominated matrix, and minor accessory phases yielded variable zonation profiles in olivine, which were frozen in below closure temperatures. Slower cooling at temperatures <600°C proceeded for an additional 4–10 Myr.

5. Summary

We experimentally determined metal/olivine element partitioning behaviors of Fe, Ni, Co, Cr, and Mn in a metal-rich environment analogous to pallasites. The experiments also produced diffusion profiles for each element, which yielded similar diffusivities for these elements for a given temperature. These new partition and diffusion parameters were used to determine the extent of olivine-metal equilibrium and to place constraints on models of processes that formed pallasites. Compositions of olivine cores suggest equilibration with metal occurred at high temperatures, likely between 1300° and 1550°C. Core-to-rim zonation profiles of olivine compositions were interpreted to result from lower temperature partial equilibration with changing boundary conditions between olivine and metal. These changing boundary conditions were driven by the appearance of minor phases such as chromite and schreibersite. The partial equilibration between olivine and metal proceeded on a shorter timescale (<5 Myr) than low- temperature taenite-kamacite subsolidus exsolution. Cooling rates (~100°C/Myr) at high- temperature were derived from olivine compositional profiles, and are consistent with gradual cooling to lower temperatures (<600°C) where metallographic relationships develop at slower cooling rates (~1°C/Myr). Post-mixing cooling at these slow rates would be consistent with insulation of pallasite meteorite precursors in a parent body.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.

Edge-to-edge Mn and Cr zoning profiles in Albin (filled circles) and Eagle Station (open circles) olivines. Note the variable “diffusion” profiles of Cr in (a), and the slight uptick in Mn at the rim of one olivine in (b). Data from Hsu (2003).

Fig. 2. Backscattered electron (BSE) images of portions of two olivine charges after high-temperature experiments and SIMS analyses (~10 μm spots). (a) Initial experiments with natural olivine experiments exsolved metal and were unsuitable for diffusion rate determination. (b) Synthetic olivine was homogeneous in major elements and did not exsolve metal. mgw = magnesiowüstite.

Fig. 3.

Comparison of diffusivities from this study (circles) to literature (lines). Literature parameters are determined for diffusion along the c-axis, and for refs 1 and 2 with α SiO_2 of 1 and IW-1. 1, Zhukova et al. (2014); 2, Jollands et al. (2016); 3, Morioka (1983); 4, Spandler and O'Neill (2010); 5, Petry et al. (2004); 6, Morioka (1981); 7, Holzapfel et al. (2007); 8, Dohmen et al. (2007) 2007; 9, Buening and Buseck (1973); 10, Meisner (1974); 11, Jurewicz and Watson (1988); 12, Chakraborty (1997); 13, Ito and Ganguly (2006).

Fig. 4.

Pallasite olivine core (filled circles) and rim (open circles) compositions compared to olivine compositions that would be in equilibrium with pallasite metal between 900°C and 1550°C (shown as a gradient). E.S., Eagle Station; G.M., Glorieta Mountain; Bren., Brenham; SPW, Springwater.

Fig. 5.

The effect of grain size and cooling rate on closure temperature and time of retention for Mn, Fe, Co, and Ni. a) T_C versus cooling rate for a range of grain sizes. b) Calculated time of retention (Myr) versus cooling rates (°C/Myr) for multiple grain sizes, assuming $T_0 = 1100^\circ\text{C}$.

Fig. 6. Schematic models of pallasite formation from (I) a differentiated chondrite body. (IIa) Protoplanet breakup by a glancing impact and reaccrction of mantle and metal components (adapted from Yang et al., 2010). (IIb) Olivine and metal mixing resulting from liquid metal convection or cumulate buildup (Boesenberg et al., 2012; McKibbin et al., 2013). Impact, convection, and accumulation may all have influenced olivine and metal mixing. (III) Downward metal solidification traps olivine and late-stage phases crystallize from interstitial melt.

Fig. 7.

Predicted changes in major and minor element concentrations in (a) metal and (b) olivine during pallasite parent body evolution. The compositions are unitless but the relative proportions are based on literature compositions of olivine in pallasite (e.g., Hsu, 2003) and partition coefficients determined in this study. Formation stages refer to schematic models of Fig. 6. (a) Liquid metal concentrations at the core-mantle boundary remain relatively constant with the evolution of a pallasite body until late stage crystallization when minor phases (e.g., chromite, phosphates, and orthopyroxene) crystallize. (b) Core-to-rim olivine transects for a hypothetical olivine extracted at the end of each stage. Changes in profile shape (black lines) from previous stages (gray lines) reflect incomplete re-equilibration with metal. Prolonged diffusion in stages II and III would result in shallower profile gradients at crystal rims.

Table 1

Representative post-run olivine and average metal compositions (wt.%).

Series	alloy	Dist.	Mg	Si	Fe	Cr	Mn	Co	Ni
		μm	wt. %	wt. %	wt. %	ppm	ppm	ppm	ppm
Olivine									
900	FeNiCo	10	34.5 (3)	17.6 (1)	0.494 (4)	3.18 (7)	6.9 (2)	20.4 (3)	7.0 (3)
	FeCo	11	34.1 (3)	20.0 (3)	1.49 (11)	0.65 (3)	30.6 (5)	162 (10)	
	FeNi	13	34.1 (3)	19.8 (3)	0.48 (4)	0.78 (4)	4.35 (7)		14 (1)
1300	FeNiCo	16	32.8 (3)	18.4 (1)	1.59 (1)	2.96 (6)	84.3 (7)	96 (1)	33 (1)
	FeCo	19	34.8 (3)	20.4 (1.0)	0.94 (1)	0.18 (2)	18.7 (2)	30.1 (3)	
	FeNi	11	34.8 (3)	19.9 (3)	0.75 (6)	1.0 (5)	5.6 (2)		13 (1)
1550	FeNiCo	12	32.7 (3)	19.6 (3)	2.29 (1)	3.25 (6)	208.7 (9)	253 (2)	75 (1)
	FeCo	10	32.6 (3)	18.8 (2)	3.37 (2)	3.44 (1)	252 (2)	629 (7)	16 (1)
	FeNi	29	32.7 (3)	17.4 (6)	2.18 (11)	1.37 (24)	139 (7)		97 (6)
1550	Fe	13	31.8 (3)	19.0 (3)	1.95 (16)	1.47 (3)	216 (8)		
metal									
900	FeNiCo		2.8 (1)	362 (446)	77.0 (4)	0.34 (2)	0.16 (1)	8.0 (1)	14.2 (2)
	FeCo		0.16 (1)	6.9 (5)	91.6 (5)	0.44 (2)	0.15 (2)	8.1 (2)	
	FeNi		0.0007 (5)	300 (150)	85.5 (3)	0.38 (2)	0.09 (1)		14.4 (3)
1300	FeNiCo		0.32 (1)	2.1 (3)	71.7 (4)	0.33 (2)	2.24 (4)	10.1 (1)	18.1 (3)
	FeCo		0.003 (1)	260 (180)	88.1 (5)	0.28 (2)	0.49 (2)	11.4 (1)	
	FeNi		0.006 (1)	0.67 (74)	80.3 (3)	0.31 (1)	0.53 (2)		18.8 (2)
1550	FeNiCo		0.009 (1)	0.41 (4)	62.5 (15)	0.50 (8)	6 (2)	12.9 (3)	24.3 (15)
	FeCo		0.003 (1)	9.0 (6)	78.4 (6)	0.51 (8)	5 (1)	20.9 (6)	
	FeNi		0.003 (1)	0.58 (8)	67.0 (25)	0.6 (1)	1.0 (2)		32.3 (25)
1550	Fe		0.012 (2)	0.22 (16)	98.9 (5)	0.50 (7)	4.3 (1)		

Dist. = distance from edge of olivine.

Values in parentheses are 2σ uncertainties on least-significant digit. For example, 2.8 (1) is 2.8 ± 0.1 .

Elements in wt. % were determined by EPMA (except olivine Fe); ppm and olivine Fe is from SIMS analysis.

Table 2

Calculated partition coefficients ($K_M^{met/ol}$) and associated uncertainties (2σ level).

Experiment	Cr	Mn	Fe	Co	Ni
900FeNiCo	0.04 ± 0.02	0.014 ± 0.001	47 ± 21	542 ± 614	2358 ± 1712
900FeCo	0.19 ± 0.07	0.005 ± 0.001	35 ± 24	448 ± 195	
900FeNi	0.49 ± 0.12	0.028 ± 0.008	125 ± 27		1123 ± 203
1300FeNiCo	0.02 ± 0.02	0.007 ± 0.001	30 ± 15	758 ± 444	3414 ± 2395
1300FeCo	0.006 ± 0.001	0.015 ± 0.002	25 ± 9	690 ± 501	
1300FeNi	0.24 ± 0.06	0.009 ± 0.001	53 ± 5		1925 ± 684
1550FeNiCo	0.13 ± 0.03	0.022 ± 0.007	24 ± 1	366 ± 98	3086 ± 335
1550FeCo	0.13 ± 0.04	0.018 ± 0.006	22 ± 2	849 ± 68	
1550FeNi	0.18 ± 0.03	0.004 ± 0.001	22 ± 3		3053 ± 708
1550Fe	0.14 ± 0.07	0.019 ± 0.012	22 ± 1		

Table 3Calculated equilibrium coefficients and weighted averages ($\pm 2\sigma$ uncertainty).

Experiment	K(Cr)	K(Mn)	K(Co)	K(Ni)
900FeNiCo	0.0008 ± 0.0005	$2.9\text{E-}04 \pm 1.3\text{E-}04$	12 ± 12	50 ± 43
900FeCo	0.0053 ± 0.0042	$1.5\text{E-}04 \pm 1.1\text{E-}04$	13 ± 10	
900FeNi	0.0039 ± 0.0013	$2.2\text{E-}04 \pm 8.2\text{E-}05$		9 ± 3
1300FeNiCo	0.0008 ± 0.0007	$2.5\text{E-}04 \pm 1.3\text{E-}04$	25 ± 20	114 ± 99
1300FeCo	0.0003 ± 0.0001	$5.9\text{E-}04 \pm 2.2\text{E-}04$	28 ± 23	
1300FeNi	0.0045 ± 0.0012	$1.7\text{E-}04 \pm 2.3\text{E-}05$		36 ± 13
1550FeNiCo	0.0054 ± 0.0012	$9.2\text{E-}04 \pm 2.9\text{E-}04$	15 ± 4	129 ± 16
1550FeCo	0.0061 ± 0.0019	$8.1\text{E-}04 \pm 2.7\text{E-}04$	39 ± 5	
1550FeNi	0.0081 ± 0.0018	$1.7\text{E-}04 \pm 4.1\text{E-}05$		140 ± 37
1550Fe	0.0066 ± 0.0033	$8.7\text{E-}04 \pm 5.6\text{E-}04$		
<i>Average</i>				
900°C	0.0012 ± 0.0005	0.00021 ± 0.00006	12 ± 8	9 ± 3
1300°C	0.0016 ± 0.0006	0.00034 ± 0.00023	27 ± 15	38 ± 13
1550°C	0.0063 ± 0.0009	0.00086 ± 0.00019	25 ± 3	131 ± 15

Table 4Calculated diffusivities ($\log D_i$; $\text{cm}^2 \text{s}^{-1}$) for experimental charges.

	Cr	Mn	Fe	Co	Ni	
900	FeNiCo	-13.47 ± 0.31	-12.96 ± 0.05	-13.02 ± 0.01	-12.87 ± 0.06	-13.41 ± 0.01
	FeCo	-12.84 ± 0.19	-12.68 ± 0.07	-12.75 ± 0.10	-12.99 ± 0.02	
	FeNi		-12.91 ± 0.26	-12.81 ± 0.05		-13.2 ± 0.05
1300	FeNiCo	-12.38 ± 0.09	-12.15 ± 0.04	-11.61 ± 0.02	-11.76 ± 0.03	-11.71 ± 0.03
	FeCo	-12.38 ± 0.13	-12.16 ± 0.06	-12.05 ± 0.03	-12.34 ± 0.01	
	FeNi		-12.71 ± 0.06	-12.15 ± 0.02		-11.99 ± 0.03
1550	FeNiCo	-11.37 ± 0.17	-10.93 ± 0.05	-10.46 ± 0.06	-10.81 ± 0.07	-9.85 ± 0.22
	FeCo		-10.74 ± 0.03	-10.5 ± 0.08	-11.13 ± 0.01	
	FeNi	-11.44 ± 0.10	-11.49 ± 0.04	-10.87 ± 0.07		-10.22 ± 0.38
1550	Fe	-11.25 ± 0.28	-11.02 ± 0.29	-9.29 ± 0.31		

Table 5

Weighted best-fit values for Arrhenius parameters.

	$\log D_0$	E_a
	$cm^2 s^{-1}$	$kJ mol^{-1}$
Cr	-7.46 ± 0.09	144 ± 23
Mn	-7.01 ± 0.04	145 ± 7
Fe	-6.30 ± 0.04	152 ± 6
Co	-7.24 ± 0.04	132 ± 8
Ni	-6.50 ± 0.05	154 ± 9