Experimentally determined subsolidus metal-olivine element partitioning with applications to pallasites

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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.

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 (900–1550 °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.
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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 (~550–300 °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

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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 ~1300 °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 ~200 °C/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 (Mg₂SiO₄) 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 (Mg# = 99.98) were created at the University of Arizona.
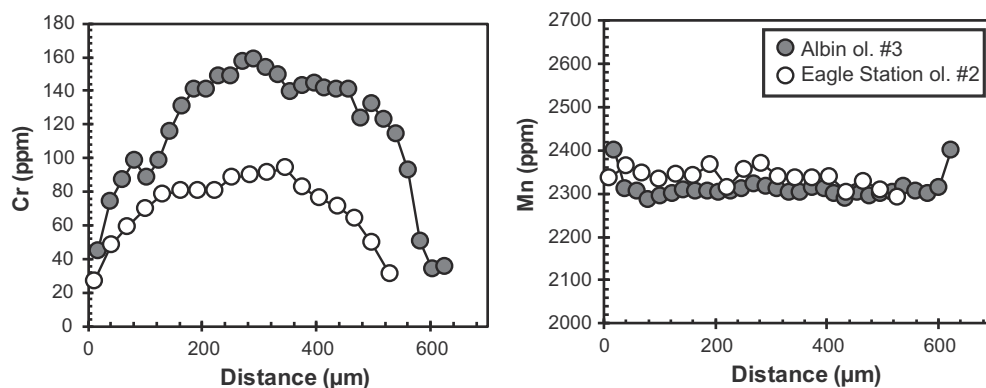

Fig. 1. Edge-to-edge Mn and Cr zoning profiles in Albin (filled circles) and Eagle Station (open circles) olivines. Note the variable "diffusion" profiles of Cr in (a), and the slight uptick in Mn at the rim of one olivine in (b). Data from Hsu (2003).