

MINOR ELEMENT BEHAVIOR OF PALLASITE OLIVINE : UNDERSTANDING PALLASITE

THERMAL HISTORY AND CHRONOLOGY. T. Tomiyama¹, G.R. Huss¹, ¹Department of Geological Sciences and Center for Meteorite Studies, Arizona State University, Tempe, AZ 85287, Takayuki.Tomiyama@asu.edu.

Introduction: Pallasites are highly differentiated meteorites composed mainly of olivines and Fe-Ni metal with comparable volumes. A standard view is that pallasites originated from the core-mantle boundary in differentiated parent bodies [e.g., 1, 2]. Fe-Ni metal in pallasites exhibits Widmanstätten structure indicative of slow cooling, and cooling rates inferred from zoning profiles in metal are $\sim 1^\circ\text{C}/\text{Myr}$ [3]. However, pallasite olivines show chemical diffusion profiles that suggest cooling rates of a few to tens of degrees per year, roughly a million times faster [4, 5]. Metal and olivine do not seem to be telling the same story. Manganese-chromium isotopic systematics are also confusing. Ion probe measurements of olivines and phosphates appear to show initial $^{55}\text{Mn}/^{53}\text{Mn}$ ratios ($(^{55}\text{Mn}/^{53}\text{Mn})_0$) on the order of 1×10^{-5} [6, 7], but thermal ionization measurements made on bulk olivines that have had the surfaces removed by abrasion give $(^{55}\text{Mn}/^{53}\text{Mn})_0$ values of $1\text{--}2 \times 10^{-6}$ [8, 9]. This discrepancy has never been adequately explained. Clearly, there is a need for a better understanding of the thermal history and isotope systematics of pallasites.

The ion probe studies of Mn-Cr systematics in pallasite olivines depend on concentration gradients, particularly in chromium, at the edges of the olivine grains. This zoning gives the required high Mn/Cr ratios. These same gradients give the fast cooling rates, so a key to understanding both the cooling rates and Mn-Cr systematics is to understand the origin of these gradients. We have begun an in-depth study to evaluate the chemical zoning in pallasite olivines and to try to understand its cause. As a first step, we performed electron probe analyses of the concentration gradients in olivines from Imilac and Esquel, and carried out preliminary ion microprobe analyses of Mn-Cr systematics on olivines from Brahin and Albin.

Methods: We acquired small slices ($\sim 4 \times 4 \times 0.5$ cm) of Esquel and Imilac pallasites that showed very little evidence of weathering. These were polished and examined using an optical microscope and electron microprobe (JEOL JXA-8600 equipped with Noran instruments Voyager EDS/WDS operating system) at Arizona State University. Larger grains with olivine-metal interfaces perpendicular to the cut surface were chosen to study the concentration gradients. Profiles of major and minor element concentrations were measured by electron microprobe in wavelength-dispersive mode using an accelerating voltage of 20 kV and a focused beam of 20 nA. Counting times were 10

sec for major elements (FeO, MgO, SiO₂) and 60–120 sec for minor elements (MnO, Cr₂O₃, CaO, Al₂O₃).

Ion-probe analyses of olivines were done on polished potted-butted samples of Albin and Brahin pallasites using Cameca IMS 6f at Arizona State University. The primary O⁺ beam of ~ 2 nA was accelerated by 9 kV to yield a 10 μm spot. The secondary-ion mass spectrometer was operated with a mass resolving power (MRP) of $m/\Delta m \sim 3500$. This MRP is sufficient to resolve $^{24}\text{Mg}^{28}\text{Si}^+$, $^{25}\text{Mg}^{28}\text{Si}^+$, $^{26}\text{Mg}^{27}\text{Al}$ and $^{28}\text{Si}^{27}\text{Al}$ from the Mn and Cr isotopes, but is not sufficient to resolve ^{52}CrH from ^{53}Cr or ^{54}CrH and ^{54}H from ^{55}Mn . The contribution of the hydride to ^{53}Cr was confirmed to be $< 1\%$ and hydrides on ^{55}Mn totaled less than 1%. Instrumental mass fractionation for Cr was corrected externally based on repeated analysis on San Carlos olivine. Correction for differential sensitivity of Mn and Cr was made based on San Carlos olivine.

Results: Fig. 1 shows line profiles of chemical variation in Esquel and Imilac olivines. Esquel has sub-angular olivines with sizes up to 19.1 mm. The CaO concentration in Esquel olivines shows zoning within ~ 500 μm from the grain boundary, decreasing from ~ 0.03 to ~ 0.01 wt% toward the rim. The Cr₂O₃ shows zoning within ~ 300 μm from the boundary, decreasing from ~ 0.07 to ~ 0.01 wt%. The Al₂O₃ data shows considerable scatter, but the concentration tends to decrease toward the rim. The Fe/(Fe+Mg) ratio shows only slight zoning, decreasing toward the edge. MnO does not show significant zoning in Esquel olivines. Imilac has sub-rounded olivines with sizes up to 14.6 mm. The CaO, Cr₂O₃ and Al₂O₃ concentrations are significantly lower than in Esquel olivine. The CaO and Cr₂O₃ concentrations are zoned from the core to rim, decreasing toward the rim from > 0.01 to < 0.01 wt% and ~ 0.04 to ~ 0.01 wt%, respectively. The Al₂O₃ again shows considerable scatter, but tends to decrease toward the rim. MnO and Fe do not show significant zoning in Imilac olivines.

Olivines in Albin have sub-rounded shapes with sizes up to 7.1 mm, whereas those in Brahin have sub-angular shapes with sizes up to 6.0 mm. Ion microprobe analyses shows wide variety of $^{55}\text{Mn}/^{52}\text{Cr}$ ratio of up to ~ 36.7 for Brahin and ~ 39.1 for Brahin. We did not resolve any excesses in ^{53}Cr , but previous detections [7] would not be resolved in our data (Fig. 2).

Discussion: Our chemical profiles data are in reasonable agreement with those of Miyamoto (1997) [4], who did the extensive work on the chemical zonings of olivines in Esquel and Imilac. In both studies, CaO

and Cr_2O_3 show strong gradients, while MnO does not. Esquel olivine is zoned in Fa content in both studies, but Imilac gives variable results with Fe content increasing, decreasing, and remaining constant in different grains ([4], Fig. 1c).

The Widmanstätten pattern in meteorite metal develops between ~ 700 - 800°C and ~ 400 - 500°C where diffusion effectively stops. Inferred time scales for cooling through this temperature range in pallasites are a few degrees per million years [3]. The profiles in olivine imply cooling rates of a few degrees per year at $\sim 1100^\circ\text{C}$ [4, 5]. Diffusion gradients in olivine imply that the olivine moved from a chemical environment where concentrations were in equilibrium to an environment where they were not. The presence of gradients means that the system failed to completely re-equilibrate, probably because of rapid cooling. Thus, the concentration gradients in pallasite olivines would appear to be a major problem for the core-mantle boundary model of pallasite formation.

Although it may be possible to construct a scenario consistent with a core-mantle boundary origin, the textures and chemical gradients in pallasite olivines suggests a different scenario. In this model, the olivine was initially equilibrated. The environment changed and the new environment provided the disequilibrium driving force to produce gradients in the olivine. But the cooling time was too short for the system to establish equilibrium. Production of phosphates and chromite through oxidation could take place if the new conditions were more oxidizing. There is a correlation between the degree of rounding of olivine grains and the length scale of the concentration gradients in the olivine, with the more-rounded olivines in Imilac having broader concentration gradients. This implies that the cooling time for Imilac was longer than that for Esquel. A two stage scenario such as this could explain the discrepancy in $^{53}\text{Mn}/^{55}\text{Mn}$ initial ratios determined by ion probe and by thermal ionization mass spectrometry in several pallasites [6-9]. If Mn and Cr were re-mobilized after at least part of the ^{53}Mn had decayed so that some of the radiogenic ^{53}Cr near the edges of the grains is unsupported by Mn.

Clearly a lot more work will have to be done to evaluate this and other scenarios to understand the thermal history of pallasites

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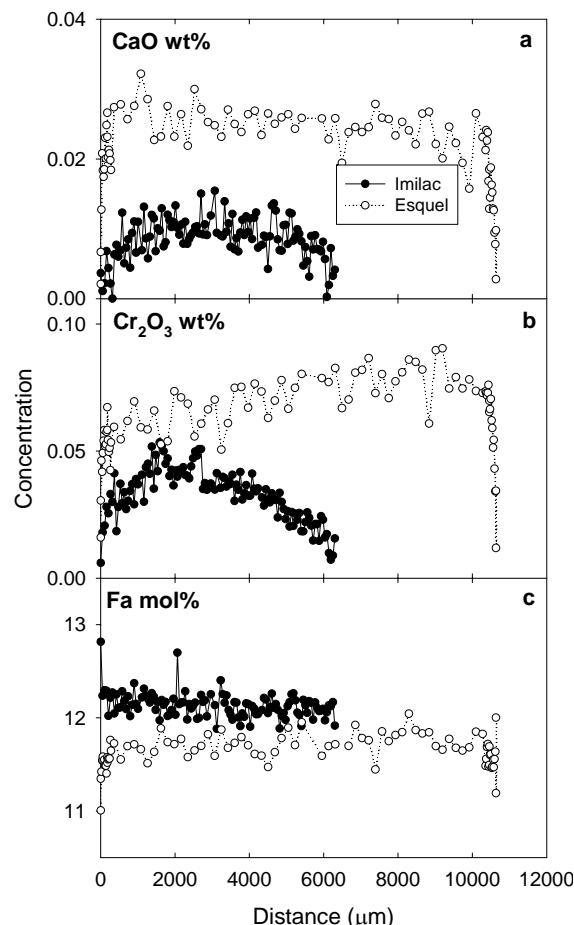


Fig. 1. Typical chemical zoning profiles of a) CaO b) Cr_2O_3 , and c) Fa of olivines in Esquel and Imilac.

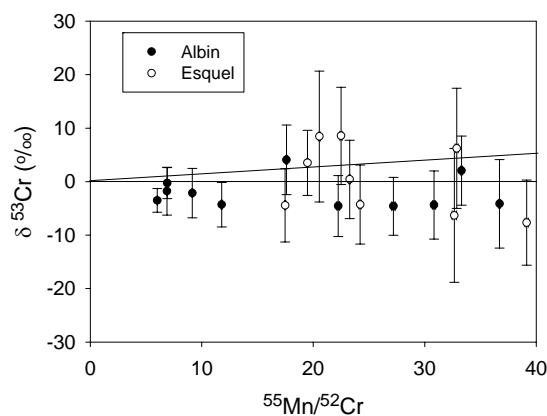


Fig. 2. Mn-Cr systematics of Albin and Esquel. Solid line [$^{53}\text{Mn}/^{55}\text{Mn}_0 = 1.5 \times 10^{-5}$] is the line determined by [7] for Albin. Error bars represent 2σ .