

CHEMICAL ZONING AND DIFFUSION OF CA, AL, MN, AND CR IN OLIVINE OF SPRINGWATER PALLASITE. Y. Zhou and Ian M. Steele, Dept. of Geophysical Sciences, University of Chicago, 5734 S. Ellis Ave., Chicago, IL 60637.

The pallasites, consisting mainly of Fe-Ni metal and olivine (1,2), are thought to represent the interior of a planetary body which slowly cooled from high temperature. Although the olivines are nearly homogeneous (3), ion microprobe studies revealed variations of Ca, Ti, Co, Cr, and Ni near grain edges (4,5). These variations were thought to represent diffusion in response to falling temperature of the parent body. Pallasite cooling rates have been estimated based on kamacite-taenite textures (6) but results differ by $\times 100$. In principle elemental profiles in olivine can allow estimates of cooling rate if diffusion coefficients are known; in addition, given a cooling rate, diffusion coefficients could be derived. Data are presented which show that apparent diffusion profiles can be measured for Al, Ca, Cr and Mn which qualitatively agree with expected diffusion rates and have the potential of providing independent estimates of pallasite cooling rates.

Experimental: Below we present electron microprobe profiles for Mn, Cr, Al, and Ca from Springwater pallasite as determined by electron microprobe. Operating conditions were selected to obtain maximum sensitivity: 20kV, 200nA, focused beam, PHA on, 1200sec count time. Concentrations (ppmw) for the 4 minor elements are approximately: Mn - 2750; Cr - 140; Al - 10; Ca - 64. Spectral scans confirmed a linear background with no interfering peaks. A total of 18 concentration profiles from edge to interior were obtained from 6 different olivine grains. Profile locations were chosen to avoid cracks and large grains were chosen so sections near the grain center were likely. The grain orientation was not known and attempts to determine orientation using backscattered electron diffraction were unsuccessful. While profiles discussed below are the most common, anomalous profiles were obtained which did not show a simple increase or decrease in concentration relative to grain edge, but there is no apparent reason for these complex profiles. Particular attention was paid to the phases adjacent to the olivine grain which may affect the profile by acting as a sink or source of a particular element.

Results: A typical profile is shown in Fig.1 where the adjacent phase is Fe-Ni metal. Two types of trends are seen which are common to nearly all profiles. The profiles for Al, Ca and Cr, all show a concentration decrease at the olivine grain edge relative to the olivine center; in contrast, the profile for Mn is highest at the grain edge and decreases toward the grain center. The profile for Mn is always much smoother than for the other three elements due to the 10 to 100x higher concentration; the apparent scatter in profiles for Al, Ca, and Cr can be attributed to counting statistics. The Mn decrease toward the grain interior can be interpreted as partitioning of Mn between olivine and metal where Mn favors olivine as temperature decreases (assuming ideal solid solution). Therefore, the Mn will migrate from the neighboring metal into olivine in response to the overall cooling. At high temperature, the diffusion is rapid and the time to reach equilibrium throughout the grain is short relative to the rate of temperature decrease. At low temperatures, on the other hand, diffusion within the olivine becomes slow and the Mn does not diffuse from the grain edge resulting in high concentrations at the metal-olivine boundary. The increasing concentrations for Al, Ca, and Cr toward the grain center indicate that these elements are diffusing out of olivine during cooling. A similar character for Ni has been observed (4). In contrast to Mn, the equilibrium Al, Ca, and Cr content in olivine decreases during cooling. This conclusion which is true for Ni (3) is speculative for the 3 elements described here because the adjacent metal phase does not contain these 3 elements in detectable quantities. It is possible that Cr is incorporated into the olivine structure as Cr^{+2} (7) at the reducing conditions indicated by the low Ni in Springwater olivine. Other phases, however, including chromite, troilite, and various phosphates (stanfieldite, whitlockite) may better act as sinks especially for Cr and Ca but require long distance grain boundary migration. A sink for Al is more difficult to identify but both phosphates and chromite may incorporate minor amounts; the bulk Al is very low in pallasites so no Al phase is required. There are indications the the slope of the profiles are dependent on the adjacent phases (metal, troilite, schreibersite) but sufficient data have not been obtained to verify relationships. If true however, limits can be placed on the distance over which equilibrium was achieved.

While crystallographic orientation of our analyzed grains is not known, there is a dependence of direction and diffusion rate (8) which has been observed for C3 (9) and terrestrial olivine (10). Fig. 2 illustrates the measured profiles for one Springwater olivine grain at 0, 45, and

90 degrees in the plane of the polished section. The profiles for Cr, Al, and Ca are essentially identical in the 3 directions, but if there are differences due to direction, they would probably be masked by the statistical fluctuation. On the other hand, Si diffusion in olivine is isotropic (11) and Al may be similar. The profiles for Mn, however are distinctly different and the 45° profile reflects rapid diffusion relative to the 0° and especially the 90° profile.

A comparison of the profiles for Al, Ca, and Cr on Fig. 2 shows that Al has the sharpest profile with a near-constant composition reached about 110µm from the grain edge. Both Ca and Cr profiles appear to extend beyond 250µm although Cr may become flat near 250µm. Qualitatively, the diffusion coefficients can be ordered as $Ca > Cr > Al$. The slow diffusion of Al is consistent with substitution in part in tetrahedral sites as concluded for C3 olivine grains (12). Quantitative interpretation suffers many uncertainties including: 1) the valance state of Cr; 2) the occurrence of Al in two sites, tetrahedral and octahedral, for charge balance; 3) unknown or poorly known diffusion coefficients for Al and Cr.

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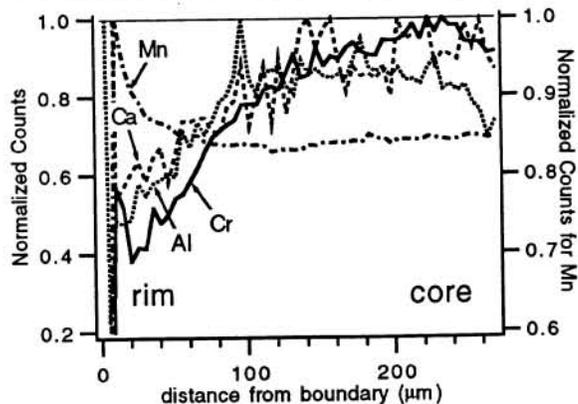


Fig. 1. Typical concentration profile for Al, Ca, Cr, and Mn in Springwater olivine. The olivine rim (left) is adjacent to Fe-Ni metal. Al, Ca, and Cr show a depletion at the olivine-metal boundary relative to the olivine center. Mn shows an enrichment at the olivine rim and rapidly levels off. The scatter for Al, Ca, and Cr is mostly due to counting statistics.

Fig. 2. Rim to core profiles for Al, Ca, Cr, and Mn in 3 directions in a single olivine grain. Fe-Ni metal occurs at the olivine rim. For Ca, Cr and Al the three profiles in the 0, 45 and 90° direction are identical within statistics suggesting no large diffusion anisotropy. For Mn, however, the profiles are distinctly different with the 0° profile indicating a fast diffusing direction. The slopes of the profiles for Ca, Cr, and Al indicate that the relative diffusion rates are $Ca > Cr > Al$.

