ZONATION OF PHOSPHORUS IN OLIVINE: DYNAMIC CRYSTALLIZATION EXPERIMENTS AND A STUDY OF CHONDRULE OLIVINE IN UNEQUILIBRATED ORDINARY CHONDRITES. M. C. McCanta, J. R. Beckett, and E. M. Stolper, Division of Geological and Planetary Sciences, California Institute of Technology, MS 170-25, Pasadena, Ca 91125 (mmccanta@caltech.edu).

Introduction: Phosphoran olivines with up to ~8 wt.% P_2O_5 have been recognized in unusual terrestrial and extraterrestrial samples (see review in [1]), but P zonation at lower concentrations appears to be a ubiquitous feature of olivine from a wide range of igneous rocks, including terrestrial basalts, komatiites, andesites, and dacites; Martian meteorites; and lunar samples [1-2]. This zonation occurs in many different patterns, including oscillatory and sector zoning, high-P cores surrounded by lower P olivine, and replacement of P-rich regions with low-P olivine [1]. Milman-Barris et al. [1] suggested that incorporation of phosphorus into olivine at the observed levels is a disequilibrium process reflecting rapid crystal growth and that the observed zoning patterns are potential indicators of magmatic processes. Moreover, P zonation is found in olivines with no correlated zonation in major or minor divalent cations, and thus it might be provide information unavailable from study of the common constituents of igneous olivine. In this abstract, we describe a series of experiments designed to determine the effects of cooling rate on the formation of P-rich zones in olivine and interpret the results in the context of varying crystal growth rates.

In some natural samples, P zonation is accompanied by zonation in Al and Cr. However, not all samples exhibit Al or Cr-zonation, specifically those samples thought to have been held at high temperature for extended periods following crystallization [1]. This suggests that retention of zoning is related to the diffusive reequilibration time for each element and that $D_{Al} > D_{Cr} > D_P$ for P-correlated cations. We have undertaken an analytical study of variably metamorphosed ordinary chondrites to investigate the T-t conditions required to wipe out P zonation in olivine; i.e., differences in metamorphic temperature and duration have resulted in chondrites that vary from unequilibrated (petrologic grade 3) to highly metamorphosed samples (grades 4-6) [3]. Provided olivines crystallized in chondrules are measurably zoned in P, it might be possible to follow diffusive reequilibration through increasing petrologic grades. As a first step in this project we present P X-ray maps for olivines from two unequilibrated chondrites, RC075 (H3.2) and LEW 86549 (L3.0), to determine if P zonation is present in chondrules from unequilibrated chondrites.

Methods:

Analytical. Kα X-ray intensity maps and major and minor element quantitative analyses were obtained on the Caltech JEOL JXA-8200 electron microprobe. We acquired Fe, Al, Cr, Ti, and P X-ray maps simultaneously at 15 kV and 400 nA, a beam diameter of 1 μm, pixel spacing of 1-2 μm, and count times of 800-2000 msec/step. Quantitative analyses were collected at 15 kV and 40 nA with a beam diameter of 1 μm (olivine) or 10 μm (glass).

Experimental. All experiments were run in a vertical 1-atm gas mixing furnace at Caltech on a Hawaiian basalt (BHVO-2) doped with 10% olivine (Fo_{92}) (bulk $P_2O_5 = 0.24$ wt.%) using the Pt-loop technique. Runs were held 10°C below the pre-determined liquidus temperature (1290°C) for 3 hours to homogenize the sample without destroying all olivine nuclei. This was done to minimize the possibility crystal growth from highly undercooled liquids [*e.g.*, 4]. f_{O2} was controlled by H_2-CO_2 gas mixing, monitored with an oxygen sensor adjacent to the sample, and buffered at QFM. Following the initial homogenization, samples were cooled at 15°, 10°, or 5°C/hr to 1150°C, held for 1 hr, and then drop quenched into deionized water.
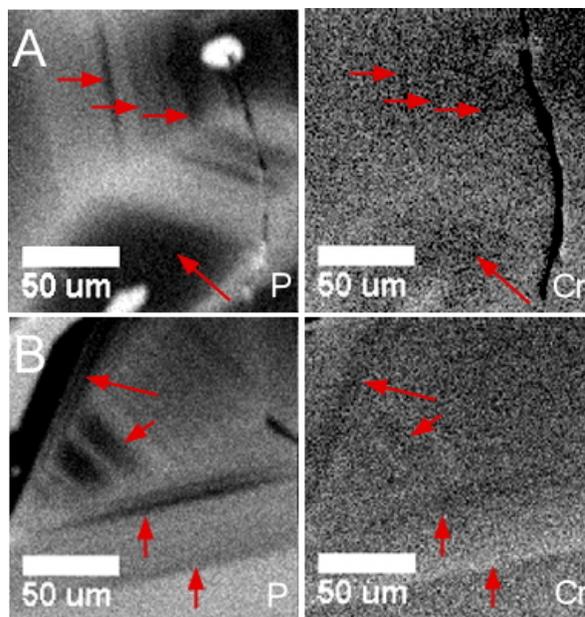

Figure 1. P and Cr X-ray maps of experimental olivine. Red arrows highlight corresponding features. (A) 5°C/hr and (B) 10°C/hr.

Results:

Cooling Rate Experiments. X-ray maps of olivines grown at cooling rates of 5 and 10°C/hr are shown in Fig. 1 (15°C/hr runs show similar features). All experiments have both equant crystals (nucleated pre-

dominantly on or near the outside surface of the bead) plus skeletal or dendritic morphologies in the interior. Oscillatory and sector zoning of P in olivine is present in all experiments. Melt inclusions are found in low P regions only (Fig. 1A). Cr and Al zoning is spatially associated with P (Fig. 2B). Fe and Al zoning near crystal rims was also observed in many samples (Fig. 1B), likely the result of insufficient reequilibration time prior to sample quench.

Fig. 2A shows an X-ray map of a sector-zoned olivine from a 5 °C/hr experiment and Figure 2B shows quantitative analyses for two transects across oscillatory zoned sectors. P oscillations in the high P sector range from 0.18 to 0.25 wt.% P, while those in the low P sector range from 0.02 to 0.11 wt%. P. Although the equilibrium partition coefficient for P is <0.1, the high P region has partition coefficients approaching 1 suggesting a disequilibrium process [1]. The range in Cr and Al concentrations is smaller than that observed for P, but they are strongly correlated spatially with P in both sectors (Fig.2B,C). This correlation could represent coupled substitution of Al, Cr, and P into the olivine and/or other factors related to the high apparent partition coefficient for P as these olivines grew.
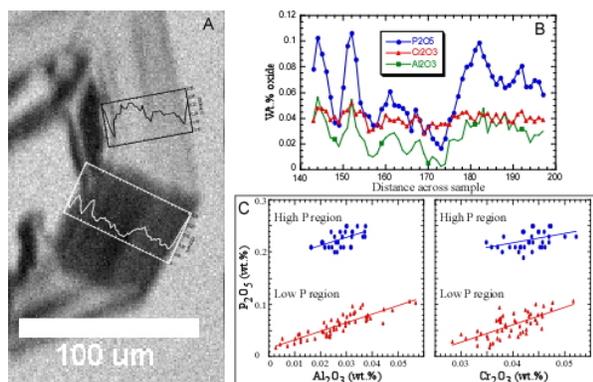

Figure 2. (**A**) Variation of P_2O_5 across sector and oscillatory zoned experimental olivine from 5°C/hr cooling rate run (different crystal from that seen in Fig. 1A). (**B**) Traverse across lower P (darker) region. (**C**) Correlation of cations within high and low P sectors.

Our cooling rate experiments and those of [1], demonstrate that complex P zonation (decoupled from zonation of the major and minor divalent cations) is present in olivines grown from basaltic melts cooled at 5-30 °C/hr. Indeed, we have yet to produce an olivine in a P-bearing bulk composition that is not zoned in P. This makes P zoning a unique feature in igneous olivines that records early crystallization processes and is not subject to subsequent modification under many geologic conditions. These results suggest that crystal growth rate (rather than cooling rate) governs the development of P zonation. This zoning does not reflect

mixing events or large-scale magma compositional changes (since these are not factors in our experiments) but rather is due to intrinsic processes dominated by the crystal-melt interface. [1] suggest that rapid growth resulting in build-up of incompatible elements at the interface (*cf.* Fig. 2) combined with "solute trapping" (the inability of a cation to diffuse away faster than crystal growth is taking place) best explain the ubiquitous presence of P zonation in igneous olivines. If this is correct, the oscillating high P to low P zones observed in our experiments imply that growth rate is highly variable in the cooling interval experienced by these samples despite the constant cooling rates. In addition, the data show that even at slow cooling rates (5°C/hr) rapid, disequilibrium crystal growth is prevalent.

Chondrite samples. We mapped olivines in porphyritic, high-FeO chondrules in the unequilibrated chondrites RC075 and LEW 86549. High-FeO chondrules were chosen for their low abundances of liquid and solid alloys and sulfides, which can potentially scavenge P. P zoning is present in chondrule olivine from both meteorites (Fig. 3) and is not correlated with major element zonation (*i.e.,* Fe). As olivine zonation is present in these unequilibrated chondrites, more extensive characterization of zoning in chondrule olivine and the study of more equilibrated meteorites is warranted.
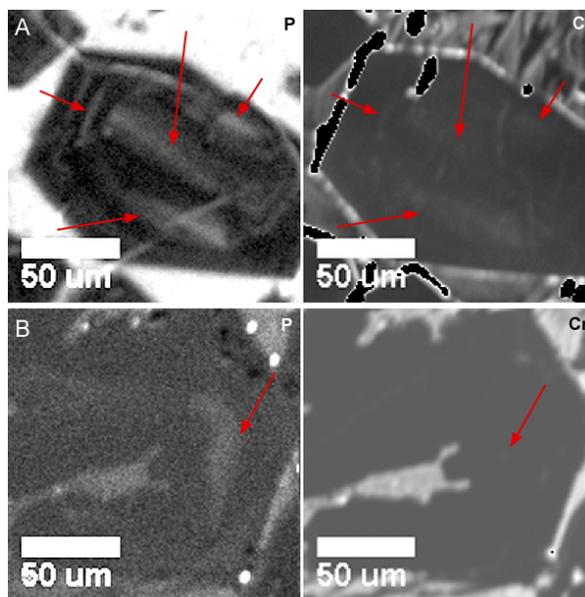

Figure 3. P and Cr X-ray maps of olivine from chondrules in (A) RC075 and (B) LEW 86549. Red arrows highlight significant features.

References: [1] Milman-Barris M.S. et al. (2008) *CMP* in press. [2] Beckett J.R. et al. (2008) *LPS*, this volume. [3] Dodd R.T. (1981) *Meteorites*. [4] Lofgren G. (1980) 487-551 in *Physics of Magmatic Processes*.