Semarkona (LL3.0)

Petrographic overview: Semarkona is recognized as one of the least metamorphosed ordinary chondrites (Sears et al., 1980; Huss et al., 1981), so it represents an important point of reference for understanding undisturbed igneous P distributions in chondrule olivines. High resolution X-ray intensity maps were collected for ten olivines from two type IIA chondrules in Semarkona. X-ray maps was collected for P and other elements (Fe, Cr, Al, and Ti as described in the Methods section). They span a range of crystal sizes and positions within the chondrule. We collected full quantitative analyses on five of the ten mapped olivines from Semarkona. Olivines are up to 250 µm in size (based on the longest dimension) and euhedral; some have abundant fractures; and they sit in a glassy groundmass (0.2-3.5 wt.% P_2O_5; Jones, 1990) that contains abundant microlites (Fig. 2a). Previous studies have suggested that some of the microlites are pigeonite (Jones, 1990). Minor metal was observed in the groundmass (< 1 wt. % of each chondrule). All ten of the mapped olivine crystals have Fo_{80-91} cores (mean = $Fo_{85.6}$; Table 1) and exhibit primary normal igneous zoning of Fe-Mg from core to rim similar to that described by Jones (1990) (Figs. 3d, h, l).

Phosphorus distribution: In Semarkona we observed concentric P-enriched bands that parallel crystal surfaces in all ten mapped olivines (mean width from background to peak concentration: 10.6 µm (n=5); Figs. 3b[A], f[A], j[A]), and three of the ten crystals have P-enriched regions near their cores that may outline the shapes of early-formed cores overgrown by subsequent olivine crystallization (e.g., Fig. 3b[B]). Similar features have been observed by Hewins (2009; see their Figs. 1, 2) in olivines from other Semarkona chondrules and by Milman-Barris et al. (2008; see their Figs. 1-5) in terrestrial and martian (i.e., SNC) igneous olivines. P_2O_5 concentrations in Semarkona olivines vary by more than an order of magnitude, ranging from below our detection limits (0.01 wt. %; 0.0003 P cations per formula unit [cpfu, based on 4 oxygens]) up to 0.21 wt. % (0.004 cpfu) with the maximum P concentrations always occurring in P-enriched zones (Table 1). This is similar to the maximum P_2O_5 concentrations of 0.2-0.4 wt. % observed by Milman-Barris et al. (2008) in zoned olivines from terrestrial basalts. Note that P zoning (and Cr zoning; see next paragraph) in Semarkona olivines is uncorrelated with the normal zoning of the divalent cations (Figs. 3d, h, l. Olivines near chondrule rims and near chondrule centers exhibited similar P-zoning patterns (Fig. 2a).

Chromium distribution: Cr contents of the olivines exhibit overall core-to-rim zonation (i.e., low Cr cores zoned to higher Cr rims) that are anti-correlated with zonation in Mg# (Figs. 3d, h, l). The concave-up profiles observed in all olivines (Figs. 3d, h, l) have been previously observed in Semarkona by Grossman and Brearley (2005) and interpreted as primary igneous zonation. Superimposed on this smoothly varying normal igneous zoning in Semarkona are perturbations to elevated Cr_2O_3 contents (~0.01-0.05 wt.%; note that although the Cr^{2+}/Cr^{3+} ratio is unknown in these samples and all Cr is reported as Cr^{3+}) that correlate with the P zoning (Figs. 3b-c[C], f-g[B], j-k[C]), although the Cr-enriched zones are more diffuse than the spatially correlated P-enriched zones (Figs. 3b-c[C], f-g[B], j-k[B]).

These perturbations in Cr content are small in Semarkona olivines, but they are similar to those observed by Milman-Barris et al. (2005) in terrestrial olivines (~0.01-0.1 wt.%). The superposition of correlated perturbations in Cr and P concentrations on the concave-up profile associated with normal igneous zoning may reflect different behaviors of Cr^{2+} and Cr^{3+} in the olivine. For example, simple igneous zonation may result from olivine Fe^{2+}-Mg^{2+}-Cr^{2+} substitution (DeHoog et al., 2010), while Cr^{3+} may play a larger role in correlated Cr-P zonation (e.g., Milman-Barris et al., 2005). Note that the perturbations in Cr that are superimposed on the dominant broad concave up patterns are small, so only a small fraction (<5%) of the total Cr in the Semarkona olivines is correlated with P zoning.

Aluminum distribution: P-correlated zoning of Al was not observed in any of the type IIA chondrule olivines we examined in Semarkona (and in any of the chondrites discussed further in the Results section), in contrast to the readily observed Al zoning in olivine from Hawaiian and martian meteorites (Milman-Barris et al. 2008; Beckett et al. 2008); indeed no Al zoning was observed at all in any studied chondrule. This likely reflects the concentration of Al_2O_3 in the melts from which the olivine crystallized. Typical bulk Al_2O_3 contents of type IIA ferromagnesian chondrules in Semarkona average ~2.7 wt. % (Jones, 1990), whereas Al_2O_3 concentrations in terrestrial and martian basalts are typically > 10 wt. %.

<u>*RC 075 (H3.1)*</u>

Petrographic overview: Like Semarkona, RC 075 is a highly unequilibrated H chondrite (McCoy et al., 1993), so igneous zoning of the divalent cations in chondrule olivines is thought to be largely preserved (McCoy et al., 1993; Sears et al., 1995). However, unlike Semarkona, RC 075 is heavily weathered (W4; Jull et al., 1991), and only traces of the original Fe-Ni metal and sulfide are preserved (24 volume % hydrated Fe oxides are present, leading McCoy et al. (1993) to calculate that the original metallic Fe-Ni metal content of the meteorite was 14.5%). Olivines are up to 300 µm in longest dimension and euhedral, and they are in a glassy groundmass with abundant microlites of unanalyzed composition (Fig. 2b). All studied olivines have ~$Fo_{76\text{-}87}$ cores (mean = $Fo_{82.1}$; Fig. 4 and Table 1), similar to the results of McCoy et al. (1993).

We mapped twelve olivine crystals from five type IIA chondrules in RC 075 for variations in P and other elements (Fe, Cr, Al, Ti); full quantitative analyses were obtained for three olivines from the two RC 075 chondrules shown in Fig. 4 (Table 1). Zonation patterns in these chondrules are similar to (and in the case of Cr, more pronounced than) those in olivines from Semarkona and terrestrial and SNC igneous olivines (Milman-Barris et al., 2008; Hewins, 2009), including such features as oscillatory zoning and high P cores.

Phosphorus distribution: All twelve mapped olivine crystals exhibit oscillatory zoning in P that has sharp boundaries (the mean width from background to peak concentration is 7.7 µm (n=7); e.g., Fig. 4j) and is uncorrelated with zoning in the divalent cations such as Fe and Mg (Figs. 4d, h, l). Moreover, the presence, intensity, and style of P enrichments are similar for olivines near chondrule edges and in chondrule centers (Fig. 2b). As in Semarkona, concentrations of P in oscillating zones vary by more than an order of magnitude, ranging from below our detection limits (0.01 wt. % P_2O_5; 0.0003 cpfu) to as much as 0.23 wt. % P_2O_5 (0.005 cpfu) (Table 1). Many RC 075 crystals also have cores with high P concentrations relative to the surrounding olivine (e.g., Fig. 4b[A], f[A]; Table 1). As we have observed in Semarkona and as previously described for igneous meteorites and terrestrial rocks, P zoning in olivine is uncorrelated with and spatially independent of zoning in divalent cations (e.g., Milman-Barris et al. 2008; Hewins, 2009; Foley et al., 2011; Balta et al., 2013; Shearer et al., 2013; except for some terrestrial veining; see supplementary material).

Chromium distribution: All twelve mapped crystals exhibit spatially correlated P-Cr zonation (Fig. 4). The broad concave up Cr patterns observed in Semarkona (Figs. 3d, h, l) that have previously been interpreted as primary igneous zoning (Grossman and Brearley, 2005) are not observed in RC 075 (Fig. 4d, h, l). This lack of Cr igneous zonation preservation as petrologic grade increased from 3.0 to 3.1 has also been observed by Grossman and Brearley (2005). Other features identified by Grossman and Brearley (2005) as occurring during the 3.0 $\rightarrow$ 3.1 increase in petrologic grade include mottled appearance in Cr X-ray intensity maps and

Cr-depleted zones near crystal edges (Figs. 4c[D], k[D]) that are surrounded by Cr-rich rims (Figs. 4c[C], g[C], k[C]). These features are visible in all of the mapped olivines (Figs. 4c[C-D], g[C], k[C-D]), are uncorrelated with the zoning in P, and differ from the Cr zoning discussed below that is correlated with P zoning. Additionally, the destruction of the primary igneous Cr zonation in RC 075 and the resulting overall decrease in the Cr contents of olivine outside of P-enriched zones and the resulting decrease in the total Cr concentration may be responsible for the fact that leads to Cr- and P-zonation being significantly more evident in meteorites more equilibrated than Semarkona.

P contents in RC 075 in each olivine crystal are positively correlated with Cr (average Cr_2O_3 for all points in all crystals = 0.35 wt. %; 0.007 cpfu) with a positive Cr intercept that differs from crystal to crystal (Figs. 5b, c). The high Cr intercept indicates that each crystal has its own background Cr concentration not associated with P enrichment (also observed in Fig. 9 of Milman-Barris et al., 2008) onto which is superimposed the observed correlated P-Cr zonation. The P-Cr coupling observed in Fig. 4 traverses was not as pronounced in Semarkona (most likely due to its significant primary core-to-rim igneous zoning).

Cr associated with P is superimposed on a background Cr concentration (i.e., the intercepts in Fig. 5b and 5c) that varies by ~0.001 cations per formula unit within a crystal, but can differ by a factor of several between crystals (Fig. 4d background Cr is 0.002 vs. Fig. 4h background Cr is 0.007). Within a P-enriched-zone, the perturbations in Cr cations above the background zoning are often much smaller than the background (i.e., the Cr correlated with P is a small fraction of the total Cr). In chondrule 2, both of the analyzed olivines have similar slopes in P-Cr space (~1:1) suggestive of a ratio of P/Cr that varies in a similar manner (Fig. 5c), although the Cr intercepts differ. This ~1:1 slope is common in igneous olivines in terrestrial and meteoritic rocks (Milman-Barris et al., 2008). The olivine crystal analyzed in chondrule 1, however, exhibits three distinct trends in P-Cr (Figs. 5a, b). One of these, labeled C in panels a and b, is the artifact of an alteration vein that passes through the crystal but the other two (A and B) are interpreted to reflect differences in olivine chemistry. P:Cr variations near A in Fig. 5b are consistent with a slope of ~4/3, comparable to the slope of ~1 observed for olivine 1 in chondrule 2 (Fig. 5c), but the slope in P-Cr space in the vicinity of B is significantly lower, ~1/3. These two trends correspond to distinct regions within the crystal (innermost core and rim vs. mid-portion of crystal), suggesting that different olivine substitution mechanisms dominated during different periods of olivine growth. Note also that the "B" trend formed during an intermediate time in the growth of the crystal as the P-Cr slope in olivine on both sides of region "B" are higher. The lack of compositional symmetry may reflect true chemical differences during growth periods or may be the result of cutting variations through this crystal.

WSG 95300 (H3.3) and BTN 00301 (H3.3)

Petrographic overview: WSG 95300 and BTN 00301are more chemically equilibrated chondrites than Semarkona or RC 075 which exhibit small amounts of weathering (A/B and B, respectively, following the descriptors set forth by the Meteorite Working Group). Olivines in these chondrules are up to 250 μm diameter, euhedral, and set in glassy groundmasses with abundant microlites of unanalyzed composition (Fig. 2c). Olivines in WSG 95300 and BTN 00301 have ~$Fo_{73\text{-}88}$ cores (mean = $Fo_{81.3}$) and ~$Fo_{73\text{-}83}$ cores (mean = $Fo_{77.9}$; Table 1), respectively. Fe-Mg zonation consistent with primary igneous zoning is present in all observed olivines (Figs. 6a-c). Minor metal is observed in the chondrule groundmasses (< 1 wt. % of each chondrule). Nineteen olivines in four type IIA chondrules in WSG 95300 (Figs. 4b and 6a, d) and nine olivines in two type IIA chondrules in BTN 00301 (Fig. 6g) were mapped for P, Fe, Cr, Al, and Ti; full quantitative analyses were completed on three olivines in WSG 95300 and two in BTN 00301.

Phosphorus distribution: P concentrations range from below our detection limits (0.01 wt. %; 0.0003 cpfu) up to 0.23 wt. % (0.005 cpfu) in WSG 95300 and up to 0.34 wt. % (0007 cpfu) in BTN 00301 (Table 1). All of the mapped olivine crystals have well-defined P zonation (mean width from background to peak concentration: 6.0 µm WSG 95300 (n=4), 8.6 µm BTN 00301 (n=2)). The presence, intensity, and style of P enrichments are similar for olivines near chondrule edges and in in chondrule centers (Fig. 2c). Observed zoning patterns are consistent with patterns seen in Semarkona and RC 075, with olivine crystals often displaying high-P cores (Fig. 6d[A]) and oscillations near crystal rims (Figs. 6a[A], d[B]), but low-P cores with oscillations of higher P olivine surrounding them, not seen in the previous two meteorites, are also observed (Fig. 6g[A]). As with Semarkona and RC 075, P zoning patterns are not correlated with zoning of the divalent cations.

Figure 8b is a BSE photomicrograph of chondrule 2 from WSG 95300 with a superimposed low-resolution P K_α X-ray map (areas of high P concentration display as orange). The threshold concentration was not calibrated but, given the counting times (10 µseconds/pixel; 25 passes), it likely exceeded several wt. % in the analyzed volume (i.e., P zoning in the olivines is not resolved in this map). Finer scale SEM examination of P hot spots in the matrix around the rim of the chondrule and in the groundmass reveals the presence of small, submicron crystals of Ca-phosphate. Similar maps of chondrules in RC 075 (Fig. 8a) and Semarkona reveal no comparable pattern of P-enriched phases localized around chondrule rims, although there are occasional P hot spots within the mesostases.

Chromium distribution: Cr zonation spatially correlated with P in olivine is observed in WSG 95300 and BTN 00301 (Figs. 6c, f, i) (average Cr_2O_3 for all points in all crystals = 0.23 and 0.12 wt. %, respectively) and the boundaries between low concentration regions and high concentration regions remain as distinct as that observed in RC 075. Cr contents in interior olivines (i.e., those not in direct contact with the chondrule rim) are uniformly lower than observed in the less equilibrated chondrites, although a systematic study of all olivines along a chondrule transect was not undertake. Cr-rich veins, similar to those observed in RC 075, dominate the Cr concentration in BTN 00301 (Fig. 6h[B]).Every olivine crystal is surrounded by a high-Cr rim similar to that reported by Grossman and Brearley (2005) (Figs. 6b [B], e [C], h[C]).

<u>*Sharps (H3.4)*</u>

Petrographic overview: Sharps is a more chemically equilibrated chondrite than the previously described meteorites; weathering grade has not been quantified, but it is low as the meteorite is a fall. Olivines in type IIA chondrules are up to 300 µm in diameter, euhedral, and set in a microlite-rich groundmass (Figs. 2d, 7d). Olivine cores are ~$Fo_{79\text{-}88}$ (mean = $Fo_{84.3}$; Table 1). Fe-Mg zonation consistent with primary igneous zoning is present in all observed olivines (Figs. 6d-e). Minor metal is observed in the chondrule matrix (< 1 wt. % of each chondrule). Nine olivines in two type IIA chondrules were mapped for P, Fe, Cr, Al, and Ti in Sharps, one of which is BSE imaged in Fig. 2d.

Phosphorus distribution: Concentrations of P_2O_5 in olivine range from below detection limits (0.01 wt. %; 0.0003 cpfu) up to 0.43 wt. % (0.009 cpfu) (Table 1). All olivine crystals have P zonation that is comparably distinct to that observed in the lower grade chondrite types described above (i.e., mean distance from background to peak concentration is 8.0 µm (n=4);

Figs. 7c, f), and they also have oscillatory P zoning that is independent of position within the chondrule (Figs. 2d, 7a[A]) and both high (Fig. 7d[A]) and low (Fig. 7a[B]) P cores.

Low-resolution P maps of whole chondrules show P concentrated into submicron Ca-phosphate crystals in the matrix immediately surrounding the objects (Fig. 8c), which is consistent with observations for WSG 95300 and BTN 00301.

Chromium distribution: Chromium zonation (average Cr_2O_3 = 0.15 wt. %; 0.003 cpfu) is spatially correlated with P zonation in all but two crystals, although the Cr concentration is less than observed in the less equilibrated H chondrites. Cr-zonation is not present in the non-P correlated crystals. Cr-rich rims are observed surrounding all crystals (Figs. 7b[C], e[C]). In addition, SEM examination shows high Cr phases in the matrix near but outside the chondrule rims and scattered throughout olivine crystals inside the chondrules (Figs. 2d, 7e[D]).

<u>*MAC 88174 (H3.5)*</u>

Petrographic overview: MAC 88174 is a more chemically equilibrated chondrite than those previously described exhibiting minor weathering (A/Be following the conventions of the Meteorite Working Group). Olivines in type IIA chondrules are up to 400 µm in diameter, euhedral, and set in a glassy groundmass containing abundant microlites (Fig. 8d). Olivine cores range in composition from ~$Fo_{71\text{-}82}$ (mean = $Fo_{76.0}$; Table 1). Fe-Mg zonation consistent with primary igneous zoning is present in all observed olivines (Fig. 7i). Minor metal is observed in the chondrule groundmass (< 1 wt. % of each chondrule). Eight olivines in two type IIA chondrules were mapped and two olivines were quantitatively analyzed in MAC 88174.

Phosphorus distribution: Concentrations of P_2O_5 in olivine range from below detection limits (0.01 wt. %; 0.0003 cpfu) up to 0.30 wt. % (0.006 cpfu) (Table 1). All olivine crystals were observed to have well-defined P oscillatory zoning (mean width from background to peak concentration: 4.3 µm (n=2); e.g., Fig. 7g[A]), including crystals near chondrule rims (Fig. 2d).

As in WSG 95300, BTN 00301, and Sharps, low-resolution P maps of whole chondrules show concentration of P in submicron Ca-phosphate crystals in the matrix immediately surrounding them (e.g., Fig. 8d).

Chromium distribution: Correlated Cr zonation (average Cr_2O_3 = 0.09 wt. %; 0.002 cpfu) is present (Fig. 7i) in two of the eight mapped crystals; Cr zoning uncorrelated with P is not observed. The two crystals observed to have Cr zoning retain indistinct oscillatory Cr zoning near crystal centers (Fig. 7h[A]) that is spatially correlated with P, but P-correlated Cr is absent near crystal edges. Cr-rich veins, similar to those observed in RC 075, dominate the Cr concentration (Fig. 7h[C]). Cr-rich rims are observed surrounding all crystals. As with Sharps, SEM examination shows high Cr phases in the matrix near but outside the chondrule rims and scattered throughout olivine crystals inside the chondrules (Fig. 8d).

<u>*Dhajala (H3.8)*</u>

Petrographic overview: Dhajala is a more chemically equilibrated chondrite than those previously described; weathering grade has not been quantified, but it is low as the meteorite is a fall. Olivines in type IIA chondrules are up to 300 µm in diameter, euhedral, and set in a devitrified glassy groundmass with abundant microlites (Figs. 2e, 8e, f). Olivine compositions range from ~$Fo_{77\text{-}81}$ (mean = $Fo_{79.6}$; Table 1). Igneous zonation of Fe-Mg was not observed in any of the studied olivines (Figs. 9c, f)); presumably it was originally present, but has been homogenized by thermal metamorphism (Van Schmus and Wood, 1967). Minor metal is observed in the chondrule matrix (< 1 wt. % of each chondrule). Nine olivines in three type IIA chondrules in Dhajala were mapped for variations in P, Fe, Cr, Al, Ti; full quantitative analyses were obtained for three olivines..

Phosphorus distribution: Phosphorus concentrations range from P_2O_5 below detection limits (0.01 wt. %; 0.0003 cpfu) up to 0.15 wt. % (0.003 cpfu) (Table 1). Eight of the nine crystals exhibit well-defined P zonation (mean width from background to peak concentration (n=3): 5.3 µm; e.g., Figs. 9a, d). The ninth, an olivine crystal near the rim of chondrule 1 was featureless in the P map (Fig. 2e). Dhajala olivine 1 (chondrule 1) exhibits oscillatory zoning (Figs. 9 a[A], 9d[A]) and a high P interior feature (Fig. 9a[B]) similar to those previously described above for the less equilibrated chondrites (cf., Fig. 2).

Low-resolution P maps of whole chondrules show P halos composed of concentrated submicron Ca-phosphate crystals within the chondrule near the chondrule-matrix interface and in the immediately surrounding matrix (Fig. 8e, f).

Chromium distribution: Chromium zonation is spatially correlated with P in two of nine mapped olivine crystals but at lower concentration and less distinctly than in RC 075 (Figs. 9c, f). Chromium concentrations in Dhajala olivines are generally much lower than observed in RC 075 (Dhajala maximum Cr_2O_3 = 0.10 wt. % (0.004 cpfu) and background Cr_2O_3 = 0.02 (0.0004 cpfu); RC 075 maximum Cr_2O_3 = 0.35 wt. % (0.007 cpfu) and background Cr_2O_3 = 0.21 wt. % (0.004 cpfu)). Cr-rich rims are observed surrounding all olivine crystals (Fig. 9b[C]). In addition, SEM examination of the Dhajala chondrules shows high Cr phases in the matrix near but outside the chondrule rims and scattered throughout olivine crystals inside the chondrules (Figs. 8e, f); of the previously described, lower grade meteorites, comparable Cr hot spots are only seen in Sharps (H3.4) and MAC 88174 (H3.5), the highest grade meteorites of those previously described.

<u>*Forest Vale (H4)*</u>

Petrographic overview: Forest Vale is a chemically equilibrated chondrite; weathering grade has not been quantified, but it is low as the meteorite is a fall. Olivines in chondrules that were suggested to be type IIA by the criteria described in the methods section are up to 250 µm in diameter, euhedral, and contained in a devitrified glass groundmass with abundant microlites were identified. Olivine compositions range from ~Fo_{81-82} (mean = $Fo_{81.9}$; Table 1). Igneous zonation of Fe-Mg was not observed in any of the studied olivines (Figs. 9i, l); presumably it was originally present, but has been homogenized by thermal metamorphism (Van Schmus and Wood, 1967). Nineteen olivines from four type IIA chondrules in Forest Vale were mapped for P, Fe, Cr, Al, and Ti and nine of these were quantitatively analyzed.

Phosphorus distribution: Phosphorus concentrations in these crystals range from P_2O_5 below detection limits (0.01 wt. %; 0.0003 cpfu) up to 0.27 wt. % (0.006 cpfu) (Table 1). Of the nine quantitatively analyzed olivines, six of the nine exhibit clear P zoning features (mean width from background to peak concentration: 19.4 µm (n=4)), including high P interiors (Fig. 9g[A]) and oscillatory zoning (Figs. 9j[A]); the other three show no P zoning features. Interior olivines (i.e., any crystal not touching the chondrule rim in the plane of the section) of small size display P-zoning, whereas small crystals near the chondrule rims (within ~15 µm of the rim) were unzoned. However, several large olivine crystals that extended from the chondrule interior (i.e., >100 µm from the rim in the plane of the section) to the rim were observed to be zoned; in one case an olivine that spanned the whole chondrule, from rim to rim was zoned. We note, however, P-zoning in an individual crystal was either clearly delineated or not observed; no intermediate states were observed.

In contrast to the H3.3-H3.8 chondrites described above, there is no P-enriched zone in the Forest Vale matrix immediately surrounding the chondrules. No further P-enriched zones surrounding chondrules were observed in the more chemically equilibrated meteorites to follow unlike in the H3.3-H3.8 chondrites.

Chromium distribution: Cr contents were very low with no observed examples of P-correlated enrichment of Cr (maximum Cr_2O_3 = 0.04 wt. % (0.0007 cpfu); average Cr_2O_3 = 0.01 wt. % (0.0003 cpfu)). Cr-rich veins, similar to those observed in RC 075, dominate the Cr concentration in olivine 1, chondrule 2 (Fig. 9h[B]). High-Cr rims surrounding olivine crystals were observed (Figs. 9h[C], k[B]).

<u>*Allegan (H5)*</u>

Petrographic overview: Allegan is an equilibrated chondrite with low weathering grade (W0) (Natural History Museum, Catalogue of Meteorites). Olivines in chondrules suggested to be type IIA by the textural criteria described in the methods section were up to 300 μm in diameter, euhedral, and contained in a devitrified glass groundmass with abundant microlites (Fig. 1b). Olivine cores range from ~Fo_{81-83} (mean = $Fo_{81.6}$; Table 1). Igneous zonation of Fe-Mg was not observed in any of the studied olivines. Minor metal is observed in the chondrule matrix (< 1 wt. % of each chondrule). Ten olivine crystals in five porphyritic olivine chondrules thought to represent altered Type IIA chondrules were mapped in Allegan for variations in P, Fe, Cr, Al, Ti; full quantitative analyses were obtained for two olivines.

Phosphorus distribution: P_2O_5 concentrations range from below the detection limit (0.01 wt. % P_2O_5; 0.0003 cpfu) to 0.17 wt. % P_2O_5 (0.004 cpfu), comparable to the ranges observed in highly unequilibrated chondrites like Semarkona and RC 075 (Table 1). Five of the ten mapped olivines exhibit well-defined high P zones (mean width from background to peak concentration: 9.0 μm (n=4); e.g., Figs. 9a, b), and all of the crystals lacking P oscillations in K_α X-ray maps were within 50 microns of chondrule rims. In all of the examined chondrules olivines exhibiting P zoning and those without were both found in the same chondrule. Features such as oscillatory zoning (Figs. 10a[A], d[A]) and high P cores (Figs. 10 a[B], d[B]) remain sharp when present.

As observed in Forest Vale, there is no P-enriched zone in the matrix immediately surrounding the chondrules.

Chromium distribution: K_α X-ray maps of Cr showed no P-correlated zoning of Cr (Figs. 10c, f), and concentrations of Cr measured quantitatively were below detection limits for all analyzed olivines (< 0.01 wt. %). Cr-rich rims were not observed surrounding olivines in Allegan.

<u>*Guareña (H6)*</u>

Petrographic overview: Guareña is a chemically equilibrated chondrite with minor to moderate weathering (W3) (Natural History Museum, Catalogue of Meteorites). Except for barred olivine chondrules whose outlines are often readily discerned, it is difficult to identify distinct chondrules in Guareña due to extensive recrystallization (especially of the matrix.) We were not able to discern whole porphyritic olivine chondrules with sharply delineated boundaries, but there are regions with the textural characteristics of type IIA chondrules (e.g., irregular shape, euhedral olivines, etc.; Fig. 1c) and it is on these areas that we concentrated. We mapped eight olivines in seven such “chondrule-like regions” for variations in P, Fe, Cr, Al, Ti; full quantitative analyses were obtained for two olivines. Olivine cores range from ~Fo_{79-81} (mean = $Fo_{80.5}$; Table 1). Minor metal is observed in the chondrule matrix (< 1 wt. % of each chondrule).

Phosphorus distribution: Phosphorus zonation is observed in five of the eight mapped olivines within these zones, including oscillatory zonation (olivine 1, chondrule 1; mean width from background to peak concentration: 12.5 μm (n=2)) (Fig. 10g[A]) and high-P crystal interiors (olivine 1, chondrule 2) (Figs. 10j[A]). Igneous zonation of Fe-Mg was not observed in any of the studied olivines. Observed P concentrations range from below the detection limit (P_2O_5 < 0.01 wt. %, 0.0003 cpfu) to 0.23 wt. % P_2O_5, comparable to ranges observed in zone crystals from the previously described meteorites (Table 1).

Olivines without P oscillations occur towards the outer portions of type II chondrule-like regions but blurring of chondrule boundaries with the matrix makes it difficult to confidently ascribe position within the original chondrule. As with Forest Vale and Allegan, no P-enriched halos were observed in the matrix near the interface with these chondrule-like regions.

Chromium distribution: Cr concentrations were below detection limits (< 0.01 wt. %). High-Cr olivine rims were also absent.

Summary of petrographic results

1. P-enriched zones are present in type IIA chondrule olivines from all studied chondrites, and, where present, they are uncorrelated with zoning in Fe/Mg (e.g., Fig. 4). Observed zoning patterns include oscillatory zoning, high-P cores surrounded by oscillatory zoned rims, and zones that appear to follow the grain boundaries of the olivine. Olivines in unequilibrated to partially chemically equilibrated chondrites (Semarkona (LL3.0) and H3.1-H3.5) are zoned in P regardless of their position within the chondrules (Table 1), but in higher-grade meteorites (H3.8 – H6), olivines in the interior portions of chondrules are zoned whereas those in contact with chondrule rims are devoid of P zonation (Table 3; Fig. 2).

2. Reconnaissance mapping of olivine from barred olivine chondrules and type I (low-FeO) chondrules (Fig. 14). K_α X-ray maps of olivines in barred olivine chondrules in RC 075 (H3.1; 1 chondrule) and Guareña (H6; 2 chondrules exhibit no zonation in any of P, Cr, or Al. Nor was oscillatory zoning in any of these elements observed in type IA chondrule olivines in RC 075 (H3.1; 3 chondrules), Dhajala (H3.8; 2 chondrules), or Forest Vale (H4; 6 chondrules; Fig. 14b) or in what appears by shape to have been a type IA chondrule in Guareña (H6; Fig. 14c).

3. Low-resolution maps of whole chondrules (e.g., Fig. 7 from H3.3-H3.8 chondrites have P-enriched “halos” (~20 μm thick) in the matrix immediately surrounding chondrule rims. Although such halos are not observed in the unequilibrated chondrites Semarkona (H3.0) and RC 075 (H3.1), P “hot spots” (Ca-phosphate crystals) are occasionally observed in the chondrule groundmass, but P-enriched regions surrounding the chondrule are absent. Neither P-enriched “halos” nor “hot spots” have been observed in the highly equilibrated chondrites Forest Vale, Allegan, and Guareña (H4-H6).

4. P-correlated zoning of Al was not observed in any of the ferromagnesian chondrules we examined, which contrasts with the observation of Al zoning in olivine from Hawaiian basalts and Martian meteorites (Milman-Barris et al. 2008; Beckett et al. 2008). This is likely due to the low concentrations of Al contents in the melt in the chondrules from which the olivine crystallized relative to terrestrial and meteoritic silicate liquids.

5. Many olivines in chondrules display P-correlated zoning of Cr. In the highly to moderately unequilibrated ordinary chondrites (Semarkona (LL3.0) and H3.1 – H3.4), P-correlated variations in Cr are present in all the studied olivines. P-correlated Cr zoning is most evident in RC 075 (H3.1) and higher than in Semarkona (LL3.0) as Semarkona still retains igneous Cr zonation that partially obscures the P-Cr correlation. As Cr becomes mobile during metamorphism, the igneous zoning is lost, but the P-correlated zoning remains. For MAC 88174 (H3.5) and Dhajala (H3.8), P-correlated zoning of Cr is present in olivines found in chondrule interiors, but absent in those crystals which are in contact with chondrule rims. P-correlated Cr

zoning was not observed in the equilibrated chondrites. Although high concentrations of Cr may be observed even in the highest metamorphic grades due to secondary veining and/or nearby chromite crystals (likely composing the Cr hotspots described earlier), this Cr is not spatially correlated with P. These observations are consistent with a previous study documenting the evolution of olivine Cr concentrations as metamorphism increases in ordinary and carbonaceous chondrites (Grossman and Brearley, 2005). Olivine Cr content has been correlated with the degree of thermal metamorphism experienced by the sample in olivines with FeO > 2 wt. % and is nearly absent in ordinary chondrites of metamorphic grade 3.6 and higher (Grossman and Brearley, 2005). P-correlated Cr zoning in olivine was not observed in previous studies and suggests a different olivine incorporation mechanism than that put forth by Grossman and Brearley (2005) as well as different diffusive reequilibration conditions.

In Fig. 11a, the Cr-P contents of studied chondrule olivines are compared. Olivines from the highly to moderately unequilibrated ordinary chondrites (LL3.0, H3.1-H3.4) show positive slopes of ~1. The notable exception is the ~1:3 slope noted in RC 075 chondrule 1, in which two distinct slopes are observed (Fig. 5b). It is also noteworthy that the Cr intercept is non-zero in all cases, consistent with substitution of most of the Cr independent of P. Additionally, the olivines in Semarkona and RC 075 chondrule 2 have a significantly higher Cr intercepts than for any other chondrule studied, likely the result of diminished olivine Cr contents at higher metamorphic grades (Grossman and Brearley, 2005). Olivines in the highly equilibrated chondrites (H3.5-H6) contain little Cr, as discussed above. The data points on Fig. 11a shift horizontally with increasing thermal metamorphism (> H3.5) and olivines begin to exhibit only P zonation (Fig. 11a). At or above metamorphic grade 3.8 olivines in contact with chondrule rims lose their P zoning while those in the chondrule interiors retain it. Olivine P zoning was found to be a binary in this study; either a crystal possessed it or did not. There was no intermediate step observed.

In Fig. 11b, Semarkona and RC 075 chondrule olivine compositions are compared with those from a range of terrestrial igneous environments including basalts, komatiites, and dacite (Milman-Barris et al., 2008). These chondrule olivines were chosen as they represent both the most unequilibrated crystals and the greatest range for the studied chondrites in Cr-P space. Data for terrestrial olivines generally have higher slopes in P-Cr space than those observed in the chondritic samples (near vertical for Volcán San Pedro, Hawaii, and Siqueiros), with the notable exception of olivine from a picritic komatiite from Gorgona whose slope is closer to the ~1:3 observed in RC 075 chondrule 1 B slope (Fig. 5b).

Finally, we note that although Semarkona and RC 075 olivines have qualitatively similar P zoning patterns, concentrations of Cr not associated with P are considerably higher in Semarkona olivines (0.01 – 0.03 cations per formula unit) than in RC 075 (0.002 – 0.008 cpfu). Also, all three olivine traverses we conducted on Semarkona olivines are concave up in Cr, consistent with the incorporation of an incompatible element during fractional crystallization (Figs. 3d, h, l). In only one of the three RC 075 traverses is the background Cr profile arguably concave up (Fig. 4h). This may result from the reducing conditions experienced by Semarkona during chondrule crystallization, where much of the Cr substituting into olivine is divalent (e.g., Sutton et al. 1996) and this Cr is unaffected by the processes leading to oscillations in P concentration.