**PHOSPHATE MINERALOGY AND THE BULK CHLORINE / FLUORINE RATIO OF ORDINARY CHONDRITES.** R. H. Jones[1] and F. M. McCubbin[1,2], [1]Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, rjones@unm.edu, [2]Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131, fmccubbi@unm.edu.

**Introduction:** The phosphate mineralogy of ordinary chondrites can provide insights into the nature and role of fluids that existed during metamorphism on OC parent asteroids. In particular, since the X anion site in apatite can host F, Cl, and OH, the composition of apatite provides direct evidence for the existence and relative abundances of volatile species. We recently studied the occurrence and compositions of phosphate minerals in the Zag, halite-bearing H chondrite breccia [1]. Apatite in different fractions of Zag has widely varying Cl/F ratios, from ~1 to ~0.5, which we interpret as a record of evolving fluid compositions on the Zag parent body. Our SIMS analyses showed that any fluid was water-poor [1]. However, we did not have a good understanding of apatite compositions within typical unbrecciated H chondrites with which to compare the Zag analyses. Here we describe the occurrence and development of apatite and merrillite in several H chondrites. We discuss variations in apatite occurrence and compositions with petrologic type, and the relationship between Zag and typical H chondrites.

Apatite is the major host for chlorine and fluorine in ordinary chondrites. Hence, one would expect that the Cl/F ratio of apatite would be comparable to bulk chondrite Cl/F ratios. Using our data for apatite in H chondrites and LL chondrites [2,3], we discuss our current understanding of halogen abundances in OCs.

**Samples and Methods:** We studied phosphate minerals in Avanhandava (H4), Richardton (H5), Oro Grande (H5) and Estacado (H6). Oro Grande is a find and is moderately weathered; the others are falls. Quantitative electron microprobe (WDS) analyses were obtained using methods described by [3].

**Results:** Phosphate minerals show textural differences in different chondrites (Fig. 1). These differences can be interpreted as progressive textural equilibration with increasing petrologic type. In Avanhandava (H4), apatite and merrillite are associated in fine-grained assemblages. In Oro Grande and Richardton (both H5), larger apatite grains occur with minor merrillite in what appears to be a reaction relationship; some apatite in Oro Grande contains pores. In Estacado (H6), apatite grains are large (>100 μm) and show no evidence for reaction. All these chondrites also contain individual merrillite grains that are not associated with apatite.

Merrillite compositions are close to the ideal formula, $Na_2(Mg,Fe^{2+})_2Ca_{18}(PO_4)_{14}$, in all the H chondrites studied. Apatite compositions, $Ca_5(PO_4)_3(X)$, have variable Cl/F ratios and each of the chondrites has a distinct average Cl/F ratio: 9.7, 21.8, 6.0 and 15.2 wt%, or 5.2, 11.7, 3.2 and 8.1 atomic percent in Avanhandava, Richardton, Oro Grande and Estacado, respectively. Figure 2 shows anion site occupancy for all apatite analyses. Most apatite analyses show approximately 10% of anions "other" than halogens: we have shown that for Zag and in LL chondrites, this component is not OH [1,3], so we label it as "other" rather than the conventional OH in this diagram.
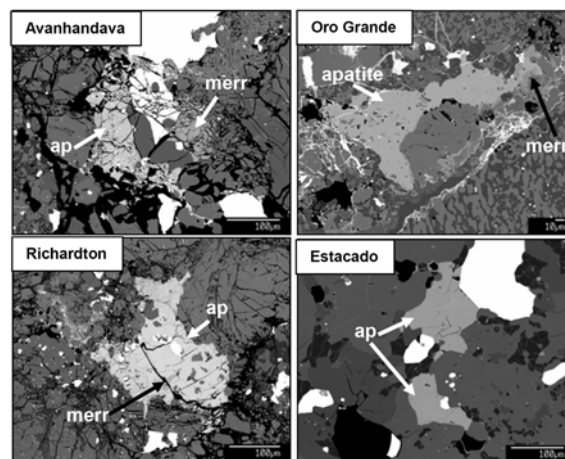


Figure 1: Phosphate minerals in H chondrites. Merrillite (merr) is slightly darker grey than apatite (ap).
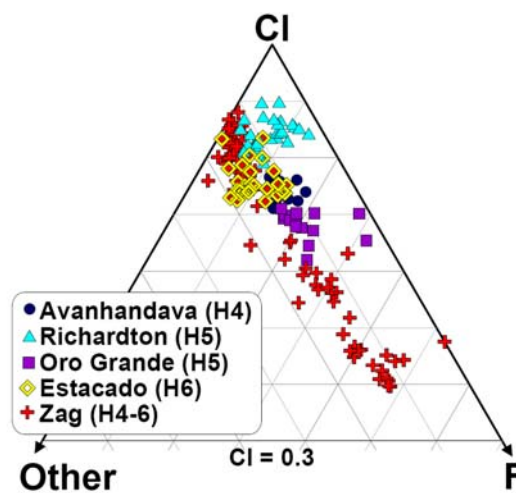


Figure 2: Anions in apatite in H chondrites.

**Discussion:** Phosphate minerals in typical, unbrecciated H chondrites show textural characteristics similar to those observed in LL chondrites [2,3]: porosity and reaction relationships with merrillite indicate reactions in the presence of fluids, and textural equilibration occurs with increasing degree of metamorphism. Apatite shows distinct Cl/F ratios in individual chondrites (Fig. 2), but there is no progressive change in this ratio with increasing petrologic type. A progressive increase in Cl/F during metamorphism could be interpreted as increasing loss of the more volatile F during heating. Since we do not see this, we suggest that apatite in each of these chondrites equilibrated with a fluid of slightly different composition. Either the H chondrite parent body was heterogeneous, or there were multiple H chondrite parent bodies.

Apatite compositions in Zag show a much wider range than those in non-brecciated H chondrites (Fig. 2). In general, apatite in the H4 fraction of Zag has a much higher Cl/F ratio than that in the H6 fraction [1]. Apatite in the H4 fraction of Zag also has a much higher Cl/F ratio than apatite in the H4 chondrite Avanhandava. In Zag, halite is associated with the H4 fraction [4,5]: we consider that the strong enrichment in Cl in this material indicated by both apatite and halite is evidence that Cl-rich fluids were pervasive and possibly indigenous [1].
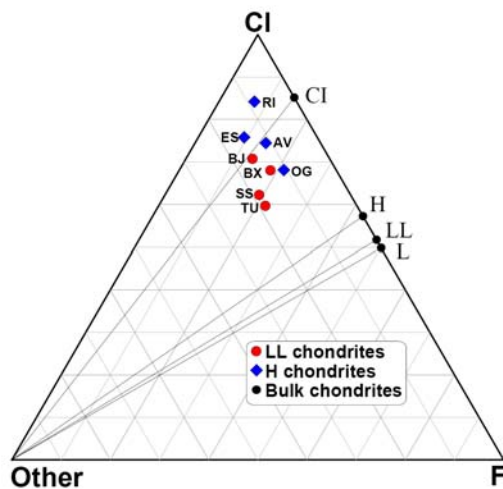


Figure 3: Average compositions of apatite in H chondrites (this work – Fig. 2) and LL chondrites [2,3]. Bulk chondrite symbols and lines are Cl/F ratios from [6]. AV = Avanhandava (H4), RI = Richardton (H5), OG = Oro Grande (H5), ES = Estacado (H6), BX = Bo Xian (LL3.9), BJ = Bjurböle (L/LL4), TU = Tuxtuac (LL5), SS = St. Séverin (LL6).

Figure 3 shows average values of anion site occupancy in H chondrites (from Fig. 2) and LL chondrites that we have studied previously [2,3]. In Fig. 3 we also show bulk chondrite Cl/F ratios of H, L, LL and CI

chondrites, taken from the compilation of [6]. Schaefer and Fegley [7] also carefully considered known OC Cl and F abundances: their values differ slightly from those of [6], with atomic Cl/F values of 0.60 (H), 0.59 (L), and 0.54 (LL). Essentially, the best estimates for bulk OC Cl/F values lie between 0.5 and 0.6.

One would expect that apatite is the major host for halogens in OCs. However, in all the unbrecciated H and LL chondrites we have analyzed, apatite has considerably higher Cl/F ratios than measured bulk OC values: Cl/F ratios are actually more comparable to the value determined for bulk CI chondrites (Fig. 3). In general, apatite in LL chondrites has lower Cl/F ratios than apatite in H chondrites. Apatite Cl/F ratios comparable to bulk OC values have only been observed in the H6 fraction of Zag (Fig. 2; [1]).

There are different possible interpretations of these observations. One possibility is that we do not have reliable determinations of bulk F abundances in ordinary chondrites. Bulk chlorine abundances are quite well known from several studies [e.g. 8-10], but F is more difficult to measure and reported abundances have large ranges and uncertainties [6,7,11]. Alternatively, it is possible that F is present in other minerals, such as feldspar [5,7] or pyroxene. The excess fluorine would be present in feldspar at a level of about 200 ppm, or in low-Ca pyroxene at approximately 100 ppm, which is much higher than typical F abundances in igneous pyroxene from high pressure experiments [12,13]. Since an understanding of the bulk Cl/F ratio of OCs is essential to an interpretation of initial halogen abundances, as well as the behavior of volatile elements, in the inner solar system, it is important to recognize the uncertainties in our current understanding of these values. New measurements of bulk F abundances in OC falls, and in the major silicate minerals in OCs, would help to resolve these questions.

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