

**PHOSPHATE MINERALS IN TYPE 4-6 LL CHONDRITES: THE NATURE OF FLUIDS ON THE LL CHONDRITE PARENT BODY.** R. H. Jones<sup>1</sup>, F. M. McCubbin<sup>1,2</sup>, L. Dreeland<sup>1</sup> and Y. Guan<sup>3</sup>, <sup>1</sup>Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, rjones@unm.edu <sup>2</sup>Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131, <sup>3</sup>Division of Geological and Planetary Sciences, Caltech, Pasadena, CA 91125.

**Introduction:** Ordinary chondrites (OCs) of petrologic types 4 to 6 exhibit a sequence of progressive chemical and textural equilibration. However, the conditions and environment of metamorphism are not well constrained. The role of fluids during metamorphism is poorly understood, although there is evidence that fluids were present [1-3]. The secondary phosphate minerals apatite and merrillite can be used to interpret the conditions of the metamorphic environment, since they can potentially preserve a record of interactions with parent body fluids. We are currently carrying out a study of the mineralogy of phosphate minerals in type 4-6 LL chondrites [3-5]. Electron microprobe analyses of chlorapatite in these chondrites indicate a significant anion deficiency, which could be attributable to the presence of the OH<sup>-</sup> anion, and hence provide evidence for the presence of aqueous fluids. Here we report SIMS measurements of OH abundance in chlorapatite, which shows that the metamorphic environment of the LL chondrites is actually extraordinarily dry.

**Analytical Methods:** We analyzed phosphate minerals in Bo Xian (LL3.9), Tuxtuac (LL5) and St. Séverin (LL6). Phosphate grains were identified in thin sections using BSE imaging and WDS elemental X-ray mapping. Electron microprobe analyses of individual grains were carried out using procedures that took into account and minimized possible volatilization of F and Cl [6,7]. Analytical conditions were typically 15 kV, 20 nA and a 5 μm diameter electron beam.

SIMS analyses of OH were carried out on the Cameca 7f Geo instrument at Caltech. Samples were measured with a ~20 μm Cs<sup>+</sup> primary beam of +10 keV and ~3.5nA, rastering over an area of 10x10 μm. Negative secondary ions (<sup>12</sup>C<sup>-</sup>, <sup>16</sup>O<sup>1</sup>H<sup>-</sup>, <sup>18</sup>O<sup>-</sup>, <sup>19</sup>F<sup>-</sup>, <sup>31</sup>P<sup>-</sup>, <sup>32</sup>S<sup>-</sup>, and <sup>35</sup>Cl<sup>-</sup>) of -10 keV were collected from the center 10 μm at a mass resolving power of ~4500. Sample charging was compensated with an electron gun at -10 keV. Secondary ion images of <sup>12</sup>C<sup>-</sup>, <sup>16</sup>O<sup>1</sup>H<sup>-</sup>, and <sup>19</sup>F<sup>-</sup> were examined before each sample measurements to avoid cracks and contamination. A calibration curve for OH was determined from five terrestrial apatite standards that had H<sub>2</sub>O contents varying from 300 to 5500 ppm. H<sub>2</sub>O contents of the standards were determined by manometry using the technique of [8], and were in close agreement with OH contents computed from electron microprobe analyses of the same apatite grains, with OH calculated from anion totals by differ-

ence. SIMS analyses of F show an excellent correlation with electron microprobe and bulk analyses of F abundances. A preliminary calibration for S is currently based solely on the published analysis of Durango apatite.

**Results:** Chlorapatite occurs in all three chondrites with typical grain sizes 10-50 μm, and individual grains up to 200 μm across. Chlorapatite is rare in both Bo Xian and St. Séverin, and is more abundant in Tuxtuac. In all three chondrites, chlorapatite shows features that suggest an origin in the presence of fluids, including fracture-filling textures, the presence of abundant pores, and reaction relationships with merrillite and other minerals including olivine [3-5] (Fig. 1). In St. Séverin, large (100-200 μm) grains are observed associated with chromite-plagioclase assemblages [4].

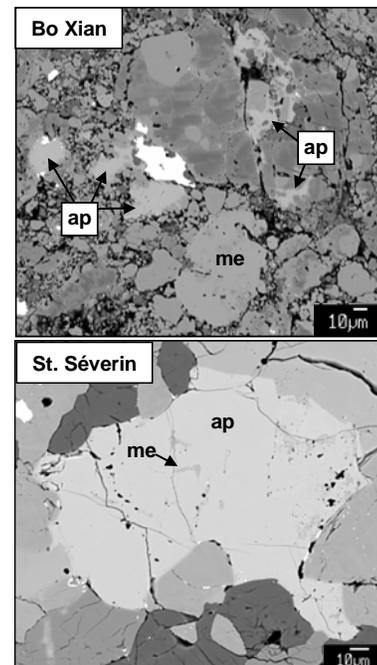


Figure 1. Occurrences of chlorapatite in LL chondrites (BSE images). Ap = apatite, Me = merrillite.

All three chondrites also contain merrillite that has similar grain sizes and textural characteristics. Merrillite compositions are close to the ideal formula, Na<sub>2</sub>(Mg,Fe<sup>2+</sup>)<sub>2</sub>Ca<sub>18</sub>(PO<sub>4</sub>)<sub>14</sub> [3-5].

Chlorapatite compositions are close to the ideal formula, Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>X, where X usually represents the anions F, Cl and OH. F and Cl abundances in all three

chondrites are similar but there are variations within each chondrite (Fig. 2). Based on microprobe analyses, there is a deficit of about 0.1 to 0.2 anions per formula unit (Fig. 2). If this deficit were attributable to OH<sup>-</sup> anions, it would represent a significant H<sub>2</sub>O content in apatite, for example 0.1 apfu OH is equivalent to ~1800 ppm H<sub>2</sub>O.

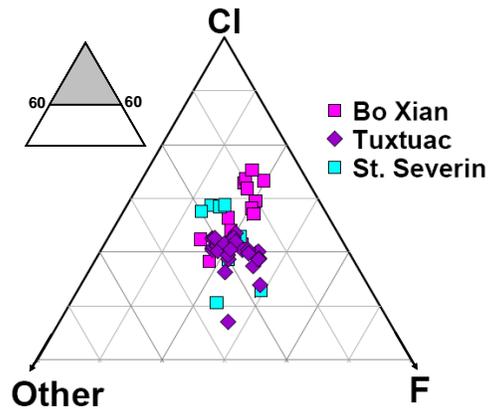


Figure 2: Anion abundances in apatite (EPMA).

However, SIMS analyses of chlorapatites show very low H<sub>2</sub>O contents, <100 ppm in all three chondrites (Fig. 3). We measured background abundances on merrillite in Bo Xian, and found comparable count rates for OH on apatite and merrillite.

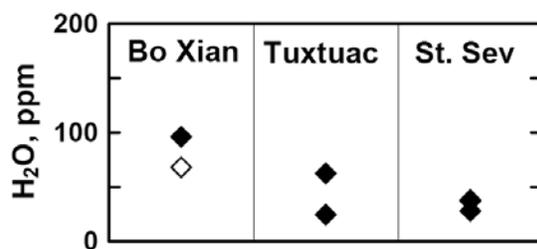


Figure 3: H<sub>2</sub>O in chlorapatite determined by SIMS (filled symbols). Open symbol = merrillite.

SIMS analyses of apatite S contents show generally low S, less than 1000 ppm. We observed an increase in S content with petrologic type, with mean S abundances of <50 ppm in Bo Xian, 335 ppm in Tuxtuac, and 610 ppm in St. Séverin.

**Discussion:** Chlorine-rich apatite is observed in layered mafic intrusions [e.g. 9] and in metamorphic rocks where fluorapatite has been metasomatized to chlorfluorapatite by Cl-rich fluids [e.g. 10]. We consider that chlorapatite in LL chondrites is unlikely to be igneous in origin. Rather, textures and compositions suggest that it formed either as a precipitate from a fluid and/or as a result of replacement of merrillite in the presence of fluid. Merrillite might have formed by

solid-state recrystallization during metamorphism, or it could have crystallized from localized partial melts resulting from impact heating.

Understanding the anion site occupancy in apatite should give us insight into the nature of fluids present during metamorphism on the LL chondrite parent body. The very low levels of measured OH indicate that any fluid that existed was extremely dry. Sulfur is present at low levels in the petrologic type 5 and 6 chondrites we analyzed. We suggest that S<sup>2-</sup> is the most likely S species, since LL chondrites contain abundant sulfide minerals. However, the amount of S we measured is insufficient to account for the anion site deficiency determined by EPMA. There is a possibility that the missing anion is carbonate, although we consider this to be unlikely since there are no indigenous carbonate minerals in type 4-6 OCs. We were unable to detect C in our SIMS analyses because the samples were C-coated. We tried to detect CO<sub>2</sub> using IR spectroscopy but our preliminary analysis was inconclusive. Another possible anion is O<sup>2-</sup>. Chlorine-rich apatite with a significant oxyapatite (O<sup>2-</sup>) component has been synthesized by reaction of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> in a dry CaCl<sub>2</sub>-CaF<sub>2</sub> flux at high temperatures (1220-1375 °C) [11,12]. A dry, sulfur- and halogen-bearing fluid may be plausible on an ordinary chondrite parent body. High Cl/OH and Cl/F ratios would be required in order to stabilize the chlorapatite compositions observed [13]. Feldspar in Bo Xian also shows evidence for reaction with a Cl-bearing fluid [3]. We suggest that such a fluid could have been derived by degassing of chondritic melts, which could have been either partial melts of chondritic material generated at depth, or shock melts generated by impacts. Compositional variability in apatite suggests that fluid interactions were localized and postdated the peak of metamorphism.

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**References:** [1] Dunn T. et al. (2010) *Meteorit. Planet. Sci.*, 45, 135-156 [2] Li et al. (2000) *Meteorit. Planet. Sci.*, 35, 561-568 [3] Jones R.H. & Brearley A.J. (2010) *73<sup>rd</sup> Meteoritical Society*, Abstract #5276. [4] Jones R.H. & Dreeland L. (2010) *LPSC XLI*, Abstract #1972 [5] Dreeland L. & Jones R.H. (2011) *LPSC XLII* [6] Stormer J.C. Jr. et al. (1993) *Am. Mineral.* 78, 641-648 [7] McCubbin et al. (2010) *Am. Mineral.* 95, 1141-1150. [8] Sharp et al. (2001) *Chem. Geo.* 178, 197-210. [9] Boudreau A.E. & McCallum I.S. (1989) *Contrib. Mineral. Petrol.* 102, 138-153 [10] Harlov D. et al. (2006) *Eur. J. Mineral* 18, 233-241 [11] Hovis G.L. & Harlov D.E. (2010) *Am. Mineral.* 95, 946-952 [12] Schettler G. et al. (2010) *Am. Mineral.* in press. [13] Zhu C. and Sverjensky D. A. (1991) *Geochim. Cosmochim. Acta* 55, 1837-1858.