

**PHOSPHATE MINERALS IN THE LL6 CHONDRITE, ST. SÉVERIN.** R. H. Jones and L. Dreeland, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, U.S.A. [rjones@unm.edu](mailto:rjones@unm.edu).

**Introduction:** The ordinary chondrites have undergone metamorphism, resulting in recrystallization and textural equilibration from petrologic types 3 to 6. Our recent studies of feldspar in ordinary chondrites [1,2] have led us to suggest that fluids may have been active during the late stages of metamorphism on OC parent bodies. As a complement to our studies of feldspar, we are investigating the occurrence of phosphate minerals in OCs, as these minerals may also record the action of any fluids that were present. There have been few systematic studies of phosphate mineralogy in chondrites: data summarized by [3] show significant variations in minor element contents, but it is not clear whether there are variations in phosphate mineral chemistry within individual meteorites, and / or among chondrites of the same group or petrologic type.

Here we report a survey of phosphate mineralogy in the LL6 chondrite, St. Séverin. U-Pb and Pb-Pb ages of phosphates in this chondrite are relatively old for type 6 OCs, ~4554 Ga [4,5]. Hence, it is of interest to interpret the formation history of phosphate minerals, especially because St. Séverin records a significant shock history as well as thermal metamorphism [6,7].

**Analytical Methods:** We examined two thin sections of St. Séverin, UNM 693 and MNHN section 2'-2397. We expected the latter to represent the "dark fraction" referred to by [8]. We carried out detailed SEM surveys of each section using X-ray mapping and BSE imaging in order to locate phosphate grains. Mineral compositions were determined using a JEOL 8200 electron microprobe, operated at 15 kV, with a beam current of 10 nA and a 5 μm beam diameter.

**Results:** In our systematic survey of UNM 693 we identified 64 merrillite grains and 10 chlorapatite grains in an area ~120 mm<sup>2</sup>. Grain sizes were variable: 70% of the chlorapatite grains were <50 μm across, and three grains were between 90 and 150 μm across. For merrillite, 60% of the grains were <50 μm across, and the other grains ranged from 50 to 275 μm. Typical occurrences are shown in Fig. 1.

Chlorapatite grains were not randomly distributed: there were higher abundances of chlorapatite in some areas of the thin section. Merrillite grains were distributed widely across the section. Several large merrillite grains were observed in an area adjacent to two large (700 μm) chromite / plagioclase assemblages, and one merrillite grain was incorporated in a chromite / plagioclase assemblage (Fig. 1a). Both merrillite and chlorapatite occurred at grain boundaries adjacent to a variety of minerals, including olivine, plagioclase,

pyroxene, chromite, metal and sulfide. Both merrillite and chlorapatite also occurred enclosed within olivine (Fig. 1b). Contacts between both phosphate minerals and olivine grains were commonly diffuse (Fig. 1b).

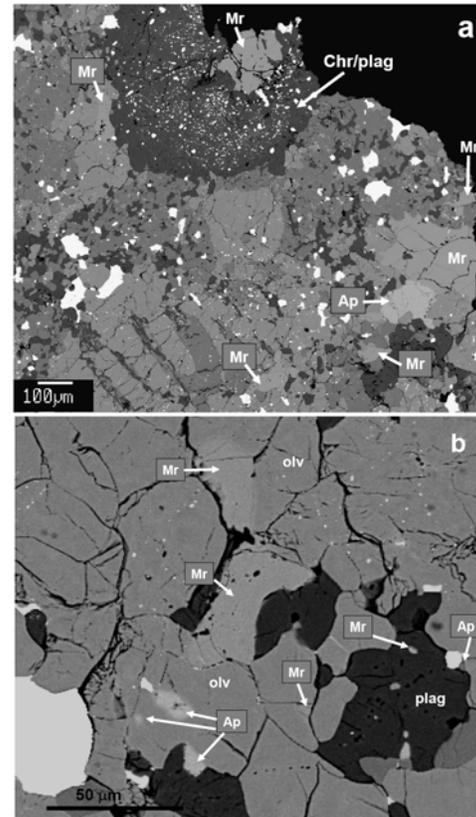


Fig. 1: BSE images showing phosphate occurrences in UNM 693. Mr = merrillite, Ap = chlorapatite.

Merrillite compositions were close to the ideal formula,  $\text{Na}_2(\text{Mg,Fe}^{2+})_2\text{Ca}_{18}(\text{PO}_4)_{14}$ . Fifty analyses of merrillites showed uniform concentrations of MgO ( $3.5 \pm 0.05$  wt%) and Na<sub>2</sub>O ( $2.9 \pm 0.05$  wt%), but significant variations in FeO (0.2 to 1.2 wt%: Fig. 2a). FeO contents varied from grain to grain, as well as within some individual grains. Grains that showed diffuse boundaries with olivine generally had higher FeO contents, and merrillite located adjacent to chromite-plagioclase assemblages had relatively low FeO contents.

Chlorapatite also showed very uniform concentrations of Na<sub>2</sub>O ( $0.28 \pm 0.02$  wt%), but significant variations in FeO (0.06 to 1.0 wt%: Fig. 2b). MgO contents were below detection limits. Individual grains had uniform FeO contents, and grains that had diffuse boundaries with olivine had higher FeO contents.

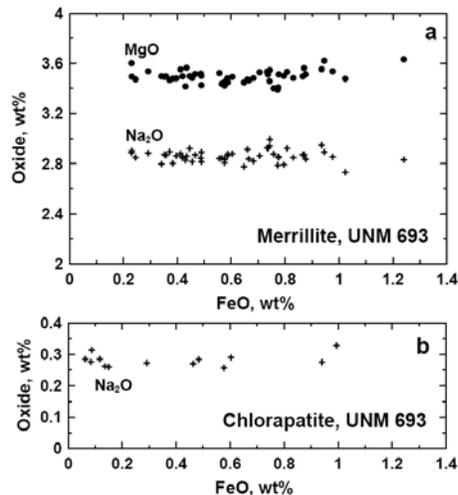


Figure 2: Minor element contents of phosphate grains.

Chlorapatite showed a range of F and Cl contents, from 0.6 to 1.2 wt% F, and 4.3 to 5.4 wt% Cl. There is a strong negative correlation between F and Cl (Fig. 3). F and Cl contents varied between chlorapatite grains, and one large (150  $\mu\text{m}$ ) grain showed variability across the grain. Grains exhibiting diffuse contacts with olivine contained lower Cl (and higher F).

In thin section MNHN 2'-2397, we did not observe any chlorapatite, contrary to the statement in [8] that the dark fraction contains 20 vol% chlorapatite. Merrillite was common, with grain sizes up to 300  $\mu\text{m}$  and compositions similar to those in UNM 693 with FeO contents varying from 0.4 to 1.2 wt%.

**Discussion:** One of the motives for our study of phosphate minerals is to investigate whether they provide evidence for the action of fluids on the LL parent body. Chlorapatite can incorporate OH in the X anion site, according to the formula  $\text{Ca}_5(\text{PO}_4)_3(\text{Cl}, \text{F}, \text{OH})$ . Our analyses show a constant sum of Cl+F anions of  $0.94 \pm 0.01$  afu, determined by the method of [9]. Based on these preliminary analyses, determination of OH by difference gives  $\text{OH} = 0.06$  afu, or 6% occupancy of the X site with OH<sup>-</sup> anions. This value is consistent with the data of [10]. If this is confirmed, it indicates the presence of an aqueous fluid.

Compositions of both chlorapatite and merrillite in St. Séverin are in close agreement with analyses reported previously for LL6 chondrites [3]. Compositional heterogeneity in FeO and F/Cl (Figs. 2a and 3) indicates that phosphates are not completely equilibrated throughout the chondrite. Diffusion coefficients for  $\text{M}^{2+}$  cations and X<sup>-</sup> anions in apatite are comparable to those of cations in olivine and pyroxene [11,12], so we would expect phosphate grains to be equilibrated in a type 6 chondrite. Hence, at least some of the phosphate grains appear to have grown at a late stage, after

the peak metamorphic temperature was reached. The association of merrillite with chromite-plagioclase assemblages, which are interpreted as indicators of shock [13], could mean that at least some phosphate growth was associated with one of the impact events known to have taken place on the parent body [6,7].

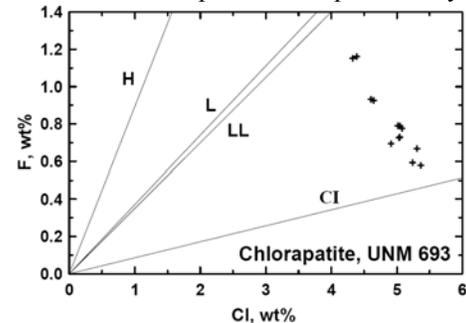


Figure 3: Cl and F abundances in chlorapatite compared with F/Cl ratios of bulk chondrites [14].

The observed range of F/Cl ratios lies between those of OC and CI chondrites (Fig. 3). Bulk chondrite F/Cl ratios should be defined by the ratios in chlorapatite, which is the major halogen-bearing phase. In the absence of a fluid, the origin of the F/Cl variability must be interpreted as reflecting local compositional heterogeneity in the material that is supplying halogens to the chlorapatite as it crystallizes, presumably chondrule mesostasis. However, in this case the compositional heterogeneity is difficult to explain. Alternatively, chlorapatite may have either grown in the presence of a fluid, or undergone late-stage equilibration with a fluid. The range of F/Cl ratios could be the result of either progressive fractionation from a fluid, or localized differences in fluid composition if there was a low fluid/rock ratio. Since the F/Cl ratio of an apatite is expected to be much higher than that of the associated fluid, such a fluid would have had an initial F/Cl ratio equivalent to or less than that of CI chondrites.

**References:** [1] Kovach H. A. & Jones R. H. (2009) *Meteorit. Planet. Sci.*, in press [2] Jones R. H. and Brearley A. J. (2010) *LPSC 2010* [3] Brearley A. J. and Jones R. H. (1998) In *Planetary Materials*, RIMS vol. 36, ed. J. Papike, Ch. 3 [4] Göpel C. et al. (1994) *Earth Planet. Sci. Lett.* 121, 153-171 [5] Bouvier A. et al. (2007) *Geochim. Cosmochim., Acta* 71, 1583-1604 [6] Ashworth J. R. (1980) *Earth Planet. Sci. Lett.* 46, 167-177 [7] Leroux H. et al. (1996) *Meteorit. Planet. Sci.*, 31, 767-776 [8] Crozaz G. and Zinner E. (1985) *Earth Planet. Sci. Lett.* 73, 41-52 [9] Piccoli P. M. and Candela P. A. (2002) In *Phosphates*, RIMS vol. 48, ed. M. J. Kohn et al., Ch. 6 [10] Van Schmus W. R. and Ribbe P. H. (1969) *Geochim. Cosmochim., Acta* 33, 637-640 [11] Brenan J. M. (1993) *Earth Planet. Sci. Lett.* 117, 251-263 [12] Cherniak D. J. (2005) *Chem. Geol.* 219, 297-308 [13] Rubin A. E. (2003) *Geochim. Cosmochim., Acta* 67, 2695-2709 [14] Lodders K. and Fegley B. Jr. (1998) *The Planetary Scientist's Companion*, Oxford, 371 pp.