

**PHOSPHATE MINERALOGY AND THE ROLE OF FLUIDS IN THE ZAG H CHONDRITE.** R. H. Jones<sup>1</sup>, F. M. McCubbin<sup>1,2</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:** Zag and Monahans (1998) are both H chondrite regolith breccia falls that contain indigeneous halite [1-4]. Zag consists of petrologic type 4 dark-colored matrix and type 6 light-colored clasts; halite occurs predominantly in the type 4 material. Halite in both chondrites contains low-temperature (<100 °C) aqueous fluid inclusions and is considered to result from evaporation of brines [1-4]. The source of water has variously been proposed to be exogenous water delivered to the parent body by cometary or asteroidal ice fragments [1,4], dehydration of the asteroid interior [2], or impact heating of phyllosilicates [3]. [1], [3] and [4] have argued that halite occurs as a clastic component of the breccia. We have studied the phosphate mineralogy of Zag, in order to determine whether apatite, which can include both chlorine and H<sub>2</sub>O in its structure, also records the process that formed halite, and thus whether apatite can help shed light on the conditions that led to halite formation.

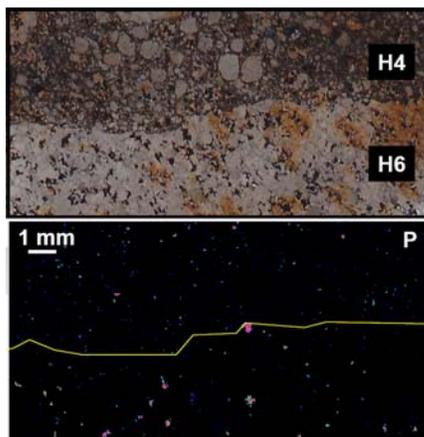


Figure 1: Zag thin section and P X-ray map.

**Analytical Methods:** We studied one thin section of Zag (UNM 1136), which includes approximately equal proportions of dark H4 and light H6 material (Fig. 1). Phosphate mineral grains were identified 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 halogens (F and Cl) in apatite ([5]; also see [6] for details).

SIMS analyses were carried out on the Cameca 7f Geo instrument at Caltech. Analytical details are given in [6]. We measured H<sub>2</sub>O and S abundances in apatite and merrillite. We also measured F abundances which

correlate closely with values determined by electron microprobe.

**Results:** The phosphate mineralogy is very distinct between the H4 and H6 fractions of Zag. In the H4 fraction, both apatite and merrillite are abundant and widely disseminated. The largest apatite grains are ~100 μm across (Fig. 1). In the H6 fraction, merrillite is significantly more abundant than apatite. Both are coarse-grained: many grains are >100 μm across and the largest grains are ~250 μm across (Figs. 1, 2). Apatite in the H4 fraction is chlorine rich (Fig. 3); the most Cl-rich grains contain 5.9 wt% Cl and only 0.03 wt% F. Apatite is considerably more F-rich in the H6 fraction and shows a range of Cl/F ratios (Fig. 3). The most F-rich grains contain 3.3 wt% Cl and 2.0 wt% F.

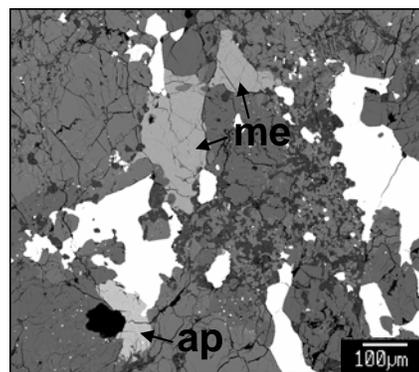


Figure 2: Phosphate grains in Zag (H6 fraction). Ap = apatite, me = merrillite.

In some areas within the H6 fraction, merrillite and sometimes apatite grains are observed along linear features. These features could either be the result of fluid flow along fractures, or possibly impact melt veins: one contains a chromite-plagioclase assemblage surrounded by merrillite. In both H4 and H6 fractions, apatite and merrillite grains contain multiple fine fractures. Inclusions of pores such as those observed in LL chondrites [6] were not observed.

All merrillite compositions are close to the ideal formula,  $\text{Na}_2(\text{Mg,Fe}^{2+})_2\text{Ca}_{18}(\text{PO}_4)_{14}$ , and there are no significant differences between compositions in the H4 and H6 fractions. In both fractions, electron microprobe analyses of apatite indicate a significant component of “other” anions (mostly in the range 0.1 to 0.2 apfu) in addition to the halogens F and Cl (Fig. 3). In general, compositions with high F contents have higher (F+Cl) anion totals.

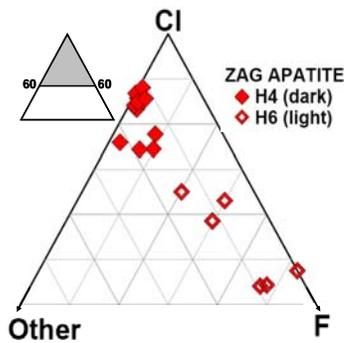


Figure 3: Apatite compositions in Zag (EPMA).

SIMS analyses of apatite in Zag show very low  $H_2O$  abundances (Fig. 4). In most grains, we measured less than 800 ppm  $H_2O$ , which must be considered as upper limits since the background abundance measured on merrillite in the same session was 843 ppm (Fig. 4). In one analysis we measured  $\sim 1700$  ppm  $H_2O$ , but this is on the same grain as an analysis with 470 ppm, and it is likely that the analysis with higher  $H_2O$  overlapped fine fractures in the grains that contain C and OH contaminants. Sulfur abundances determined by SIMS are also low,  $<500$  ppm (Fig. 4). The background S content measured on merrillite is  $<30$  ppm. Neither OH nor S abundances correlate with F content.

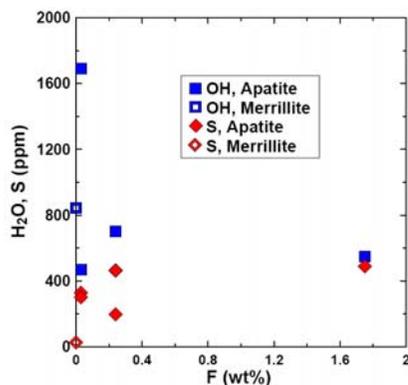


Figure 4. SIMS analyses of  $H_2O$  and S abundances in apatite and merrillite from Zag.

**Discussion:** Marked differences in apatite and merrillite distribution, and apatite compositions, between the H4 and H6 fractions of Zag indicate that formation conditions of apatites in this chondrite were locally controlled. Hence, apatite formation preceded final assembly of the brecciated sample. Apatite in the H4 fraction is highly enriched in chlorine, consistent with the observation that halite occurs predominantly in this material [1-4]. Since halite is suggested to have precipitated from a brine [1-4], one might expect that if apatite growth was contemporaneous with halite formation, it would contain a significant hydroxyapatite

(OH<sup>-</sup>) component. However, the apatite in both H4 and H6 fractions is remarkably dry. A possible interpretation is that formation of apatite and halite are decoupled: the chlorine required for halite formation may have been derived, for example, from dissolution of pre-existing chlorapatite.

In [6] we discuss apatite in LL chondrites, that has similar Cl-rich and halogen-deficient compositions to those in Zag. We suggest that there may be a significant oxyapatite ( $O^{2-}$ ) component in the anion site, as has been observed in synthetic apatites grown in the presence of a  $CaCl_2$ - $CaF_2$  flux [7,8]. Hence, Cl-rich apatite in Zag may be the result of replacement reactions that occurred when halogen-rich fluids interacted with previously existing merrillite grains, in a similar manner to the partial replacement of merrillite with apatite in GRA 06128/06129 [9]. Merrillite could have formed initially during metamorphic recrystallization of the chondrite and/or as a result of localized impact melting. The absence of  $H_2O$  in apatite is consistent with formation from a highly Cl-rich fluid at low pressures and temperatures [10].

We propose that on the Zag / Monahans parent body, peak metamorphic temperatures increased with burial depth. Partial melting occurred in the interior of the body, resulting in degassing that produced a halogen-rich (and S-bearing) fluid. This fluid interacted with merrillite in petrologic type 6 material, producing fluor-chlor-apatites. Since F partitions strongly into apatite, the fluid became progressively depleted in F and enriched in Cl. Hence, when the fluid reached higher levels of the asteroid (petrologic type 4 material), it reacted with merrillite to form Cl-rich apatite. The fluid also became progressively enriched in Na as a result of breakdown of merrillite, and in its final stages precipitated halite. Aqueous fluid inclusions in halite would thus represent the final stages of crystallization of extremely  $H_2O$ -poor fluids. Subsequent brecciation preserved the original halogen-bearing minerals in each petrologic type fraction. According to this scenario, halite formed in situ in H4 type material, from fluids indigenous to the Zag parent body.

**References:** [1] Zolensky M. E. et al. (1999) *Science* 285, 1377-1379 [2] Whitby J. et al. (2000) *Science* 288, 1819-1821 [3] Rubin A. E. et al. (2002) *Meteor. Planet. Sci.* 37, 125-141 [4] Bridges J. et al. (2004) *Meteor. Planet. Sci.* 39, 657-666 [5] Stormer J.C. Jr. et al. (1993) *Am. Mineral.* 78, 641-648 [6] Jones R. H. et al. (2011) *LPSC* [7] Hovis G.L. & Harlov D.E. (2010) *Am. Mineral.* 95, 946-952 [8] Schettler G. et al. (2010) *Am. Mineral.* in press. [9] Shearer C. et al. (2010) *Geochim. Cosmochim. Acta* 74, 1172-1199 [10] Zhu C. and Sverjensky D. A. (1991) *Geochim. Cosmochim. Acta* 55, 1837-1858.