Phosphate minerals in the H group of ordinary chondrites, and fluid activity recorded by apatite heterogeneity in the Zag H3-6 regolith breccia

DOI:

[10.2138/am-2016-5728](https://doi.org/10.2138/am-2016-5728)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Jones, R., McCubbin, F. M., & Guan, Y. (2016). Phosphate minerals in the H group of ordinary chondrites, and fluid activity recorded by apatite heterogeneity in the Zag H3-6 regolith breccia. *The American Mineralogist*, 101(11). <https://doi.org/10.2138/am-2016-5728>

Published in:

The American Mineralogist

Citing this paper

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1 **REVISION 1**

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5 **Phosphate minerals in the H group of ordinary chondrites, and fluid activity recorded by**
6 **apatite heterogeneity in the Zag H3-6 regolith breccia**

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8 Rhian H. Jones^{1,2}, Francis M. McCubbin^{2,3,4} and Yunbin Guan⁵
9

10 ¹School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, M13
11 9PL, U.K. Rhian.jones-2@manchester.ac.uk

12 ²Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM
13 87131, U.S.A.

14 ³Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131, U.S.A.

15 ⁴NASA Johnson Space Center, Mailcode XI2, 2101 NASA Parkway, Houston, TX 77058,
16 U.S.A. francis.m.mccubbin@nasa.gov

17 ⁵Division of Geological and Planetary Sciences, Caltech, Pasadena, CA 91125, U.S.A.
18 yunbin@gps.caltech.edu
19
20
21
22
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25 *Submitted to American Mineralogist, February 2016: Apatite thematic issue*

26 *Revised: June 2016*
27

Abstract

Phosphate minerals in ordinary chondrites provide a record of fluids that were present during metamorphic heating of the chondrite parent asteroids. We have carried out a petrographic study of the phosphate minerals, merrillite and apatite, in metamorphosed H group ordinary chondrites of petrologic type 4-6, in order to understand development of phosphate minerals and associated fluid evolution during metamorphism. In unbrecciated chondrites, apatite is Cl-rich and shows textural evolution from fine-grained apatite-merrillite assemblages in type 4 towards larger, uniform grains in type 6. The Cl/F ratio in apatite shows a similar degree of heterogeneity in all petrologic types, and no systematic change in compositions with metamorphic grade, which suggests that compositions in each meteorite are dictated by localized conditions, possibly because of a limited fluid / rock ratio. The development of phosphate minerals in H chondrites is similar to that of L and LL chondrites, despite the fact that feldspar equilibration resulting from albitization is complete in H4 chondrites but not in L4 or LL4 chondrites. This suggests that albitization took place during an earlier period of the metamorphic history than that recorded by preserved apatite compositions, and chemical equilibrium was not achieved throughout the H chondrite parent body or bodies during the late stages of metamorphism. A relict igneous clast in the H5 chondrite, Oro Grande has apatite rims on relict phenocrysts of (possibly) diopside that have equilibrated with the host chondrite. Apatite in the Zag H3-6 regolith breccia records a complex fluid history, which is likely related to the presence of halite in this meteorite. The porous dark H4 matrix of Zag, where halite is observed, has a high apatite / merrillite ratio, and apatite is extremely Cl-rich. One light H6 clast contains similarly Cl-rich apatite. In a second light H6 clast, apatite compositions are very heterogeneous

and more F-rich. Apatites in both H4 matrix and H6 clasts have very low H₂O contents. Heterogeneous apatite compositions in Zag record multiple stages of regolith processing and shock at the surface of the H chondrite parent body, and apatite records either the passage of fluids of variable compositions resulting from different impact-related processes, or the passage of a single fluid whose composition evolved as it interacted with the chondrite regolith. Unraveling the history of apatite can potentially help to interpret the internal structure of chondrite parent bodies, with implications for physical and mechanical properties of chondritic asteroids. The behavior of halogens recorded by apatite is important for understanding the behavior of volatile elements in general: if impact-melt materials close to the surface of a chondritic asteroid are readily degassed, the volatile inventories of terrestrial planets could be considerably more depleted than the CI carbonaceous chondrite abundances that are commonly assumed.

Keywords:

ANALYSIS, CHEMICAL (MINERAL): merrillite, apatite

MAJOR AND MINOR ELEMENTS: merrillite, apatite

METEORITE: ordinary chondrite, H chondrite, Avanhandava, Estacado, Oro Grande, Richardton, Zag

PETROGRAPHY: ordinary chondrite, H chondrite

Introduction

One of the important considerations related to the formation and geological evolution of the terrestrial planets is the initial abundance of volatile species such as water and the halogens: these species can play a major role in determining the geochemical behavior of planetary interiors. Since determinations of bulk compositions of the terrestrial planets are largely based on our understanding of elemental abundances in chondritic meteorites, it is important to understand the behavior of volatile species in these meteorites. For the halogens in particular there are considerable uncertainties and unknowns with respect to their elemental abundances as well as their mineralogical hosts in chondrites (Brearley and Jones 2016). Overall, we have a rather poor understanding of the distribution of the halogens in early solar system materials, and hence in materials that were accreting to form the planets.

The ordinary chondrites (OCs) consist of three groups, H, L and LL, which have all undergone metamorphism on their separate parent bodies (e.g. Huss et al. 2006). The degree of metamorphism is identified by a scheme of petrologic types (Van Schmus and Wood 1967) that range from 3.00 (pristine aggregates of solar nebula materials) to 6 (peak temperatures up to the onset of melting at $\sim 950^\circ\text{C}$). Secondary minerals that form during equilibration of OCs include merrillite, apatite, and feldspar (e.g. Brearley and Jones 1998). The phosphate minerals merrillite $[\text{Na}_2(\text{Mg}, \text{Fe}^{2+})_2\text{Ca}_{18}(\text{PO}_4)_{14}]$ and apatite $[\text{Ca}_5(\text{PO}_4)_3(\text{X})]$ can provide insights into processes that redistribute halogens in the early solar system, by providing a window into processes that take place on chondritic parent asteroids. Because the X anion site in apatite can host F^- , Cl^- , and OH^- , apatite can provide direct evidence for the presence and relative abundances of volatile species, and hence the nature and role of fluids that existed during the period of metamorphism which

took place in the first few million years of solar system history. In a recent study of petrologic type 4-6 LL chondrites, we showed that chlorapatite grains record the presence of metasomatizing fluids throughout the metamorphic history of the LL parent body (Jones et al. 2014), and that in at least the late stages of metamorphism, these fluids are dry (water-poor) and halogen-bearing. Metasomatizing fluids are also likely responsible for albitization reactions that produce albitic feldspar in ordinary chondrites (Kovach and Jones 2011; Jones and Brearley 2010a,b; Lewis and Jones 2014, 2015, 2016). The three groups of ordinary chondrites all record the effects of similar metamorphic and metasomatic environments. However, there are also significant differences. Feldspar in H4 chondrites is albitic and homogeneous in composition, whereas feldspar in L4 and LL4 chondrites is highly heterogeneous, ranging from almost end-member An to Ab (Kovach and Jones 2011; Lewis and Jones 2016). In L and LL chondrites, equilibration to albitic feldspar is only complete in petrologic type 6. Hence, it appears that complete albitization took place at significantly lower temperatures in the H chondrites (<600 °C for petrologic type 3: Huss et al. 2006) than in the L and LL chondrites, possibly as a result of differences in fluid composition and / or availability. In this study, we examine the occurrence and development of apatite and merrillite in H chondrites, and we address the question of whether phosphate minerals also record differences in the conditions of secondary processing between the parent bodies of H vs. L and LL chondrites.

We have also studied the H chondrite regolith breccia fall, Zag. Zag and a similar meteorite, Monahans (1998) (hereafter Monahans) contain indigenous (extraterrestrial) halite (Zolensky et al. 1999; Whitby et al. 2000; Rubin et al. 2002; Bridges et al. 2004). Halite contains low-temperature (<100 °C) aqueous fluid inclusions and is considered to result from evaporation of brines. The source of water has variously been proposed to be exogenous water delivered to

the parent body by cometary or asteroidal ice fragments (Zolensky et al. 1999; Bridges et al. 2004), dehydration of the asteroid interior (Whitby et al. 2000), or impact heating of phyllosilicates (Rubin et al. 2002). Alternatively, halite may be exogenous, derived from either a carbonaceous asteroid such as Ceres (Fries et al. 2014; Yurimoto et al. 2014) or via cryovolcanism on a body such as the Saturnian satellite Enceladus (Zolensky et al. 2013). We have studied the phosphate mineralogy of Zag, in order to examine whether apatite can help shed light on the conditions that led to halite formation and halogen redistribution in the regolith of the H chondrite asteroid.

Samples and Methods

We studied phosphate minerals in Avanhandava (H4), Richardton (H5), Oro Grande (H5) Estacado (H6), and Zag (H3-6) (Table 1). Phosphate minerals were identified and analyzed in the following thin sections: Avanhandava, UNM 88; Richardton, UNM 384; Oro Grande, UNM 55; Estacado, UNM 609; and Zag, UNM 1136. Oro Grande is a find and is moderately weathered; the others are falls. All the samples have nominally low shock levels, between S1 and S3 (Stöffler et al. 1991; Rubin 1994, 2002, 2004; Folco et al. 1996; Grossman 1999). The Zag thin section we studied contains both dark matrix and light clast lithologies.

We used WDS/EDS X-ray mapping to locate phosphate mineral grains, using the JEOL 8200 electron microprobe at the University of New Mexico (UNM). For mapping, we typically used a defocused electron beam, 10 μm in diameter, and a counting time of 20 milliseconds per pixel, in order to minimize volatile loss from susceptible phases. Back-scattered electron (BSE) images were obtained using the electron microprobe and the JEOL 5800LV SEM at UNM, as

well as an FEI XL30 ESEM-FEG at the University of Manchester. We determined modal abundances of phosphate minerals from X-ray maps using the ImageJ image analysis program (Schneider et al. 2012). Modal abundances of total phosphates were determined from P X-ray maps, modal abundances of Cl-apatite were determined from Cl X-ray maps, and modal abundances of merrillite were calculated by subtracting the abundance of Cl-apatite from total phosphates. Estimated errors for modal abundances determined with this method are less than 10% relative.

Electron microprobe analyses of merrillite and chlorapatite were obtained using the JEOL 8200 electron microprobe. We used conditions that were designed to minimize volatilization of halogens (F and Cl) in chlorapatite: operating conditions were 15kV and a 20nA beam current, and we used a defocused (usually 5 μ m) electron beam to analyze both standards and unknowns. The problem of fluorine migration in apatite under the electron beam has been recognized in previous studies (Stormer et al. 1993; McCubbin et al. 2010a, 2011). We monitored the F and Cl count rates during analyses using the live chart recorder on the electron microprobe and discarded analyses in which we observed significant changes in F and/or Cl counts during peak counting times. The following standards were used for calibration: Taylor apatite and Apatite 020 (see below) for Ca, P, and F (McCubbin et al. 2012); sodalite for Na and Cl, Taylor olivine for Mg and Fe, and Y and Ce end-member phosphates for Y and Ce. Detection limits for F and Cl were 0.04 and 0.01 wt% respectively, and detection limits for Y₂O₃ and Ce₂O₃ were 0.05 wt%. Detection limits for all other elemental oxides were 0.01 or 0.02 wt%. For apatite analyses, we defined criteria for an acceptable analysis where each cation site is populated by $\pm 2\%$ of values in the ideal structural formula. Thus an acceptable analysis was defined as follows: Total oxide wt% between 97 and 102; Sum of tetrahedral site cations

(Σ Tetrahedral) between 2.94 and 3.06; Sum of octahedral site cations (Σ Octahedral) between 4.9 and 5.1. For Oro Grande only, most analyses fitted all criteria except for (Σ Tetrahedral) which was relaxed to values lying between 4.9 and 5.15. For several analyses in Richardton, the total structural formulae values for F+Cl were slightly >1: for these analyses only, Cl was calculated as $Cl = 1 - F$ (c.f. McCubbin et al. 2013).

Secondary ion mass spectrometry (SIMS) analyses of volatile anion elements (H, F, and S) were obtained using the Cameca IMS 7f-GEO ion microprobe at Caltech. Samples were measured with a $\sim 20\ \mu\text{m}$ Cs^+ primary beam of +10 keV and $\sim 3.5\text{nA}$, rastering over an area of $10 \times 10\ \mu\text{m}$. Negative secondary ions ($^{12}\text{C}^-$, $^{16}\text{O}^{1}\text{H}^-$, $^{18}\text{O}^-$, $^{19}\text{F}^-$, $^{31}\text{P}^-$, $^{32}\text{S}^-$, and $^{35}\text{Cl}^-$) of -10 keV were collected from the center $10\ \mu\text{m}$ at a mass resolving power of ~ 4500 . Sample charging was compensated with an electron gun at -10 keV. Secondary ion images of $^{12}\text{C}^-$, $^{16}\text{O}^{1}\text{H}^-$, and $^{19}\text{F}^-$ were examined before each sample measurement to avoid cracks and contamination. A calibration curve for OH was determined from five terrestrial apatite standards that had H_2O contents varying from 300 to 5500 ppm (McCubbin et al. 2010b, 2012; Jones et al. 2014). A calibration curve for S, based on the five apatite standards, was determined by Jones et al. (2014). SIMS analyses of F in this study show an excellent correlation with electron microprobe and bulk analyses of F abundances, measured in terrestrial standards and apatite grains in LL chondrites (Jones et al. 2014).

Results

Non-brecciated H chondrites

Abundances and distributions of phosphate minerals. Distributions and sizes of phosphate grains in Avanhandava, Oro Grande, Richardton and Estacado are illustrated in the P and Cl X-ray maps shown in Fig. EA1. Abundances of phosphate mineral grains in each chondrite, determined using ImageJ software, are summarized in Table 1. The total abundance of phosphate minerals (apatite + merrillite) is similar in all four chondrites, 0.4-0.5 vol%, but the apatite / merrillite ratio is highly variable, ranging from 0.4 to 1.5. Both minerals are distributed evenly throughout the thin sections studied, although there is some heterogeneity on a scale of millimeters that could account for the observed differences in apatite / merrillite ratios. A large inclusion in Oro Grande that contains apatite is described in more detail below.

Textures of phosphate minerals in Avanhandava, Richardton and Estacado. Figures 1, 2 and 3 illustrate textures of phosphate minerals in the H4-5-6 petrologic sequence represented by Avanhandava, Richardton and Estacado respectively. In all cases, both apatite and merrillite occur as irregularly shaped grains up to 200 μm in length. In Avanhandava (H4), both apatite and merrillite are commonly fragmented into small angular pieces (Fig. 1a). The two minerals can be associated (Fig. 1a), and both are commonly associated with metal / sulfide grains (Fig. 1a-c). Grains of merrillite up to 200 μm in length also occur along and close to the perimeter of relict chondrules (Fig. 1c,d). In Richardton (H5), large apatite grains up to 200 μm in length often contain a small inclusion of merrillite (Fig. 2a,b). Similar to Avanhandava, both apatite and merrillite are commonly associated with metal / sulfide grains (Fig. 2a-d). Apatite grains occur in intergrowths with olivine, in which case they contain rounded olivine inclusions and show a curved interface, concave to the apatite (Fig. 2a,c). Several grains of both apatite and merrillite are connected to vein-like networks of similar material (Fig. 2a,c). In Estacado (H6), apatite and merrillite grains are more angular than those in Richardton, and do not contain many inclusions

of olivine or any merrillite inclusions (Fig. 3). Associations between both phosphate minerals and metal / sulfide grains are common, but many grains of both minerals occur independently of metal in the plane of the thin section. Phosphate minerals occur in the vicinity of chromite-plagioclase assemblages: in the example in Fig. 3d, a merrillite grain is located at the periphery of a chromite-plagioclase assemblage in association with metal / sulfide.

Oro Grande host and igneous inclusion. In the Oro Grande H5 chondrite host, both apatite and merrillite occur as grains up to 200 μm in length, many of which are associated with metal / sulfide grains (Fig. 4). Apatite and merrillite are closely associated (Fig. 4c), and in some grains appear to show a reaction relationship (Fig. 4a,d). Also, some apatite grains contain what appear to be pores (Fig. 4d). Both minerals are present along and close to the boundary of a large (5 mm) inclusion within the H chondrite host (Fig. 4c,d). This inclusion has previously been described as an igneous inclusion that has equilibrated with the host chondrite (Fodor et al. 1972; Jones 2007). The inclusion is dominated by a fine-grained mixture of barred olivine and plagioclase, with olivine bar widths $<10\ \mu\text{m}$ (Fig. 4c,d; 5a,b). Throughout the inclusion there are also numerous objects ($\sim 50\ \text{vol}\%$) that appear to be pseudomorphs of euhedral phenocrysts, 100 to 500 μm in length, which have complex internal textures. Some pseudomorphic regions are dominated by diopside, with minor low-Ca pyroxene and plagioclase, and rims of plagioclase. Apatite occurs as $\sim 20\ \mu\text{m}$ wide rims on these features, between the core region and plagioclase. Other euhedral pseudomorphic regions consist of fine-grained intergrowths of low-Ca pyroxene, diopside, olivine, plagioclase, pigeonite and minor chromite. These regions have thin rims of diopside, overgrown with plagioclase. Throughout the inclusion, iron metal and troilite are minor phases, and chromite is present as ubiquitous but finely dispersed sub-micrometer crystals. Compositions of all phases are essentially identical to those in the host chondrite, and are typical

of equilibrated H chondrites, with average compositions as follows: olivine, Fa_{18} ; low-Ca pyroxene, $\text{En}_{82}\text{Fs}_{17}\text{Wo}_1$; diopside, $\text{En}_{48}\text{Fs}_6\text{Wo}_{46}$; feldspar, $\text{An}_{12}\text{Ab}_{82}\text{Or}_6$ (Jones 2007).

Phosphate mineral compositions. Merrillite compositions are close to the ideal formula, $\text{Na}_2(\text{Mg,Fe}^{2+})_2\text{Ca}_{18}(\text{PO}_4)_{14}$, in all the H chondrites studied (Table 2: individual analyses are given in Table EA1). Apatite compositions, $\text{Ca}_5(\text{PO}_4)_3(\text{X})$, have variable Cl/F ratios and each of the chondrites has a distinct average Cl/F ratio: 9.1, 19.5, 6.2 and 14.4 wt% ratio, or 4.9, 10.2, 3.3 and 7.7 atomic ratio, in Avanhandava, Richardton, Oro Grande (host) and Estacado, respectively (Table 3: individual analyses are given in Table EA2). We also define a value of $\text{Cl}\# = \text{Cl}/(\text{Cl}+\text{F})$ (atomic), which has a value of 0.83, 0.91, 0.77, 0.89 for these four chondrites, respectively. Figure 6a shows anion site occupancy for all apatite analyses in these four non-brecciated H chondrites. Apatite analyses contain up to 0.15 atoms per formula unit (apfu) “other” than halogens: we have shown that for LL chondrites, this component is not OH^- (Jones et al. 2014), so we label it as “other” rather than the conventional OH^- in this diagram (see also the discussion of the Zag data below). For each chondrite, there is considerable variability in apatite compositions around the chondrite mean, for example $\text{Cl}\#$ values in Richardton vary in the range 0.85 to 0.97. Apatite compositions in the Oro Grande igneous inclusion are very similar to compositions in the H5 host (Table 3, Table EA2). For all apatite analyses, Y_2O_3 and Ce_2O_3 contents are close to or below detection limits. These elements are not included in Table 3, but are given in Table EA2.

The Zag H3-6 regolith breccia

Petrography. Zag is a regolith breccia that contains mainly light-colored metamorphic clasts, and some dark clasts, set within a dark clastic matrix (e.g. Rubin et al. 2002). The thin

section of Zag we studied (UNM 1136) includes both dark and light material (Fig. 7a). The dark matrix includes clearly defined chondrules and unequilibrated low-Ca pyroxene, and although it is possibly clastic, with some regions showing a higher degree of recrystallization to petrologic type 5, we describe it here as H4 matrix. There are two light regions (clasts) within the thin section, both of petrologic type H6, in which chondrules are poorly defined: H6-1 is a large area, approximately half of the total area, and H6-2 is a smaller area on the left hand side of Fig. 7a. Fig. 7b shows the boundary between dark matrix and H6-2 material: H6-2 contains very few fine-grained metal / sulfide particles compared with the H4 matrix. Figures 7c-f show X-ray maps for an area that consists of approximately equal areas of matrix and H6-1 material. The Fe map does not distinguish the two areas clearly, but the S map shows fine-grained sulfides disseminated throughout the matrix, and larger sulfide grains in H6-1. The finely disseminated sulfides are likely responsible for darkening in the matrix. Rubin et al. (2002) observed extensive silicate darkening within this material, in the form of veinlets of troilite and curvilinear trails of troilite blebs cutting through olivine and pyroxene grains, but in our thin section such linear features are not abundant and fine-grained sulfides more typically occur at silicate grain boundaries (Fig. 8).

The distribution of phosphate minerals is very different in the H4 and H6-1 regions: this is illustrated in the P and Cl X-ray maps of Fig. 7e,f and summarized in Table 1. In the H4 matrix, the abundance of both phosphate minerals is low compared with other H chondrites (total of 0.28 vol%), and apatite is much more abundant than merrillite (apatite / merrillite ratio of 4.6). In contrast, in H6-1, the abundance of both phosphates is much higher (total of 0.64 vol%), and merrillite is much more abundant than apatite (apatite / merrillite ratio of 0.16). Also, merrillite

grains are much larger in H6-1 compared with H4 matrix: many grains are >100 μm across and the largest grains are ~ 250 μm across in H6-1.

Textures of apatite and merrillite grains in the H4 matrix are illustrated in Fig. 8.

Abundant apatite grains, up to about 100 μm across, are mostly irregular in shape. Most apatite grains are not associated with metal. One of the apatite grains in Fig. 8c has a vein-like protuberance into surrounding material. Merrillite occurs as small, mostly <20 μm , rounded or subhedral grains throughout the H4 lithology (Fig. 8b,c), and can be associated with metal (Fig. 8a).

In the H6-1 region, both merrillite and apatite grains are very irregular in shape (Fig. 9). Large merrillite grains >100 μm across are common (Fig. 9a,b), and some show faint features that appear to be multiple parallel sets of striations that could be crystallographically controlled (Fig. 9b). Apatite can occur as independent grains (Fig. 9c), but can also occur intergrown with merrillite (Fig. 9d). Two occurrences of apatite-merrillite-chromite assemblages were observed: in the one illustrated in Fig. 9e, apatite encloses an olivine core and the assemblage is adjacent to an Fe,Ni metal grain.

The H6-2 light clast differs significantly from H6-1. Abundant large apatite grains, typically 100 μm (Fig. 7b) but one over 400 μm across (Fig. 9f), are distributed throughout the H6-2 region. The large apatite grain in Fig. 9f encloses a region of merrillite close to the centre.

In a few areas within both H4 matrix and H6-1, merrillite and sometimes apatite grains are observed along linear features (Fig. 10). These features could either be the result of fluid flow along fractures, or possibly impact melt veins, as discussed below. In the example in Fig. 10a, merrillite is distributed throughout a sinuous feature that has a high concentration of plagioclase, and which contains a chromite-plagioclase assemblage surrounded by merrillite

(Fig. 10b). The merrillite grain in the top left of Fig. 1b shows evidence of flow around the chromite-plagioclase assemblage. We also observed other textures where phosphate minerals in H6-1 appear to have undergone melting in association with plagioclase. The large apatite grain in Fig. 10c shows evidence for incipient melting where it is in contact with plagioclase. The equigranular assemblage shown in Fig. 10d consists of low-Ca pyroxene, Ca-rich pyroxene and plagioclase, with fine-grained ($<5\ \mu\text{m}$) merrillite distributed along grain boundaries. We interpret this texture as a region that has undergone melting and recrystallization, possibly while entrained in an impact-generated melt.

Mineral compositions. Merrillite compositions in Zag are close to the ideal formula, $\text{Na}_2(\text{Mg},\text{Fe}^{2+})_2\text{Ca}_{18}(\text{PO}_4)_{14}$, and there are no significant differences between compositions in the two H6 clasts (Table 2). We did not obtain any merrillite analyses in the H4 lithology. In contrast, the different lithologies have distinct apatite compositions (Table 3, Fig. 6b). Apatite in H4 and H6-2 is very chlorine-rich; the most Cl-rich grains, in H4 matrix, contain 6.2 wt% Cl and only 0.03 wt% F, with $\text{Cl}\# = 0.99$. Two analyses in the H6-2 clast have lower Cl/F ratios (Fig. 6b): this appears to reflect compositional heterogeneity within individual apatite grains. In the H6-1 clast, apatite is considerably more F-rich and shows a wide range of Cl/F ratios. The most F-rich grain contains 2.9 wt% Cl and 1.9 wt% F, $\text{Cl}\# = 0.45$, and the most Cl-rich grain contains 4.7 wt% Cl and 0.8 wt% F, $\text{Cl}\# = 0.76$. There are no apparent differences in texture that distinguish high-F apatite grains. Apatite in the mixed apatite / merrillite grain shown in Fig. 9d is F-rich, with F = 1.6 to 1.9 wt%, $\text{Cl}\# = 0.46$ to 0.54. Electron microprobe analyses of apatite indicate a significant component of “other” anions, up to 0.13 apfu, in addition to the halogens F and Cl (Fig. 6). In general, compositions with high F contents have higher (F+Cl) anion totals and a lower “other” component.

SIMS analyses of apatite in Zag show very low H₂O abundances, in the range 350-600 ppm, irrespective of the lithology (Table 4). These are maximum values, because many apatite grains in Zag have fine fractures (Fig. 8, 9) that likely contain C and OH contaminants. Also, we measured the background abundance on a merrillite grain in the same session, and obtained a value of 744 ppm. The high background resulted from strong outgassing of the thin section, and short residence time in the vacuum. As a result, the H₂O abundances we obtained for apatite should be considered to be below the detection limit. Although our measurements cannot be considered quantitative, we can confidently state that H₂O abundances are low, and significantly lower than 1000 ppm. This H₂O abundance clearly does not entirely account for the amount of the “other” anion determined from our EPMA analyses: for OH⁻, 0.1 apfu would correspond to 1800 ppm H₂O.

Sulfur abundances determined by SIMS are also low, <200 ppm (Table 4). The background S content measured on merrillite is <30 ppm. Neither OH nor S abundances correlate with F content. F contents measured by SIMS are consistent with EPMA analyses on the same grains.

Discussion

Non-brecciated H chondrites

Origin of phosphate minerals: Metamorphism and metasomatism. Phosphate minerals show textural differences in different chondrites, which can be interpreted as progressive textural equilibration with increasing petrologic type. In the H4 chondrite, Avanhandava, apatite occurs in fine-grained assemblages, commonly in association with merrillite (Figs. 1a,b). By petrologic type 5 (Richardton, Oro Grande), apatite grains are larger

and more uniform in appearance, but retain islands of merrillite (Figs. 2, 4), and in petrologic type 6 (Estacado), apatite grains are smooth and uniform in appearance with little evidence of association with merrillite. Merrillite shows less textural evolution, although merrillite regions are more fractured and fine-grained in H4 (Fig. 1) than in H5 and H6 (Figs. 2 and 3). In all the H chondrites, there is a notable association of phosphate minerals with metal grains, consistent with derivation of P from its initial source dissolved in metal (Rubin and Grossman, 1985; Zanda et al. 1994; Jones et al. 2014; McCubbin and Jones 2015). Possible sources of halogens could include chondrule mesostasis glass or chondrite matrix (Jones et al. 2014).

Textural changes through the sequence of petrologic types could be interpreted as occurring in the solid state as a result of diffusive equilibration of the host chondrite assemblage, and are most likely at least partly attributable to this process. However, there is evidence for fluid-derived growth in the form of vein-filling phosphate minerals such as those illustrated in Figs. 1a,b, 2a,c, and 4d, as well as porosity in a limited number of grains (e.g. Fig. 4d). Also, compositional heterogeneity of apatite within each H chondrite (Fig. 6a) suggests that compositions are dictated by localized conditions, possibly because of a limited fluid / rock ratio, which argues against diffusive equilibration over a scale of centimeters. Differences in apatite compositions among individual H chondrites (Fig. 6a), and the lack of a systematic trend in Cl/F ratio with petrologic type, argue that chemical communication was limited within the H chondrite parent body, and that chemical equilibrium was not achieved throughout the body. This observation contrasts with essentially complete equilibration of feldspar throughout petrologic types 4, 5, and 6 (Kovach and Jones 2011) and suggests that apatite compositions record a later stage of the metamorphic history than albitization reactions which appear to have been completed before type 4 conditions were reached. In terms of late-stage fluids recorded in

apatite, we infer that the H chondrite parent body was heterogeneous, which could be the result of limited availability of fluid, or differences in the mechanism for generation of fluid. Alternatively, there could have been multiple H chondrite parent bodies that evolved in a similar manner but with different compositions of late-stage fluids, specifically with different Cl/F ratios. However, the entire range of Cl/F ratios observed for H chondrites is encompassed within a single regolith breccia, Zag, which almost certainly represents a sample from a single parent body. The ordinary chondrite parent bodies also show heterogeneity in oxidation state on a kilometer scale and oxygen isotope compositions on a 100-km scale (Rubin et al. 2008).

Comparison of H chondrites with L and LL chondrites. A comparison of the distribution and occurrence in phosphate minerals among the different OC groups allows us to consider differences in the metasomatic / metamorphic environment on the three parent bodies. Abundances of phosphate minerals in petrologic type 4-6 chondrites of the three OC groups are very similar, mostly totaling between 0.4 – 0.5 vol.% (Table 1; Jones et al. 2014; Lewis and Jones 2016). In all three groups, total phosphate abundance is low in type 4 compared with types 5 and 6. However, the ratio of apatite / merrillite varies widely and shows no systematic relationship with either petrologic type or OC group: values for this ratio that we have observed range from 0.4-1.5 in H chondrites (Table 1), 0.25 – 1.0 in L chondrites (Lewis and Jones 2016) and 0.1 to 0.5 in LL chondrites (Jones et al. 2014). The wide range in apatite / merrillite ratios most likely results from the heterogeneity in distribution of apatite on the scale of a thin section.

Textural equilibration of both apatite and merrillite through the petrologic sequence of H chondrites, described above, is also generally observed in LL chondrites (Jones et al. 2014; McCubbin and Jones 2015). and L chondrites (Lewis and Jones 2016). Also, in all three OC groups, phosphate minerals occur in association with chromite-plagioclase assemblages (Fig. 3d;

Jones et al. 2014; Lewis and Jones 2016). These assemblages are considered to be a shock feature (Rubin 2003): if they represent low degrees of partial melting of the host chondrite, it is likely that phosphate minerals would dissolve in the melt and re-precipitate as the melt pocket cools (Jones et al. 2014). Phosphate minerals in association with chromite-plagioclase assemblages do not appear to have notably different compositions to grains that are located elsewhere in the chondrite, which suggests that either melting and crystallization resulted in the same compositions, or that any compositional differences resulting from formation in a small impact melt pocket have been overprinted by later metamorphic or/and metasomatic processes.

Overall, phosphate minerals do not appear to record a significant difference in the metamorphic environment between the H vs. L and LL groups, unlike feldspar, and the phosphate minerals in petrologic type 4-6 H chondrites shed little light on different conditions that might have prevailed on the H vs. the L and LL parent bodies. Apatite in H chondrites tends to be more Cl-rich than apatite in L and LL chondrites (Fig. 6a; Jones et al. 2014; Lewis and Jones 2016). However, there is considerable overlap between H and L apatite compositions in the anion ternary diagram (Lewis and Jones 2016), and given the heterogeneity both within each OC group and among groups, the difference is not resolvable. Relationships between the different OC groups are therefore complicated. Our interpretation is that there is decoupling of the period during which extensive albitization took place from the period recorded by preserved apatite compositions, which is likely to be the case if apatite compositions are determined at a late stage of the metamorphic history of the different parent bodies, possibly during cooling.

Igneous inclusion in Oro Grande. Igneous or lithic inclusions have been described in numerous ordinary chondrites (Hutchison et al. 1988; Bridges and Hutchison 1997; Ruzicka et al. 1998, 2000, 2012). These are igneous-textured inclusions, large relative to chondrules, which

often have low abundances of metal and sulfides. There are several different proposed origins for the melts, including shock, vapor condensation, and melts derived from differentiated planetesimals (e.g. see Ruzicka et al. 2012). Igneous inclusions in the L6 chondrite Barwell have I-Xe ages 4565-4566 Ma, suggesting they formed on a parent body that differentiated prior to formation of chondrites (Hutchison 1988; Gilmour et al. 2000; Crowther et al. 2014). The inclusion in Oro Grande is broadly similar to several previously described inclusions, for example Fodor and Keil (1976) described an inclusion with olivine phenocrysts and an interstitial spinifex texture in the Eva H5 chondrite, and Ruzicka et al. (2012) described an inclusion with a porphyritic texture in Buzzard Coulee (H4). Fodor et al. (1972) interpreted the Oro Grande inclusion as an impact melt formed from the silicate portion of equilibrated H5 material. However, X-ray mapping (Fig. 5) highlights features that resemble textures seen in terrestrial porphyritic volcanic rocks: we suggest that the fine-grained pseudomorphic features represent aggregates of euhedral phenocrysts that have undergone decompositional breakdown reactions, possibly as a result of shock (Jones 2007). The original porphyritic igneous rock could have contained olivine and / or pyroxene phenocrysts, possibly diopside and pigeonite, which broke down into multi-phase assemblages. Also as a result of the shock, an olivine / plagioclase impact melt was generated, which was injected among the phenocryst clusters and quenched into a barred olivine texture. Chemical equilibration of the inclusion with the Oro Grande host chondrite indicates that formation of the original porphyritic rock, as well as the proposed impact event, and incorporation into the H chondrite host, must have occurred prior to H chondrite parent body metamorphism.

The origin of the chlorapatite grains that surround pseudomorphs dominated by diopside is not clear. Possibly, Ca for the chlorapatite originated in diopside, which could have reacted

with a P- and Cl-bearing melt or fluid during the impact event that melted the inclusion. Since formation of the inclusion has been overprinted by metamorphic equilibration with the host H5 chondrite, it is difficult to speculate further.

The Zag H3-6 regolith breccia

Phosphate minerals: Comparison with unbrecciated H chondrites. In Zag, the distribution and grain sizes of phosphate minerals differs significantly between the type 4 matrix and type 6 clast lithologies (Fig. 7). We can compare the phosphate occurrences in the different Zag lithologies with non-brecciated chondrites of comparable petrologic type.

For the H4 matrix lithology of Zag, both merrillite and apatite consist predominantly of individual grains, and apatite grains tend to be larger (several tens μm) than merrillite grains (typically $<20 \mu\text{m}$) as well as significantly more abundant (apatite / merrillite ratio of 4.6) (Figs. 7,8). This distribution is markedly different from Avanhandava (H4), in which the apatite / merrillite ratio is 0.7 (Table 1), apatite consists of fine-grained aggregates that are commonly associated with merrillite, and merrillite occurs as large grains up to $200 \mu\text{m}$ (Fig. 1). The apatite / merrillite ratio in Zag H4 matrix material is the highest of all we have measured in our studies of type 4-6 ordinary chondrites: all apatite / merrillite ratios are <1 in LL and L chondrites studied by Jones et al. (2014) and Lewis and Jones (2016). We attribute the high apatite / merrillite ratio to the fact that the H4 material in Zag is a regolith component that has seen a more complex history than a typical petrologic type 4 H chondrite. Apatite compositions in the H4 lithology are mostly very Cl-rich (Fig. 6b), with higher Cl/F ratios than Avanhandava (H4), up to compositions containing almost no F. Although apatite in the H chondrites in general are

quite Cl-rich (Fig. 6a), these Zag compositions are the most Cl-rich of all the OCs we have studied.

We examined two clasts with type 6 lithology, H6-1 and H6-2. In both, merrillite is much more abundant than apatite (apatite / merrillite ratio of 0.16 in H6-1), and grains of both apatite and merrillite are large, up to 200 μm (Fig. 9). Also, intergrowths of apatite and merrillite are observed (Fig. 9d,f). Occurrences of both minerals are similar to those observed in Estacado (H6: Fig. 3), although intergrowths are more similar to Richardton (H5: Fig. 2). The abundance of merrillite and the apatite / merrillite ratio differ from the non-brecciated H chondrites, but since these values have a wide range (0.4-1.5: Table 1), it is not meaningful to attach much significance to these differences. Despite comparable petrographic observations, apatite compositions in the two H6 clasts differ significantly. In the H6-2 clast, apatite compositions are Cl-rich and comparable to the H4 matrix lithology (Fig. 6b). In contrast, in the H6-1 material, apatite compositions are highly heterogeneous, much more F-rich, and compositions extend to lower Cl/F (atomic) ratios of around 1.

The overall picture of apatite in Zag is complex. The H4 and H6-2 clasts have apatite compositions that are close to normal for H chondrites, but the high apatite/merrillite ratio in H4 is unusual. In H6-1, apatite petrography can be considered to be normal, but compositions are heterogeneous and F-rich. Interpreting the evolution of this regolith breccia requires an understanding of these observations, as well as an understanding of the relationship between apatite and halite: since halite is also a halogen-bearing mineral, it is important to question whether the two minerals have a common source.

Relationship between apatite and halite. Halite in Zag, as well as in the related H5

chondrite, Monahans, is demonstrably pre-terrestrial (Zolensky et al. 1999; Whitby et al. 2000; Rubin et al. 2002; Bridges et al. 2004). Previous studies have shown that halite occurs predominantly within the dark matrix of these two chondrites, as grains a few hundred microns across (Zolensky et al. 1999; Whitby et al. 2000; Rubin et al. 2002; Bridges et al. 2004). Halite in both Zag and Monahans contains low-temperature (<100 °C) aqueous fluid inclusions, and is considered to result from evaporation of brines (Zolensky et al. 1999; Whitby et al. 2000; Rubin et al. 2002). In Monahans, halite also contains inclusions of sylvite (KCl) (Zolensky et al. 1999). Halides in both Zag and Monahans have been dated by K-Ar, Rb-Sr and I-Xe methods (Zolensky et al. 1999; Bogard et al. 2001; Whitby et al. 2000; Busfield et al. 2004), and have ages consistent with the timing of metamorphism on the OC parent bodies, with the best interpretation of I-Xe ages around 4559 Ma (Busfield et al. 2004).

Various models have been proposed to account for the origin of halite and the source of water in the brines. One group of models assumes that halite formed on the H chondrite parent body: possible sources of water include exogenous water delivered to the parent body by cometary or asteroidal ice fragments (Zolensky et al. 1999; Bridges et al. 2004), dehydration of the asteroid interior (Whitby et al. 2000), and impact heating of phyllosilicates (Rubin et al. 2002). Bridges et al. (2004) argued that halite occurs as a clastic component of the breccia and did not precipitate in situ. More recent work has shown that halite contains a disequilibrium assemblage of diverse solid inclusions including silicates, phosphates, sulfides, oxides, macromolecular carbon, and light organic species (Fries et al. 2011; Zolensky et al. 2013). This assemblage is not obviously derived from an H chondrite parent body. Fries et al. (2011, 2013) suggest that halite could be derived from a carbonaceous asteroid, such as Ceres, or it could be

the product of cryovolcanism similar to what is observed on the Saturnian satellite Enceladus (Fries et al. 2011; Zolensky et al. 2013). Disequilibrium hydrogen and oxygen isotope ratios of fluid inclusions in halite indicate a D-rich and ^{16}O -poor source for the fluid, which is consistent with an origin on a carbonaceous parent body that had mixed with cometary water (Yurimoto et al. 2014). The presence of organic inclusions, as well as studies of the aqueous fluid inclusions in halite (Zolensky et al. 1999), provide strong evidence that halite has not been heated above 25 °C (Zolensky et al. 2013).

The predominance of halite in dark matrix and the highly Cl-rich compositions of apatite in matrix suggest that there may be a relationship between the two minerals and that their formation mechanisms could be coupled. In addition, the high apatite / merrillite ratio suggests a high fluid / rock ratio, since the overall abundance of phosphates is not unusually high (Table 1). Fluids would need to have a high Cl/F ratio, and the very low H_2O contents of apatite (Table 4) would also require such a fluid to be extremely H_2O -poor. Such a briny fluid might also precipitate halite: this could be a mechanism for an indigenous origin for halite. If halite is exogenous, one could argue that the halogens required to reset apatite compositions are delivered by the same mechanism as the halite, and that some of the impact material that included halite might vaporize and release Cl-rich fluids. An alternative model is that the presence of clastic halite (either indigenous or exogenous) contributed to secondary production of localized Cl-rich fluids: halite in Zag (and Monahans) contains fluid-filled fractures, providing evidence for fracturing and healing, most likely as a result of micrometeorite impacts in the regolith (Zolensky et al. 1999; Rubin et al. 2002), and this could have released Cl-rich fluids. If apatite compositions and the presence of halite are coupled, we might also expect halite to occur in H6-2 material. Unfortunately, we do not know if this is the case, since the thin section was not

prepared in water-absent conditions, and any halite present would have been lost in sample preparation. The Cl-rich apatite compositions in H6-2 could mean that the H6-2 clast was emplaced within matrix before H6-1, at the time when Cl-rich fluids were active.

The chlorine isotopic composition of halite in Zag is significantly lighter than that in typical ordinary chondrite material, $\delta^{37}\text{Cl} \sim -2\%$ (Bridges et al. 2004; also, water-soluble chloride analysis in Zag from Sharp et al. 2013), vs. a mean bulk value of -0.4% for all ordinary chondrites (Sharp et al. 2013). Since little isotopic fractionation would be expected between halite and the brine from which it precipitates, the brine must have been isotopically light. Bridges et al. (2004) suggested that isotopic fractionation producing an isotopically light fluid was unlikely to be a parent body process, and that the isotopically light fluid represents a separate isotopic reservoir in the early solar system. Alternatively, we propose that an isotopically light fluid could have formed as a result of degassing of metal chlorides in an H-poor system, the counterpart of the analogous process that led to high $^{37}\text{Cl}/^{35}\text{Cl}$ ratios measured in Apollo samples which were attributed to Cl degassing of anhydrous magmas (Sharp et al. 2010). Sharp et al. (2013) also observed isotopically light chlorine in the LL3.6 chondrite Parnallee, in both the water-soluble fraction ($\delta^{37}\text{Cl} = -2.65\%$), and the structurally-bound chloride component (mean $\delta^{37}\text{Cl} = -4.1\%$, indicating that a mechanism for producing isotopically light chlorine must be reproducible, although uncommon, on ordinary chondrite parent bodies.

We also need to consider the source of the more F-rich apatite compositions of H6-1. One might argue that Cl-rich apatite compositions represent the final stages of evolution of a halogen-rich fluid that was initially F-bearing, which evolved to more Cl-rich compositions due to the relative partitioning behavior of F and Cl between apatite and fluid or melt (Boyce et al.

2014; McCubbin et al. 2015), in a process of fractional precipitation (similar to fractional crystallization). For example, halogen-bearing fluids may have been derived from the interior of the H chondrite parent body, either as a result of solid-state breakdown of halogen-bearing phases such as chondrule mesostasis at high metamorphic temperatures, or possibly as a result of degassing of a partial melt in the interior of the body (Elkins-Tanton et al. 2011; Weiss et al. 2012). The latter mechanism would be consistent with light chlorine isotopes, if the fluid was H-poor. As the fluid migrated towards the asteroid surface, it would have interacted with merrillite or apatite already present in petrologic type 6 material, producing fluor-chlor-apatites (F-Cl-apatites). Apatite / merrillite intergrowth textures such as those illustrated in Fig. 9d,f are similar to textures in the unique primitive achondrite GRA 06128/06129 which are interpreted as replacement reactions that occurred when halogen-rich fluids interacted with previously existing merrillite grains (Shearer et al. 2011). Since F partitions strongly into apatite (Boyce et al. 2014; McCubbin et al. 2015), the fluid would become progressively depleted in F and enriched in Cl as it migrated through the parent body, resulting in more Cl-rich apatite compositions at lower depths (petrologic type 4). Extreme enrichment in Na and Cl could lead to precipitation of halite in the final stages. Further insight into this model would be gained by a better understanding of the relationship between F and H₂O contents, as well as D/H ratios, in apatite. A complication for this scenario is that apatite in the H6-2 clast is Cl-rich, not F-rich, so we cannot simply consider the parent body to have an onion-shell structure in which all H6 material records alteration by the same fluid. The parent body must have already been brecciated when fluid evolution occurred, i.e. the parent body would have had a rubble-pile structure, with H6-1 material located towards the centre and H4 and H6-2 material located closer to the surface.

If halite is exogenous, a relationship between apatite and halite is not required. An alternative model for the formation of F-Cl-apatite is that it represents interactions with an F-bearing fluid generated from localized, impact-related shock melting. Features that appear to be impact melt veins and pockets occur in H6-1 material (Fig. 10), as well as chromite-plagioclase assemblages (Fig. 10b) which are interpreted as being produced by shock (Rubin et al. (2002) also describe shock features in H6 material in Zag. We suggest that impact melts could have degassed volatiles, including F, and that the F-bearing vapor derived from such an event either interacted with pre-existing apatite or precipitated apatite, resulting in heterogeneous apatite compositions. F-Cl-apatite compositions would form initially, followed by Cl-rich apatite as the F inventory of the fluid is rapidly depleted due to the relative partitioning behavior of F relative to Cl between apatite and fluid. Alternatively, F-Cl-apatite could have precipitated from an impact melt that had degassed Cl. Further support for an impact-related scenario is that F-Cl-apatite is also observed in the L4 host of the L chondrite regolith breccia, Kendleton (Lewis and Jones 2016), suggesting that F-bearing fluids might be more generally associated with regolith breccias and surface processing. Since heterogeneous Cl/F ratios of apatite would become homogenized by diffusion over metamorphic timescales (see Jones et al. 2014), continuous impact processing would need to extend into the time period when the asteroid was cooling.

Although we cannot argue for a unique scenario to explain the apatite compositions in Zag, it is clear that formation conditions of apatites in different lithologies must have been locally controlled, which in turn means that compositions were set prior to assembly of the material we now observe as the Zag brecciated chondrite. Our preferred interpretation of the complex nature of this rock is as follows. Merrillite and apatite were formed initially in a similar way to unbrecciated chondrites, at varying depths in the H chondrite parent body. Repeated

impacts resulted in brecciation and regolith formation, mixing clasts of different lithologies at the asteroid surface. Impacts into this material produced F-bearing, Cl-rich and H₂O-poor fluids, and fractional precipitation of these fluids led to formation of F-Cl-apatite, followed by Cl-rich apatite, and finally halite. In this scenario, both apatite and halite are retrograde phases that form during cooling, and halite forms at the lowest temperatures. This model argues against the interpretation that halite is exogenous. We suggest that the mélange of solid inclusions found in halite (Fries et al. 2011, Zolensky et al. 2013) may represent fine-grained detritus at the surface of the H asteroid, derived from regolith formation as well as bombardment by interplanetary dust and micrometeorites. The D-rich and ¹⁶O-poor cometary signature of the fluid inclusions in halite (Yurimoto et al. 2014) could be derived from a cometary impactor, as proposed by Zolensky et al. (1999) and Bridges et al. (2004). Further clarification of the behavior of halogens in Zag will need detailed observations of a range of lithologies in multiple thin sections, to investigate relationships between apatite compositions, the presence of halite, and host petrography in more detail.

Implications

The factors affecting the formation and evolution of apatite in ordinary chondrites are varied and complex, but unraveling them can potentially help to interpret the complex behavior of fluids on the asteroids that represent chondritic parent bodies. Compositions of apatites are heterogeneous on a scale of individual chondrites from the same chondrite group, and on a scale of individual lithologies within brecciated chondrites, indicating that fluid compositions are highly localized and that fluids were active as the asteroids cooled. This observation is an important consideration for understanding the internal structure of chondritic asteroids, with

619 implications for physical as well as mechanical properties of the bulk asteroid. The suggestion
620 that F-Cl-apatites may be associated with regolith breccias could have important broader
621 implications: if halogens are readily degassed from impact-melt materials close to an asteroid
622 surface, significant volatile loss could have occurred, even on chondritic asteroids. For an
623 asteroid that underwent extensive melting, such as the parent body of an achondrite, volatile loss
624 would have been considerable. The volatile inventories of terrestrial planets are probably
625 considerably more depleted than the CI carbonaceous chondrite abundances that are commonly
626 assumed.

627 **Acknowledgements**

629
630 We wish to thank reviewers S. Itoh and A. Rubin for useful comments, Michael Spilde
631 for assistance with electron microprobe analyses, and Jonathan Lewis for helpful discussions.
632 Electron microprobe and SEM work was carried out in the Electron Microbeam Analysis
633 Facility, Department of Earth and Planetary Sciences and Institute of Meteoritics, University of
634 New Mexico. The work was partially funded by NASA grant NNX12AH61G (P.I. R. Jones).
635 FMM acknowledges support from the NASA Cosmochemistry Program through grant
636 NNX14AK43G (P.I. FMM).

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Tables

Table 1: Modal abundances of phosphate minerals

Chondrite	Pet type	Shock stage ¹	Area mm ²	% Phosphate Minerals			
				Apatite	Merrillite	Total	Ap/Merr
Avanhandava	H4	S2	64	0.17	0.24	0.41	0.72
Oro Grande	H5	S1	96	0.21	0.29	0.50	0.72
Richardton	H5	S2	64	0.28	0.18	0.46	1.49
Estacado	H6	S1	73.5	0.15	0.38	0.52	0.39
Zag matrix	H4	S2-S5	67.5	0.23	0.05	0.28	4.60
Zag clast H6-1	H6	S2-S5	60.5	0.09	0.55	0.64	0.16

¹Shock stages from Stöffler et al. (1991); Rubin (1994, 2004); Folco et al. (1996); Grossman (1999); Rubin et al. (2002)

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Table 2: Average compositions of merrillite in H chondrites (EPMA data)

	Avan.	1-sig	Rich.	1-sig	Oro Gr.	1-sig	Est.	1-sig	Zag H6-1	1-sig	Zag H6-2
CaO	47.1	0.2	47.1	0.2	47.1	0.1	46.9	0.3	46.8	0.5	46.3
MgO	3.7	0.1	3.7	0.0	3.7	0.0	3.5	0.0	3.5	0.0	3.5
FeO	0.4	0.1	0.5	0.2	0.4	0.1	0.5	0.3	0.5	0.2	0.3
Na ₂ O	2.8	0.0	2.8	0.0	2.7	0.0	2.8	0.0	2.7	0.1	2.8
P ₂ O ₅	45.5	0.2	45.3	0.3	45.1	0.3	45.6	0.4	46.0	0.4	45.3
Total	99.5		99.3		99.0		99.3		99.6	0.7	98.2
<i>Merrillite formula on the basis of 56 oxygens</i>											
Ca	18.2	0.1	18.2	0.1	18.3	0.1	18.1	0.1	18.0	0.1	18.1
Mg	2.0	0.0	2.0	0.0	2.0	0.0	1.9	0.0	1.9	0.0	1.9
Fe	0.1	0.0	0.1	0.1	0.1	0.0	0.2	0.1	0.2	0.1	0.1
Na	1.9	0.0	2.0	0.0	1.9	0.0	1.9	0.0	1.9	0.1	1.9
P	13.9	0.0	13.9	0.0	13.8	0.0	13.9	0.0	14.0	0.0	14.0
Total	36.1	0.1	36.2	0.1	36.2	0.1	36.1	0.1	35.9	0.1	36.0
mg#	0.94		0.94		0.94		0.93		0.93		0.96
n	15		19		20		28		41		1

Avan: Avanhandava; Rich: Richardton; Oro Gr: Oro Grande; Est: Estacado

n = number of analyses

mg# = mg/(mg+fe)

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Table 3: Apatite compositions in H chondrites (EPMA data)

	Avan.	1-sig	Rich.	1-sig	Oro Gr.	1-sig	Oro Gr.	1-sig	Est.	1-sig	Zag	1-sig	Zag	1-sig	Zag	1-sig
					host		inclusion				H4		H6-1		H6-2	
CaO	53.5	0.2	53.1	0.3	53.7	0.3	53.6	0.1	53.6	0.2	52.3	0.3	53.4	0.4	52.5	0.2
MgO	0.05	0.03	0.05	0.06	0.09	0.03	0.06	0.01	0.05	0.03	0.10	0.04	0.05	0.03	0.09	0.04
FeO	0.44	0.16	0.27	0.11	0.41	0.16	0.28	0.03	0.18	0.12	0.61	0.39	0.47	0.31	0.38	0.30
Na ₂ O	0.35	0.01	0.42	0.02	0.31	0.03	0.35	0.01	0.43	0.03	0.50	0.09	0.27	0.04	0.48	0.04
P ₂ O ₅	40.7	0.2	40.3	0.2	40.2	0.4	39.8	0.2	40.8	0.3	40.4	0.2	40.7	0.3	40.6	0.3
F	0.60	0.07	0.32	0.11	0.80	0.11	0.71	0.08	0.38	0.12	0.16	0.08	1.43	0.34	0.24	0.18
Cl	5.4	0.1	6.2	0.2	4.9	0.2	5.0	0.1	5.5	0.2	5.8	0.2	3.7	0.5	5.7	0.4
-O=F+Cl	1.5	0.0	1.5	0.1	1.5	0.0	1.4	0.0	1.4	0.1	1.4	0.0	1.4	0.0	1.4	0.0
Total	99.6	0.4	99.2	0.3	99.1	0.4	98.4	0.2	99.5	0.4	98.6	0.6	98.6	0.5	98.6	0.5
Cl/F (wt)	9.3	1.2	23.4	14.3	6.4	1.1	7.1	0.9	16.0	5.9	52.6	45.4	2.8	1.2	34.9	18.8
<i>Apatite formula on the basis of 13 anions</i>																
Ca	4.97	0.01	4.98	0.02	5.01	0.03	5.04	0.02	4.97	0.01	4.91	0.03	4.96	0.02	4.91	0.02
Mg	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.01
Fe	0.03	0.01	0.02	0.01	0.03	0.01	0.02	0.00	0.01	0.01	0.04	0.03	0.03	0.02	0.03	0.02
Na	0.06	0.00	0.07	0.00	0.05	0.01	0.06	0.00	0.07	0.01	0.09	0.01	0.05	0.01	0.08	0.01
P	2.98	0.01	2.98	0.01	2.97	0.01	2.96	0.01	2.99	0.01	3.00	0.01	2.99	0.01	3.00	0.01
F	0.16	0.02	0.09	0.03	0.22	0.03	0.20	0.02	0.11	0.03	0.04	0.02	0.39	0.09	0.07	0.05
Cl	0.80	0.02	0.90	0.02	0.73	0.03	0.74	0.01	0.81	0.03	0.87	0.03	0.54	0.08	0.84	0.06
"Other" anion by diff	0.04	0.02	0.01	0.02	0.05	0.02	0.06	0.01	0.08	0.04	0.09	0.02	0.07	0.02	0.09	0.02
Σ Tetrahedral	2.98	0.01	2.98	0.01	2.97	0.01	2.96	0.01	2.99	0.01	3.00	0.01	2.99	0.01	3.00	0.01
Σ Octahedral	5.07	0.01	5.07	0.02	5.11	0.03	5.13	0.02	5.07	0.02	5.05	0.02	5.05	0.03	5.04	0.01
Cl/F (atomic)	5.0	0.6	12.4	7.7	3.4	0.6	3.8	0.5	8.6	3.2	28.2	24.3	1.5	0.6	18.7	10.1
Cl/(Cl+F) (atomic)	0.83	0.02	0.91	0.03	0.77	0.03	0.79	0.02	0.89	0.03	0.95	0.02	0.58	0.09	0.93	0.06
n	9		16		9		3		21		13		26		16	

Avan: Avanhandava; Rich: Richardton; Oro Gr: Oro Grande; Est: Estacado

n = number of analyses

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Table 4: Volatile anion analyses of merrillite and apatite in Zag

Grain	Host material	H ₂ O, ppm SIMS ¹	S, ppm SIMS ¹	F, wt% SIMS ¹	F, wt% EPMA ²
Apatite M2D	H6-2	599	97	0.11	0.10-0.28
Apatite P11	H4	358	117	0.05	0.13
Apatite P7	H6-1	439	154	1.58	1.05-1.78
Merrillite P1	H6-1	744	64	-0.08	0

¹OH, S and F determined by SIMS based on calibrations from apatite standards

²F wt% measured directly by electron microprobe: ranges are for multiple analyses on a single grain

Figure Captions

Fig. 1. BSE images showing occurrences of phosphate minerals in Ahanhandava (H4): ap = apatite, merr = merrillite. The silicate mineral assemblage in all images includes olivine (olv), which is lighter grey than low-Ca pyroxene (pyx), and feldspar (dark grey – noticeable in chondrule interiors in (c) and (d)). White phases include Fe,Ni metal and troilite (FeS). a) Fine-grained assemblage of apatite and merrillite intergrown with pyroxene and metal; b) Fine-grained apatite adjacent to metal; c,d) occurrence of merrillite at the margins of relict chondrules (rounded objects).

Fig. 2. BSE images showing occurrences of phosphate minerals in Richardton (H5): ap = apatite, merr = merrillite. The silicate mineral assemblage in all images includes olivine (olv), which is lighter grey than low-Ca pyroxene (pyx), and feldspar (dark grey). White phases include Fe,Ni metal and troilite (FeS). a) Apatite grain with inclusions of merrillite, olivine (dark grey) and metal (white). Apatite also occurs in fine veins adjacent to the large grain. b) Fractured apatite grain with an inclusion of merrillite. c) Individual grains of merrillite and apatite. Merrillite also occurs in fine veins adjacent to the large grain. d) Individual grain of merrillite. In (b), (c), and (d), phosphate grains are in contact with metal.

Fig. 3. BSE images showing occurrences of phosphate minerals in Estacado (H6): ap = apatite, merr = merrillite. The silicate mineral assemblage in all images includes olivine (olv), which is lighter grey than low-Ca pyroxene (pyx), and feldspar (dark grey). White phases include Fe,Ni metal and troilite (FeS). Both phosphate minerals are distributed throughout the chondrite with

similar grain sizes and as mostly uniform individual grains. Fig. 3(d) shows merrillite and apatite grains that appear to be associated with a chromite-plagioclase assemblage (CPA).

Fig. 4. BSE images showing occurrences of phosphate minerals in Oro Grande (H5): ap = apatite, merr = merrillite. The silicate mineral assemblage in all images includes olivine (olv), which is lighter grey than low-Ca pyroxene (pyx), and feldspar (dark grey). White phases include Fe,Ni metal and troilite (FeS). White veins throughout the images are the product of terrestrial weathering. Both phosphate minerals occur as individual grains as well as intergrown together e.g. in (a), (c) and (d). Both phosphate minerals occur at the margins of the large (5 mm) igneous inclusion which is visible in (c) and (d).

Fig. 5. Texture and occurrence of apatite (ap) in the 5 mm igneous inclusion in Oro Grande (H5). a,b) BSE images showing large apatite grains surrounding features that appear to be fine-grained pseudomorphs of phenocrysts in a porphyritic rock. The groundmass is a fine-grained mixture of olivine (light grey) and feldspar (dark grey) with a barred texture. Small white grains are predominantly chromite. c,d,e) X-ray maps of the area shown in (b), highlighting phenocrystic texture. (e) Combined X-ray map, RGB = Mg,Na,Ca. Apatite shows as pink in the Ca map and blue in the combined map. Olivine is pink in the Mg map and bright red in the combined map. Albitic feldspar is green in the combined map. Low-Ca pyroxene is yellow in the Mg map and dull red in the combined map. Diopside is light blue in the Mg and Ca maps and purple in the combined maps.

Fig. 6. Anions in apatite in H chondrites. The apex of the ternary labeled “other” is usually assigned to OH^- , but we prefer to label it “other” since there is little evidence for OH in chondritic apatite (see text). a) Apatite compositions in non-brecciated chondrites. b) Apatite compositions in the H3-6 breccia, Zag. Lithologies identified as H4 matrix, H6-1 and H6-2 are identified in Fig. 7.

Fig. 7. Thin section of the Zag H3-6 chondrite studied. a) Optical scan of thin section UNM 1136: circular thin section is 2.5 cm in diameter. H4 matrix material is dark, and two H6 clasts, H6-1 and H6-2, are light. The small box with solid outline is the region shown in (b) and the larger box with dashed outline is the region shown in the X-ray maps, (c)-(f). Fine-dashed line outlines the contact between H4 matrix and H6-1 regions. b) BSE image showing the contact between regions H6-2 and H4 matrix, which is highlighted with a dashed line. The H6 lithology is coarse-grained and contains coarse-grained metal and sulfide aggregates (white). Apatite (ap) occurs as large individual grains (light grey) in both lithologies. c-f) X-ray maps showing distributions of Fe, S, P and Cl in the region outlined in (a). Sulfide is fine-grained in H4 matrix and coarser-grained in H6-1. Apatite is concentrated in the H4 matrix material (see Cl map) and merrillite occurs in both matrix and H6-1 lithologies, but has significantly larger grain size in H6-1.

Fig. 8. BSE images of phosphate grains in the H4 matrix of Zag: ap = apatite, me = merrillite. The silicate mineral assemblage in all images includes feldspar, olivine, low-Ca pyroxene, and Ca-rich pyroxene, in order of increasing grey-level. White grains include Fe,Ni metal and troilite (FeS). a) Several irregular shaped apatite grains and a small merrillite grain associated with

metal (top). b) Several apatite grains and two small merrillite grains (center). Chondrules are clearly defined. c) Apatite and small merrillite grains: elongate apatite in the center has a vein-like extension from the right side of the grain.

Fig. 9. BSE images of phosphate grains in the H6 lithologies of Zag: ap = apatite, merr = merrillite. The silicate mineral assemblage in all images includes olivine (olv), which is lighter grey than low-Ca pyroxene (pyx), and feldspar (dark grey). White phases include Fe,Ni metal and troilite (FeS). a) Individual merrillite grain in H6-1. b) Merrillite grains in H6-1 showing lineations that appear to be crystallographically controlled. c) Apatite grains in H6-1 (d) Intergrown apatite and merrillite in H6-1. (e) Apatite in an assemblage with chromite (chro) and olivine (olv) in H6-1. (f) Large apatite grain with an inclusion of merrillite in H6-2.

Fig. 10. a) Region of Zag region H6-1 showing merrillite (light grey: red arrows) that appears to occur in a sinuous feature interpreted as an annealed melt vein. The sinuous feature is defined by plagioclase (plag: dark grey) and includes a chromite-plagioclase assemblage (CPA). b) Higher magnification image of the chromite-plagioclase assemblage in (a), chro = chromite, plag = plagioclase, merr = merrillite. c) Apatite and merrillite in H6-1. The lower part of the large apatite grain appears to have undergone incipient melting into a feldspathic melt. d) Merrillite in H6-1. A fine-grained equigranular region of low-Ca pyroxene (pyx), Ca-rich pyroxene (cpx) and plagioclase contains fine-grained (<5 μm) merrillite distributed along grain boundaries.

Fig. 1

Avanhandava

Fig. 2

Richardton

Fig. 3

Estacado

Fig. 4

Oro Grande

Fig. 5

Oro Grande Inclusion

Fig. 6

Fig. 7

Zag

Fig. 8
Zag: H4 matrix

Fig. 9
Zag: a-e) H6-1; f) H6-2

Fig. 10
Zag: H6-1