



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

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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**

7  
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## Abstract

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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

51 and more F-rich. Apatites in both H4 matrix and H6 clasts have very low H<sub>2</sub>O contents.  
52 Heterogeneous apatite compositions in Zag record multiple stages of regolith processing and  
53 shock at the surface of the H chondrite parent body, and apatite records either the passage of  
54 fluids of variable compositions resulting from different impact-related processes, or the passage  
55 of a single fluid whose composition evolved as it interacted with the chondrite regolith.  
56 Unraveling the history of apatite can potentially help to interpret the internal structure of  
57 chondrite parent bodies, with implications for physical and mechanical properties of chondritic  
58 asteroids. The behavior of halogens recorded by apatite is important for understanding the  
59 behavior of volatile elements in general: if impact-melt materials close to the surface of a  
60 chondritic asteroid are readily degassed, the volatile inventories of terrestrial planets could be  
61 considerably more depleted than the CI carbonaceous chondrite abundances that are commonly  
62 assumed.

63

64 **Keywords:**

65 ANALYSIS, CHEMICAL (MINERAL): merrillite, apatite

66 MAJOR AND MINOR ELEMENTS: merrillite, apatite

67 METEORITE: ordinary chondrite, H chondrite, Avandava, Estacado, Oro Grande, Rich-  
68 ardton, Zag

69 PETROGRAPHY: ordinary chondrite, H chondrite

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## 73 **Introduction**

74

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

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

106 took place in the first few million years of solar system history. In a recent study of petrologic  
107 type 4-6 LL chondrites, we showed that chlorapatite grains record the presence of  
108 metasomatizing fluids throughout the metamorphic history of the LL parent body (Jones et al.  
109 2014), and that in at least the late stages of metamorphism, these fluids are dry (water-poor) and  
110 halogen-bearing. Metasomatizing fluids are also likely responsible for albitization reactions that  
111 produce albitic feldspar in ordinary chondrites (Kovach and Jones 2011; Jones and Brearley  
112 2010a,b; Lewis and Jones 2014, 2015, 2016). The three groups of ordinary chondrites all record  
113 the effects of similar metamorphic and metasomatic environments. However, there are also  
114 significant differences. Feldspar in H4 chondrites is albitic and homogeneous in composition,  
115 whereas feldspar in L4 and LL4 chondrites is highly heterogeneous, ranging from almost end-  
116 member An to Ab (Kovach and Jones 2011; Lewis and Jones 2016). In L and LL chondrites,  
117 equilibration to albitic feldspar is only complete in petrologic type 6. Hence, it appears that  
118 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.

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

119 the parent body by cometary or asteroidal ice fragments (Zolensky et al. 1999; Bridges et al.  
120 2004), dehydration of the asteroid interior (Whitby et al. 2000), or impact heating of  
121 phyllosilicates (Rubin et al. 2002). Alternatively, halite may be exogenous, derived from either a  
122 carbonaceous asteroid such as Ceres (Fries et al. 2014; Yurimoto et al. 2014) or via  
123 cryovolcanism on a body such as the Saturnian satellite Enceladus (Zolensky et al. 2013). We  
124 have studied the phosphate mineralogy of Zag, in order to examine whether apatite can help shed  
125 light on the conditions that led to halite formation and halogen redistribution in the regolith of  
126 the H chondrite asteroid.

127

## 128 **Samples and Methods**

129

130 We studied phosphate minerals in Avanhandava (H4), Richardton (H5), Oro Grande (H5)  
131 Estacado (H6), and Zag (H3-6) (Table 1). Phosphate minerals were identified and analyzed in  
132 the following thin sections: Avanhandava, UNM 88; Richardton, UNM 384; Oro Grande, UNM  
133 55; Estacado, UNM 609; and Zag, UNM 1136. Oro Grande is a find and is moderately  
134 weathered; the others are falls. All the samples have nominally low shock levels, between S1 and  
135 S3 (Stöffler et al. 1991; Rubin 1994, 2002, 2004; Folco et al. 1996; Grossman 1999). The Zag  
136 thin section we studied contains both dark matrix and light clast lithologies.

137 We used WDS/EDS X-ray mapping to locate phosphate mineral grains, using the JEOL  
138 8200 electron microprobe at the University of New Mexico (UNM). For mapping, we typically  
139 used a defocused electron beam, 10  $\mu\text{m}$  in diameter, and a counting time of 20 milliseconds per  
140 pixel, in order to minimize volatile loss from susceptible phases. Back-scattered electron (BSE)  
141 images were obtained using the electron microprobe and the JEOL 5800LV SEM at UNM, as

142 well as an FEI XL30 ESEM-FEG at the University of Manchester. We determined modal  
143 abundances of phosphate minerals from X-ray maps using the ImageJ image analysis program  
144 (Schneider et al. 2012). Modal abundances of total phosphates were determined from P X-ray  
145 maps, modal abundances of Cl-apatite were determined from Cl X-ray maps, and modal  
146 abundances of merrillite were calculated by subtracting the abundance of Cl-apatite from total  
147 phosphates. Estimated errors for modal abundances determined with this method are less than  
148 10% relative.

149         Electron microprobe analyses of merrillite and chlorapatite were obtained using the  
150 JEOL 8200 electron microprobe. We used conditions that were designed to minimize  
151 volatilization of halogens (F and Cl) in chlorapatite: operating conditions were 15kV and a 20nA  
152 beam current, and we used a defocused (usually 5  $\mu\text{m}$ ) electron beam to analyze both standards  
153 and unknowns. The problem of fluorine migration in apatite under the electron beam has been  
154 recognized in previous studies (Stormer et al. 1993; McCubbin et al. 2010a, 2011). We  
155 monitored the F and Cl count rates during analyses using the live chart recorder on the electron  
156 microprobe and discarded analyses in which we observed significant changes in F and/or Cl  
157 counts during peak counting times. The following standards were used for calibration: Taylor  
158 apatite and Apatite 020 (see below) for Ca, P, and F (McCubbin et al. 2012); sodalite for Na and  
159 Cl, Taylor olivine for Mg and Fe, and Y and Ce end-member phosphates for Y and Ce. Detection  
160 limits for F and Cl were 0.04 and 0.01 wt% respectively, and detection limits for  $\text{Y}_2\text{O}_3$  and  
161  $\text{Ce}_2\text{O}_3$  were 0.05 wt%. Detection limits for all other elemental oxides were 0.01 or 0.02 wt%. For  
162 apatite analyses, we defined criteria for an acceptable analysis where each cation site is  
163 populated by  $\pm 2\%$  of values in the ideal structural formula. Thus an acceptable analysis was  
164 defined as follows: Total oxide wt% between 97 and 102; Sum of tetrahedral site cations

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

170 Secondary ion mass spectrometry (SIMS) analyses of volatile anion elements (H, F, and  
171 S) were obtained using the Cameca IMS 7f-GEO ion microprobe at Caltech. Samples were  
172 measured with a  $\sim 20 \mu\text{m}$   $\text{Cs}^+$  primary beam of +10 keV and  $\sim 3.5\text{nA}$ , rastering over an area of  
173  $10 \times 10 \mu\text{m}$ . 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  
174 collected from the center  $10 \mu\text{m}$  at a mass resolving power of  $\sim 4500$ . Sample charging was  
175 compensated with an electron gun at -10 keV. Secondary ion images of  $^{12}\text{C}^-$ ,  $^{16}\text{O}^{1}\text{H}^-$ , and  $^{19}\text{F}^-$   
176 were examined before each sample measurement to avoid cracks and contamination. A  
177 calibration curve for OH was determined from five terrestrial apatite standards that had  $\text{H}_2\text{O}$   
178 contents varying from 300 to 5500 ppm (McCubbin et al. 2010b, 2012; Jones et al. 2014). A  
179 calibration curve for S, based on the five apatite standards, was determined by Jones et al.  
180 (2014). SIMS analyses of F in this study show an excellent correlation with electron microprobe  
181 and bulk analyses of F abundances, measured in terrestrial standards and apatite grains in LL  
182 chondrites (Jones et al. 2014).

183

184

## Results

185

186 **Non-brecciated H chondrites**

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

196           **Textures of phosphate minerals in Avanhandava, Richardton and Estacado.** Figures  
197 1, 2 and 3 illustrate textures of phosphate minerals in the H4-5-6 petrologic sequence represented  
198 by Avanhandava, Richardton and Estacado respectively. In all cases, both apatite and merrillite  
199 occur as irregularly shaped grains up to 200  $\mu\text{m}$  in length. In Avanhandava (H4), both apatite  
200 and merrillite are commonly fragmented into small angular pieces (Fig. 1a). The two minerals  
201 can be associated (Fig. 1a), and both are commonly associated with metal / sulfide grains (Fig.  
202 1a-c). Grains of merrillite up to 200  $\mu\text{m}$  in length also occur along and close to the perimeter of  
203 relict chondrules (Fig. 1c,d). In Richardton (H5), large apatite grains up to 200  $\mu\text{m}$  in length  
204 often contain a small inclusion of merrillite (Fig. 2a,b). Similar to Avanhandava, both apatite and  
205 merrillite are commonly associated with metal / sulfide grains (Fig. 2a-d). Apatite grains occur in  
206 intergrowths with olivine, in which case they contain rounded olivine inclusions and show a  
207 curved interface, concave to the apatite (Fig. 2a,c). Several grains of both apatite and merrillite  
208 are connected to vein-like networks of similar material (Fig. 2a,c). In Estacado (H6), apatite and  
209 merrillite grains are more angular than those in Richardton, and do not contain many inclusions

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

215 **Oro Grande host and igneous inclusion.** In the Oro Grande H5 chondrite host, both  
216 apatite and merrillite occur as grains up to 200  $\mu\text{m}$  in length, many of which are associated with  
217 metal / sulfide grains (Fig. 4). Apatite and merrillite are closely associated (Fig. 4c), and in some  
218 grains appear to show a reaction relationship (Fig. 4a,d). Also, some apatite grains contain what  
219 appear to be pores (Fig. 4d). Both minerals are present along and close to the boundary of a large  
220 (5 mm) inclusion within the H chondrite host (Fig. 4c,d). This inclusion has previously been  
221 described as an igneous inclusion that has equilibrated with the host chondrite (Fodor et al. 1972;  
222 Jones 2007). The inclusion is dominated by a fine-grained mixture of barred olivine and  
223 plagioclase, with olivine bar widths  $<10 \mu\text{m}$  (Fig. 4c,d; 5a,b). Throughout the inclusion there are  
224 also numerous objects ( $\sim 50 \text{ vol}\%$ ) that appear to be pseudomorphs of euhedral phenocrysts, 100  
225 to 500  $\mu\text{m}$  in length, which have complex internal textures. Some pseudomorphic regions are  
226 dominated by diopside, with minor low-Ca pyroxene and plagioclase, and rims of plagioclase.  
227 Apatite occurs as  $\sim 20 \mu\text{m}$  wide rims on these features, between the core region and plagioclase.  
228 Other euhedral pseudomorphic regions consist of fine-grained intergrowths of low-Ca pyroxene,  
229 diopside, olivine, plagioclase, pigeonite and minor chromite. These regions have thin rims of  
230 diopside, overgrown with plagioclase. Throughout the inclusion, iron metal and troilite are minor  
231 phases, and chromite is present as ubiquitous but finely dispersed sub-micrometer crystals.  
232 Compositions of all phases are essentially identical to those in the host chondrite, and are typical

233 of equilibrated H chondrites, with average compositions as follows: olivine,  $\text{Fa}_{18}$ ; low-Ca  
234 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).

235 **Phosphate mineral compositions.** Merrillite compositions are close to the ideal formula,  
236  $\text{Na}_2(\text{Mg},\text{Fe}^{2+})_2\text{Ca}_{18}(\text{PO}_4)_{14}$ , in all the H chondrites studied (Table 2: individual analyses are given  
237 in Table EA1). Apatite compositions,  $\text{Ca}_5(\text{PO}_4)_3(\text{X})$ , have variable Cl/F ratios and each of the  
238 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  
239 and 7.7 atomic ratio, in Avanhandava, Richardton, Oro Grande (host) and Estacado, respectively  
240 (Table 3: individual analyses are given in Table EA2). We also define a value of  $\text{Cl}\# = \text{Cl}/(\text{Cl}+\text{F})$   
241 (atomic), which has a value of 0.83, 0.91, 0.77, 0.89 for these four chondrites, respectively.  
242 Figure 6a shows anion site occupancy for all apatite analyses in these four non-brecciated H  
243 chondrites. Apatite analyses contain up to 0.15 atoms per formula unit (apfu) “other” than  
244 halogens: we have shown that for LL chondrites, this component is not  $\text{OH}^-$  (Jones et al. 2014),  
245 so we label it as “other” rather than the conventional  $\text{OH}^-$  in this diagram (see also the discussion  
246 of the Zag data below). For each chondrite, there is considerable variability in apatite  
247 compositions around the chondrite mean, for example  $\text{Cl}\#$  values in Richardton vary in the range  
248 0.85 to 0.97. Apatite compositions in the Oro Grande igneous inclusion are very similar to  
249 compositions in the H5 host (Table 3, Table EA2). For all apatite analyses,  $\text{Y}_2\text{O}_3$  and  $\text{Ce}_2\text{O}_3$   
250 contents are close to or below detection limits. These elements are not included in Table 3, but  
251 are given in Table EA2.

252

### 253 **The Zag H3-6 regolith breccia**

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



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

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

278 grains are much larger in H6-1 compared with H4 matrix: many grains are >100  $\mu\text{m}$  across and  
279 the largest grains are  $\sim$ 250  $\mu\text{m}$  across in H6-1.

280 Textures of apatite and merrillite grains in the H4 matrix are illustrated in Fig. 8.  
281 Abundant apatite grains, up to about 100  $\mu\text{m}$  across, are mostly irregular in shape. Most apatite  
282 grains are not associated with metal. One of the apatite grains in Fig. 8c has a vein-like  
283 protuberance into surrounding material. Merrillite occurs as small, mostly <20  $\mu\text{m}$ , rounded or  
284 subhedral grains throughout the H4 lithology (Fig. 8b,c), and can be associated with metal (Fig.  
285 8a).

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

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

296 In a few areas within both H4 matrix and H6-1, merrillite and sometimes apatite grains  
297 are observed along linear features (Fig. 10). These features could either be the result of fluid  
298 flow along fractures, or possibly impact melt veins, as discussed below. In the example in Fig.  
299 10a, merrillite is distributed throughout a sinuous feature that has a high concentration of  
300 plagioclase, and which contains a chromite-plagioclase assemblage surrounded by merrillite

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

309 **Mineral compositions.** Merrillite compositions in Zag are close to the ideal formula,  
310  $\text{Na}_2(\text{Mg,Fe}^{2+})_2\text{Ca}_{18}(\text{PO}_4)_{14}$ , and there are no significant differences between compositions in the  
311 two H6 clasts (Table 2). We did not obtain any merrillite analyses in the H4 lithology. In  
312 contrast, the different lithologies have distinct apatite compositions (Table 3, Fig. 6b). Apatite in  
313 H4 and H6-2 is very chlorine-rich; the most Cl-rich grains, in H4 matrix, contain 6.2 wt% Cl and  
314 only 0.03 wt% F, with  $\text{Cl}\# = 0.99$ . Two analyses in the H6-2 clast have lower Cl/F ratios (Fig.  
315 6b): this appears to reflect compositional heterogeneity within individual apatite grains. In the  
316 H6-1 clast, apatite is considerably more F-rich and shows a wide range of Cl/F ratios. The most  
317 F-rich grain contains 2.9 wt% Cl and 1.9 wt% F,  $\text{Cl}\# = 0.45$ , and the most Cl-rich grain contains  
318 4.7 wt% Cl and 0.8 wt% F,  $\text{Cl}\# = 0.76$ . There are no apparent differences in texture that  
319 distinguish high-F apatite grains. Apatite in the mixed apatite / merrillite grain shown in Fig. 9d  
320 is F-rich, with F = 1.6 to 1.9 wt%,  $\text{Cl}\# = 0.46$  to 0.54. Electron microprobe analyses of apatite  
321 indicate a significant component of “other” anions, up to 0.13 apfu, in addition to the halogens F  
322 and Cl (Fig. 6). In general, compositions with high F contents have higher (F+Cl) anion totals  
323 and a lower “other” component.

324 SIMS analyses of apatite in Zag show very low H<sub>2</sub>O abundances, in the range 350-600  
325 ppm, irrespective of the lithology (Table 4). These are maximum values, because many apatite  
326 grains in Zag have fine fractures (Fig. 8, 9) that likely contain C and OH contaminants. Also, we  
327 measured the background abundance on a merrillite grain in the same session, and obtained a  
328 value of 744 ppm. The high background resulted from strong outgassing of the thin section, and  
329 short residence time in the vacuum. As a result, the H<sub>2</sub>O abundances we obtained for apatite  
330 should be considered to be below the detection limit. Although our measurements cannot be  
331 considered quantitative, we can confidently state that H<sub>2</sub>O abundances are low, and significantly  
332 lower than 1000 ppm. This H<sub>2</sub>O abundance clearly does not entirely account for the amount of  
333 the “other” anion determined from our EPMA analyses: for OH<sup>-</sup>, 0.1 apfu would correspond to  
334 1800 ppm H<sub>2</sub>O.

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

## 339 Discussion

340

### 341 Non-brecciated H chondrites

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

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

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

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

378 **Comparison of H chondrites with L and LL chondrites.** A comparison of the  
379 distribution and occurrence in phosphate minerals among the different OC groups allows us to  
380 consider differences in the metasomatic / metamorphic environment on the three parent bodies.  
381 Abundances of phosphate minerals in petrologic type 4-6 chondrites of the three OC groups are  
382 very similar, mostly totaling between 0.4 – 0.5 vol.% (Table 1; Jones et al. 2014; Lewis and  
383 Jones 2016). In all three groups, total phosphate abundance is low in type 4 compared with types  
384 5 and 6. However, the ratio of apatite / merrillite varies widely and shows no systematic  
385 relationship with either petrologic type or OC group: values for this ratio that we have observed  
386 range from 0.4-1.5 in H chondrites (Table 1), 0.25 – 1.0 in L chondrites (Lewis and Jones 2016)  
387 and 0.1 to 0.5 in LL chondrites (Jones et al. 2014). The wide range in apatite / merrillite ratios  
388 most likely results from the heterogeneity in distribution of apatite on the scale of a thin section.

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

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

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

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

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

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



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

442

### 443 **The Zag H3-6 regolith breccia**

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

448 For the H4 matrix lithology of Zag, both merrillite and apatite consist predominantly of  
449 individual grains, and apatite grains tend to be larger (several tens  $\mu\text{m}$ ) than merrillite grains  
450 (typically  $<20 \mu\text{m}$ ) as well as significantly more abundant (apatite / merrillite ratio of 4.6) (Figs.  
451 7,8). This distribution is markedly different from Avanhandava (H4), in which the apatite /  
452 merrillite ratio is 0.7 (Table 1), apatite consists of fine-grained aggregates that are commonly  
453 associated with merrillite, and merrillite occurs as large grains up to  $200 \mu\text{m}$  (Fig. 1). The apatite  
454 / merrillite ratio in Zag H4 matrix material is the highest of all we have measured in our studies  
455 of type 4-6 ordinary chondrites: all apatite / merrillite ratios are  $<1$  in LL and L chondrites  
456 studied by Jones et al. (2014) and Lewis and Jones (2016). We attribute the high apatite /  
457 merrillite ratio to the fact that the H4 material in Zag is a regolith component that has seen a  
458 more complex history than a typical petrologic type 4 H chondrite. Apatite compositions in the  
459 H4 lithology are mostly very Cl-rich (Fig. 6b), with higher Cl/F ratios than Avanhandava (H4),  
460 up to compositions containing almost no F. Although apatite in the H chondrites in general are

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

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

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

482           **Relationship between apatite and halite.** Halite in Zag, as well as in the related H5  
483 chondrite, Monahans, is demonstrably pre-terrestrial (Zolensky et al. 1999; Whitby et al. 2000;  
484 Rubin et al. 2002; Bridges et al. 2004). Previous studies have shown that halite occurs  
485 predominantly within the dark matrix of these two chondrites, as grains a few hundred microns  
486 across (Zolensky et al. 1999; Whitby et al. 2000; Rubin et al. 2002; Bridges et al. 2004). Halite  
487 in both Zag and Monahans contains low-temperature (<100 °C) aqueous fluid inclusions, and is  
488 considered to result from evaporation of brines (Zolensky et al. 1999; Whitby et al. 2000; Rubin  
489 et al. 2002). In Monahans, halite also contains inclusions of sylvite (KCl) (Zolensky et al. 1999).  
490 Halides in both Zag and Monahans have been dated by K-Ar, Rb-Sr and I-Xe methods (Zolensky  
491 et al. 1999; Bogard et al. 2001; Whitby et al. 2000; Busfield et al. 2004), and have ages  
492 consistent with the timing of metamorphism on the OC parent bodies, with the best interpretation  
493 of I-Xe ages around 4559 Ma (Busfield et al. 2004).

494           Various models have been proposed to account for the origin of halite and the source of  
495 water in the brines. One group of models assumes that halite formed on the H chondrite parent  
496 body: possible sources of water include exogenous water delivered to the parent body by  
497 cometary or asteroidal ice fragments (Zolensky et al. 1999; Bridges et al. 2004), dehydration of  
498 the asteroid interior (Whitby et al. 2000), and impact heating of phyllosilicates (Rubin et al.  
499 2002). Bridges et al. (2004) argued that halite occurs as a clastic component of the breccia and  
500 did not precipitate in situ. More recent work has shown that halite contains a disequilibrium  
501 assemblage of diverse solid inclusions including silicates, phosphates, sulfides, oxides,  
502 macromolecular carbon, and light organic species (Fries et al. 2011; Zolensky et al. 2013). This  
503 assemblage is not obviously derived from an H chondrite parent body. Fries et al. (2011, 2013)  
504 suggest that halite could be derived from a carbonaceous asteroid, such as Ceres, or it could be

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

512         The predominance of halite in dark matrix and the highly Cl-rich compositions of apatite  
513 in matrix suggest that there may be a relationship between the two minerals and that their  
514 formation mechanisms could be coupled. In addition, the high apatite / merrillite ratio suggests a  
515 high fluid / rock ratio, since the overall abundance of phosphates is not unusually high (Table 1).  
516 Fluids would need to have a high Cl/F ratio, and the very low  $\text{H}_2\text{O}$  contents of apatite (Table 4)  
517 would also require such a fluid to be extremely  $\text{H}_2\text{O}$ -poor. Such a briny fluid might also  
518 precipitate halite: this could be a mechanism for an indigenous origin for halite. If halite is  
519 exogenous, one could argue that the halogens required to reset apatite compositions are delivered  
520 by the same mechanism as the halite, and that some of the impact material that included halite  
521 might vaporize and release Cl-rich fluids. An alternative model is that the presence of clastic  
522 halite (either indigenous or exogenous) contributed to secondary production of localized Cl-rich  
523 fluids: halite in Zag (and Monahans) contains fluid-filled fractures, providing evidence for  
524 fracturing and healing, most likely as a result of micrometeorite impacts in the regolith  
525 (Zolensky et al. 1999; Rubin et al. 2002), and this could have released Cl-rich fluids. If apatite  
526 compositions and the presence of halite are coupled, we might also expect halite to occur in H6-  
527 2 material. Unfortunately, we do not know if this is the case, since the thin section was not

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

531         The chlorine isotopic composition of halite in Zag is significantly lighter than that in  
532 typical ordinary chondrite material,  $\delta^{37}\text{Cl} \sim -2\%$  (Bridges et al. 2004; also, water-soluble  
533 chloride analysis in Zag from Sharp et al. 2013), vs. a mean bulk value of  $-0.4\%$  for all ordinary  
534 chondrites (Sharp et al. 2013). Since little isotopic fractionation would be expected between  
535 halite and the brine from which it precipitates, the brine must have been isotopically light.  
536 Bridges et al. (2004) suggested that isotopic fractionation producing an isotopically light fluid  
537 was unlikely to be a parent body process, and that the isotopically light fluid represents a  
538 separate isotopic reservoir in the early solar system. Alternatively, we propose that an  
539 isotopically light fluid could have formed as a result of degassing of metal chlorides in an H-  
540 poor system, the counterpart of the analogous process that led to high  $^{37}\text{Cl}/^{35}\text{Cl}$  ratios measured  
541 in Apollo samples which were attributed to Cl degassing of anhydrous magmas (Sharp et al.  
542 2010). Sharp et al. (2013) also observed isotopically light chlorine in the LL3.6 chondrite  
543 Parnallee, in both the water-soluble fraction ( $\delta^{37}\text{Cl} = -2.65\%$ ), and the structurally-bound  
544 chloride component (mean  $\delta^{37}\text{Cl} = -4.1\%$ , indicating that a mechanism for producing  
545 isotopically light chlorine must be reproducible, although uncommon, on ordinary chondrite  
546 parent bodies.

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

551 2014; McCubbin et al. 2015), in a process of fractional precipitation (similar to fractional  
552 crystallization). For example, halogen-bearing fluids may have been derived from the interior of  
553 the H chondrite parent body, either as a result of solid-state breakdown of halogen-bearing  
554 phases such as chondrule mesostasis at high metamorphic temperatures, or possibly as a result of  
555 degassing of a partial melt in the interior of the body (Elkins-Tanton et al. 2011; Weiss et al  
556 2012). The latter mechanism would be consistent with light chlorine isotopes, if the fluid was H-  
557 poor. As the fluid migrated towards the asteroid surface, it would have interacted with merrillite  
558 or apatite already present in petrologic type 6 material, producing fluor-chlor-apatites (F-Cl-  
559 apatites). Apatite / merrillite intergrowth textures such as those illustrated in Fig. 9d,f are similar  
560 to textures in the unique primitive achondrite GRA 06128/06129 which are interpreted as  
561 replacement reactions that occurred when halogen-rich fluids interacted with previously existing  
562 merrillite grains (Shearer et al. 2011). Since F partitions strongly into apatite (Boyce et al. 2014;  
563 McCubbin et al. 2015), the fluid would become progressively depleted in F and enriched in Cl as  
564 it migrated through the parent body, resulting in more Cl-rich apatite compositions at lower  
565 depths (petrologic type 4). Extreme enrichment in Na and Cl could lead to precipitation of halite  
566 in the final stages. Further insight into this model would be gained by a better understanding of  
567 the relationship between F and H<sub>2</sub>O contents, as well as D/H ratios, in apatite. A complication  
568 for this scenario is that apatite in the H6-2 clast is Cl-rich, not F-rich, so we cannot simply  
569 consider the parent body to have an onion-shell structure in which all H6 material records  
570 alteration by the same fluid. The parent body must have already been brecciated when fluid  
571 evolution occurred, i.e. the parent body would have had a rubble-pile structure, with H6-1  
572 material located towards the centre and H4 and H6-2 material located closer to the surface.

573           If halite is exogenous, a relationship between apatite and halite is not required. An  
574 alternative model for the formation of F-Cl-apatite is that it represents interactions with an F-  
575 bearing fluid generated from localized, impact-related shock melting. Features that appear to be  
576 impact melt veins and pockets occur in H6-1 material (Fig. 10), as well as chromite-plagioclase  
577 assemblages (Fig. 10b) which are interpreted as being produced by shock (Rubin 2003). Rubin et  
578 al. (2002) also describe shock features in H6 material in Zag. We suggest that impact melts could  
579 have degassed volatiles, including F, and that the F-bearing vapor derived from such an event  
580 either interacted with pre-existing apatite or precipitated apatite, resulting in heterogeneous  
581 apatite compositions. F-Cl-apatite compositions would form initially, followed by Cl-rich apatite  
582 as the F inventory of the fluid is rapidly depleted due to the relative partitioning behavior of F  
583 relative to Cl between apatite and fluid.       Alternatively, F-Cl-apatite could have precipitated  
584 from an impact melt that had degassed Cl. Further support for an impact-related scenario is that  
585 F-Cl-apatite is also observed in the L4 host of the L chondrite regolith breccia, Kendleton (Lewis  
586 and Jones 2016), suggesting that F-bearing fluids might be more generally associated with  
587 regolith breccias and surface processing. Since heterogeneous Cl/F ratios of apatite would become  
588 homogenized by diffusion over metamorphic timescales (see Jones et al. 2014), continuous  
589 impact processing would need to extend into the time period when the asteroid was cooling.

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

596 impacts resulted in brecciation and regolith formation, mixing clasts of different lithologies at  
597 the asteroid surface. Impacts into this material produced F-bearing, Cl-rich and H<sub>2</sub>O-poor fluids,  
598 and fractional precipitation of these fluids led to formation of F-Cl-apatite, followed by Cl-rich  
599 apatite, and finally halite. In this scenario, both apatite and halite are retrograde phases that form  
600 during cooling, and halite forms at the lowest temperatures. This model argues against the  
601 interpretation that halite is exogenous. We suggest that the mélange of solid inclusions found in  
602 halite (Fries et al. 2011, Zolensky et al. 2013) may represent fine-grained detritus at the surface  
603 of the H asteroid, derived from regolith formation as well as bombardment by interplanetary dust  
604 and micrometeorites. The D-rich and <sup>16</sup>O-poor cometary signature of the fluid inclusions in  
605 halite (Yurimoto et al. 2014) could be derived from a cometary impactor, as proposed by  
606 Zolensky et al. (1999) and Bridges et al. (2004). Further clarification of the behavior of halogens  
607 in Zag will need detailed observations of a range of lithologies in multiple thin sections, to  
608 investigate relationships between apatite compositions, the presence of halite, and host  
609 petrography in more detail.

### 610 **Implications**

611  
612 The factors affecting the formation and evolution of apatite in ordinary chondrites are  
613 varied and complex, but unraveling them can potentially help to interpret the complex behavior  
614 of fluids on the asteroids that represent chondritic parent bodies. Compositions of apatites are  
615 heterogeneous on a scale of individual chondrites from the same chondrite group, and on a scale  
616 of individual lithologies within brecciated chondrites, indicating that fluid compositions are  
617 highly localized and that fluids were active as the asteroids cooled. This observation is an  
618 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.

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## Tables

Table 1: Modal abundances of phosphate minerals

Chondrite	Pet type	Shock stage <sup>1</sup>	Area mm <sup>2</sup>	% 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

<sup>1</sup>Shock 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 <sub>2</sub> O	2.8	0.0	2.8	0.0	2.7	0.0	2.8	0.0	2.7	0.1	2.8
P <sub>2</sub> O <sub>5</sub>	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: Avandhandava; 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 <sub>2</sub> 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 <sub>2</sub> O <sub>5</sub>	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
∑ 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
∑ 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: Avandhandava; 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 <sub>2</sub> O, ppm SIMS <sup>1</sup>	S, ppm SIMS <sup>1</sup>	F, wt% SIMS <sup>1</sup>	F, wt% EPMA <sup>2</sup>
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

<sup>1</sup>OH, S and F determined by SIMS based on calibrations from apatite standards

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

812 **Figure Captions**

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

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

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

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

836

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

844

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

855

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

861  
862 Fig. 7. Thin section of the Zag H3-6 chondrite studied. a) Optical scan of thin section UNM  
863 1136: circular thin section is 2.5 cm in diameter. H4 matrix material is dark, and two H6 clasts,  
864 H6-1 and H6-2, are light. The small box with solid outline is the region shown in (b) and the  
865 larger box with dashed outline is the region shown in the X-ray maps, (c)-(f). Fine-dashed line  
866 outlines the contact between H4 matrix and H6-1 regions. b) BSE image showing the contact  
867 between regions H6-2 and H4 matrix, which is highlighted with a dashed line. The H6 lithology  
868 is coarse-grained and contains coarse-grained metal and sulfide aggregates (white). Apatite (ap)  
869 occurs as large individual grains (light grey) in both lithologies. c-f) X-ray maps showing  
870 distributions of Fe, S, P and Cl in the region outlined in (a). Sulfide is fine-grained in H4 matrix  
871 and coarser-grained in H6-1. Apatite is concentrated in the H4 matrix material (see Cl map) and  
872 merrillite occurs in both matrix and H6-1 lithologies, but has significantly larger grain size in  
873 H6-1.

874  
875 Fig. 8. BSE images of phosphate grains in the H4 matrix of Zag: ap = apatite, me = merrillite.  
876 The silicate mineral assemblage in all images includes feldspar, olivine, low-Ca pyroxene, and  
877 Ca-rich pyroxene, in order of increasing grey-level. White grains include Fe,Ni metal and troilite  
878 (FeS). a) Several irregular shaped apatite grains and a small merrillite grain associated with

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

882

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

890

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

899

900



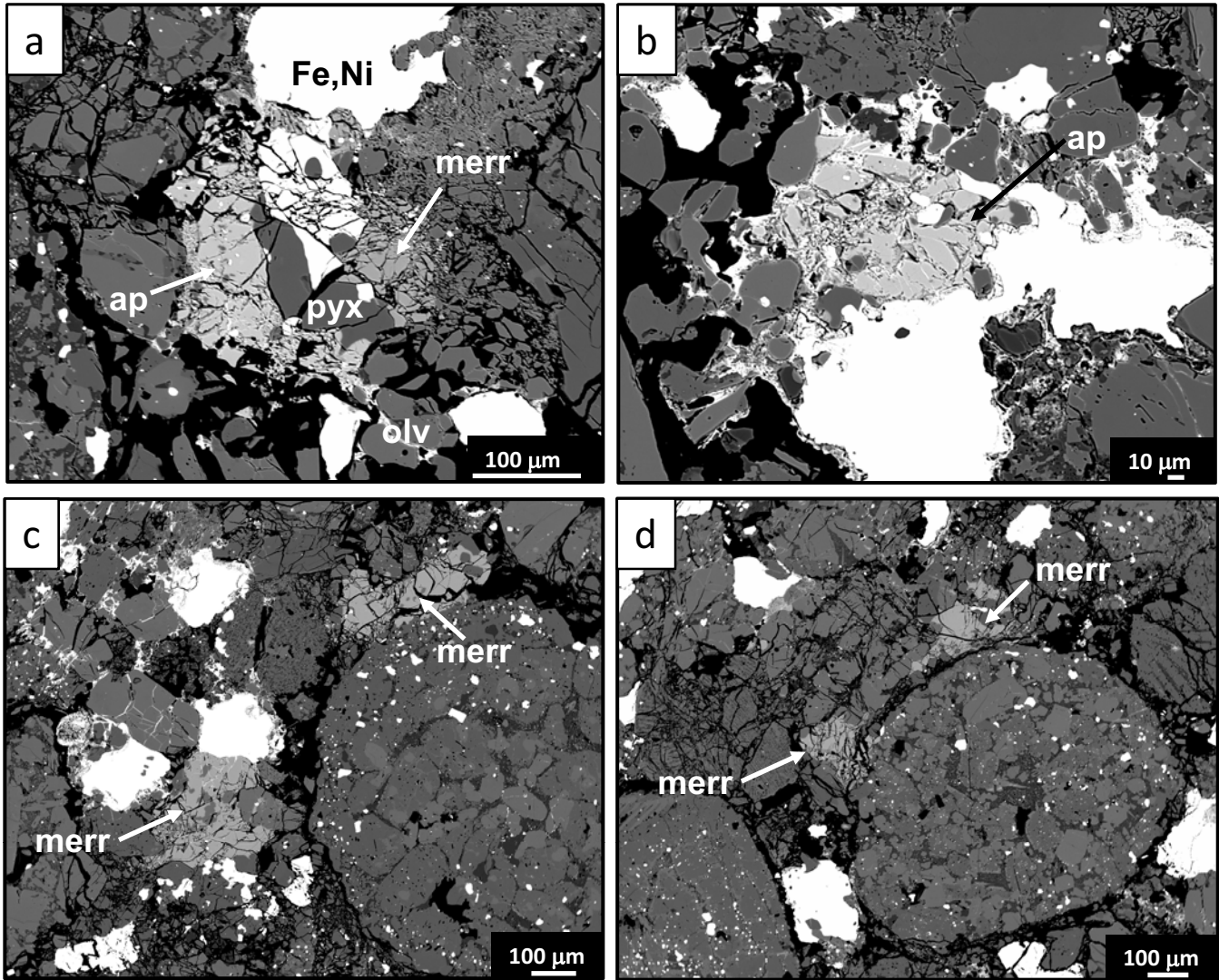


Fig. 1

Avanhandava

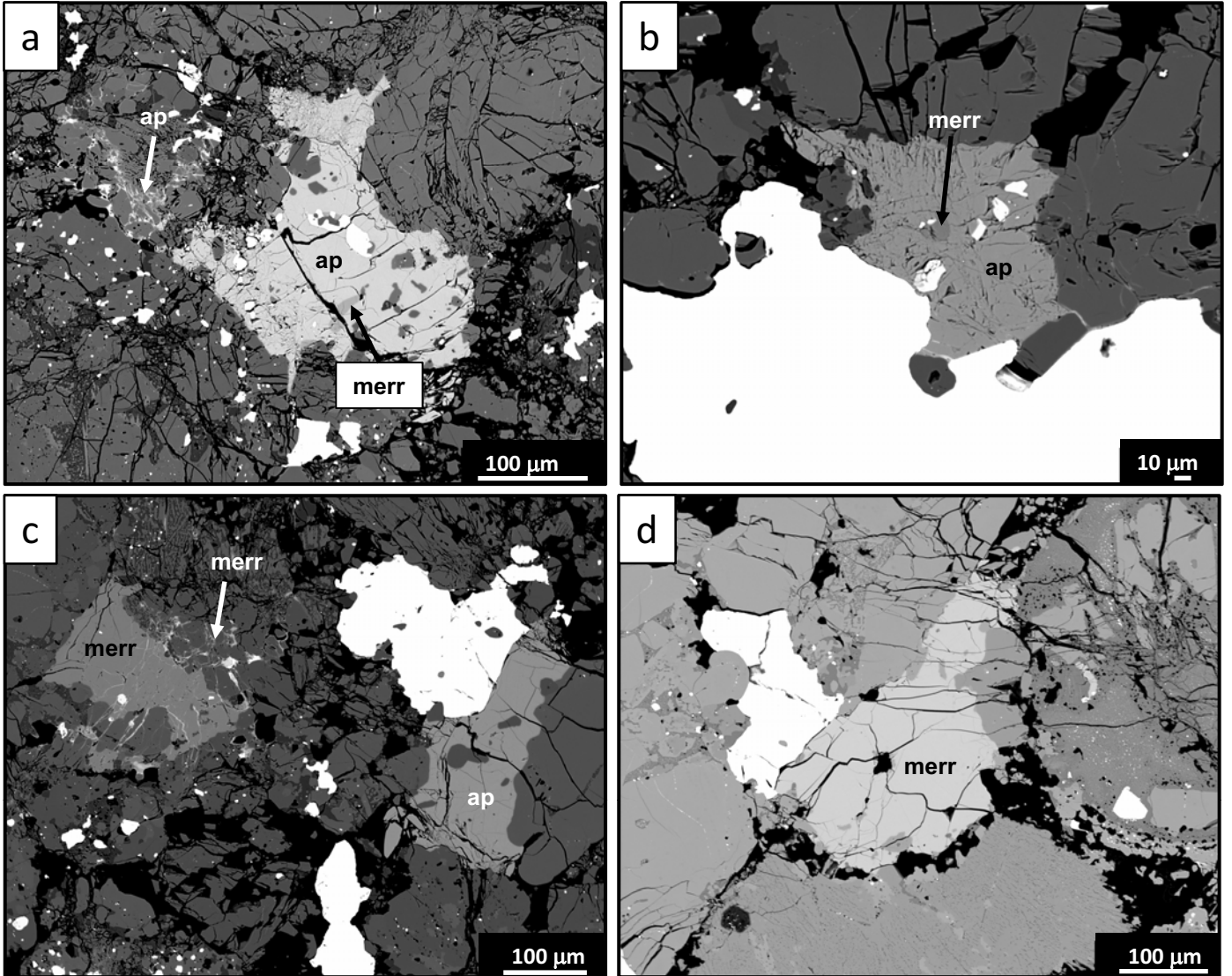


Fig. 2

Richardton

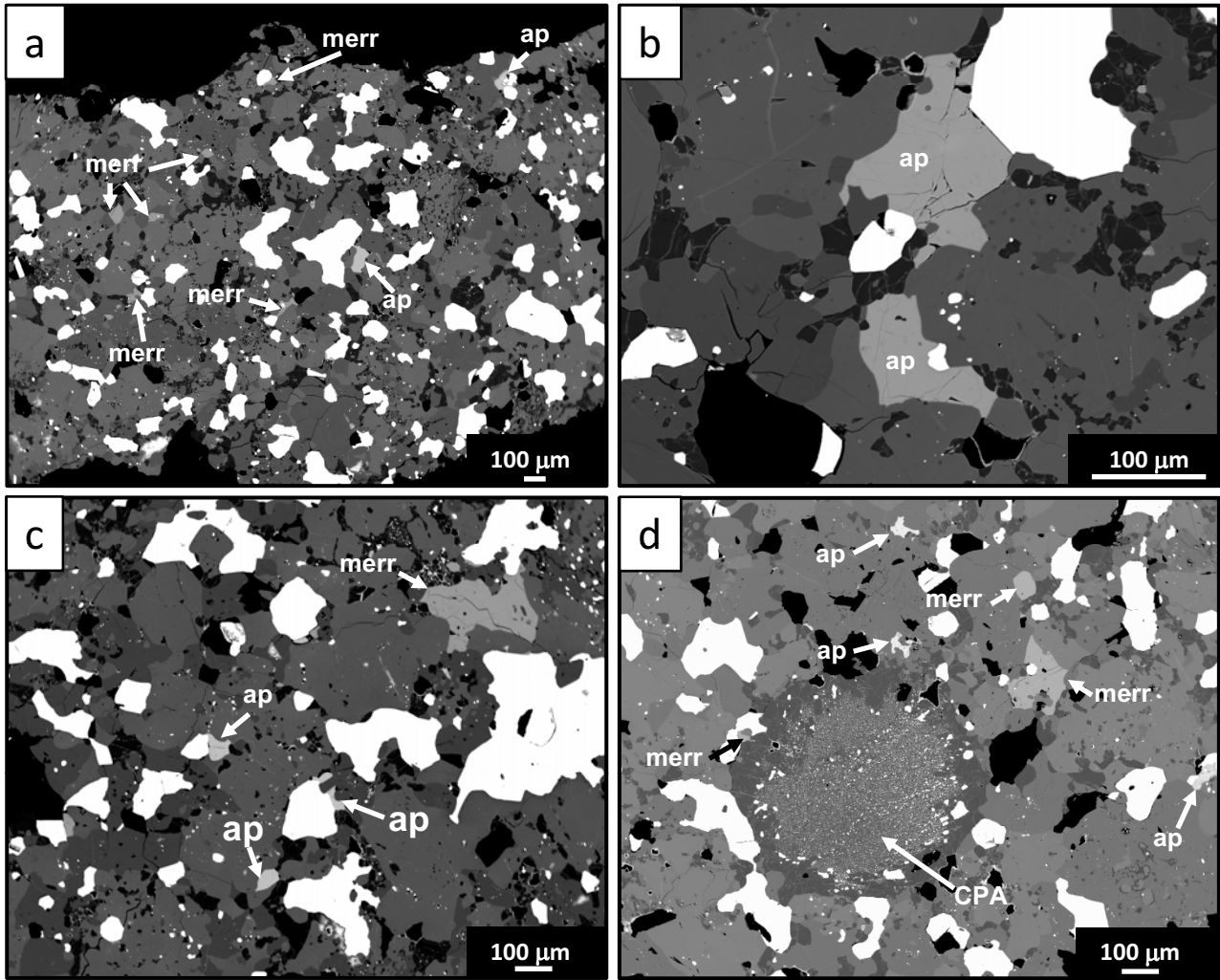


Fig. 3

Estacado

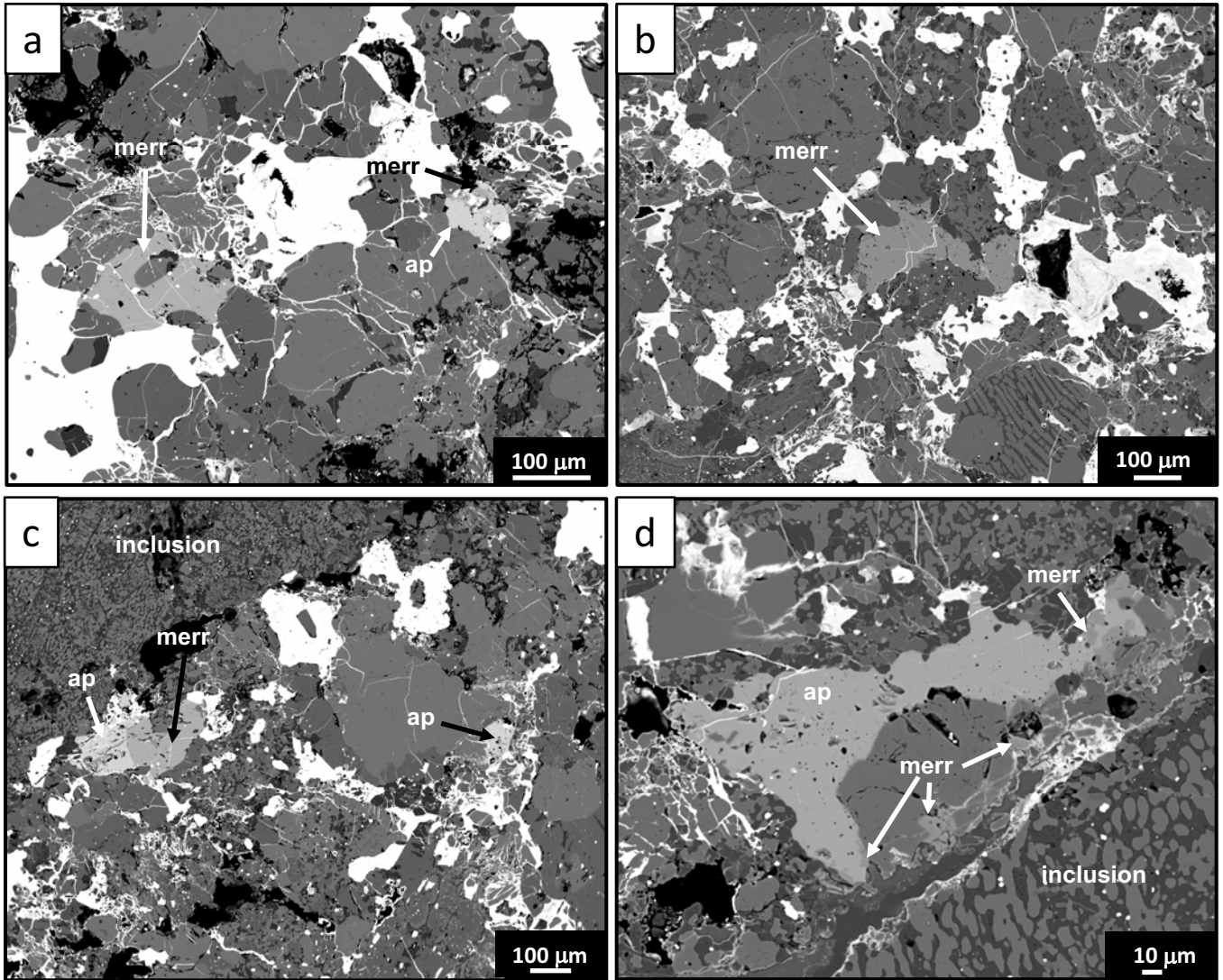


Fig. 4

Oro Grande



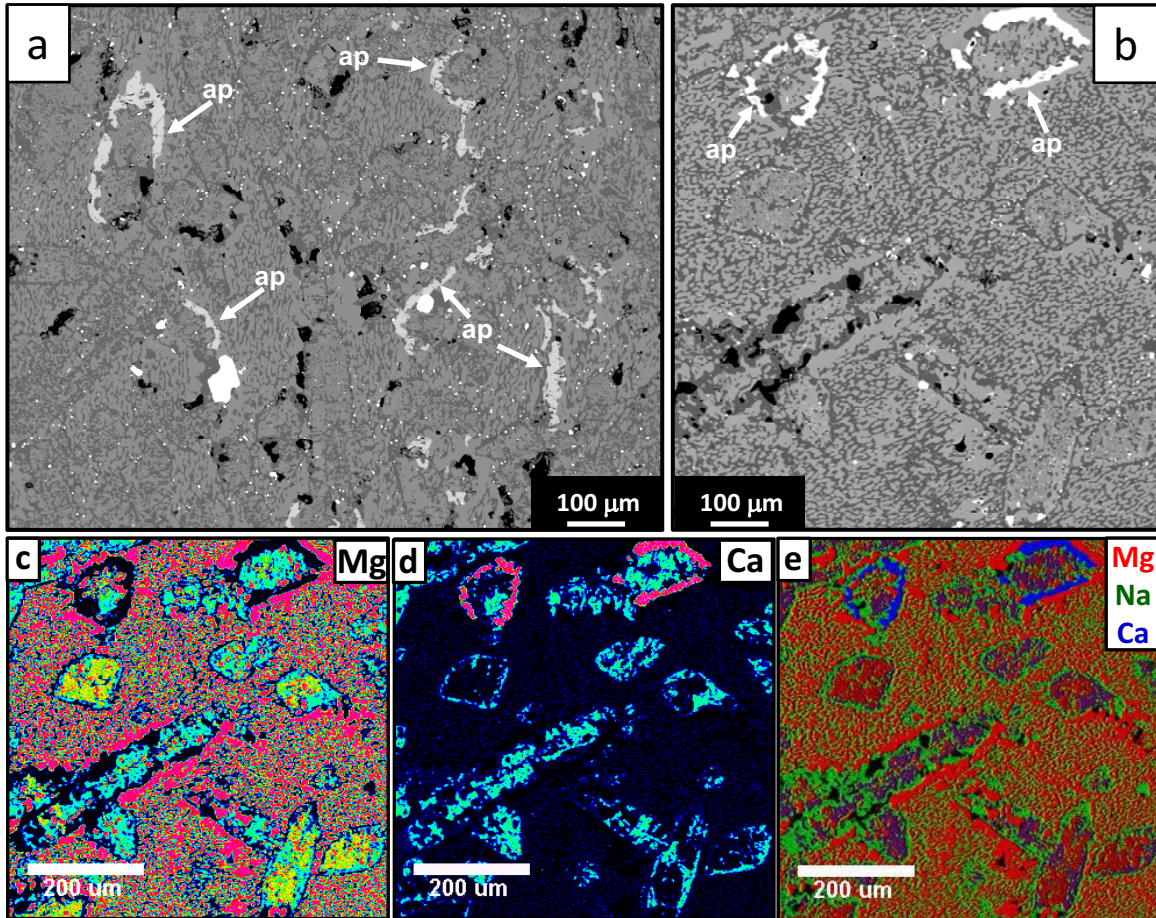


Fig. 5

Oro Grande Inclusion

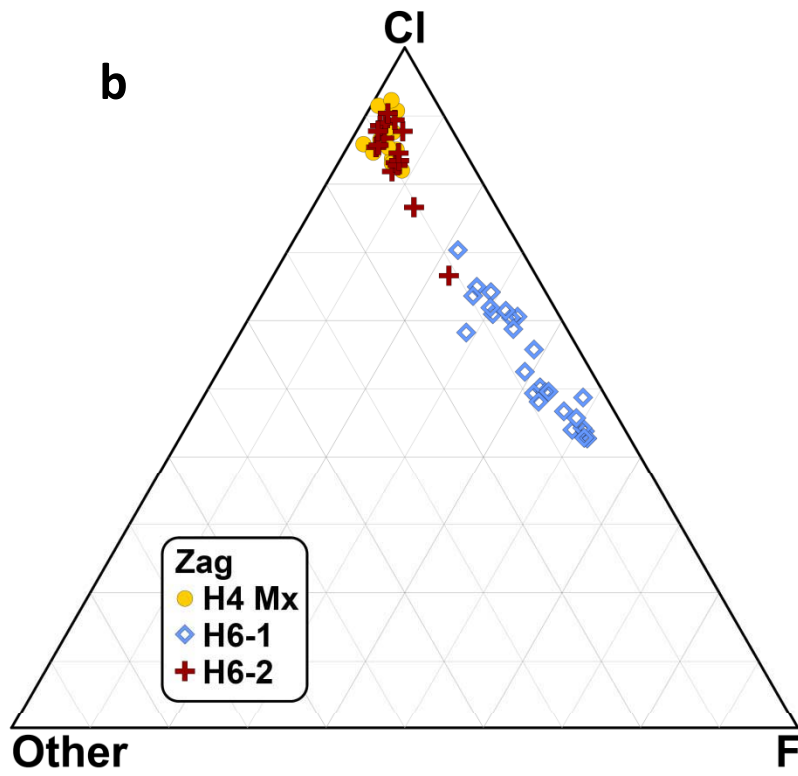
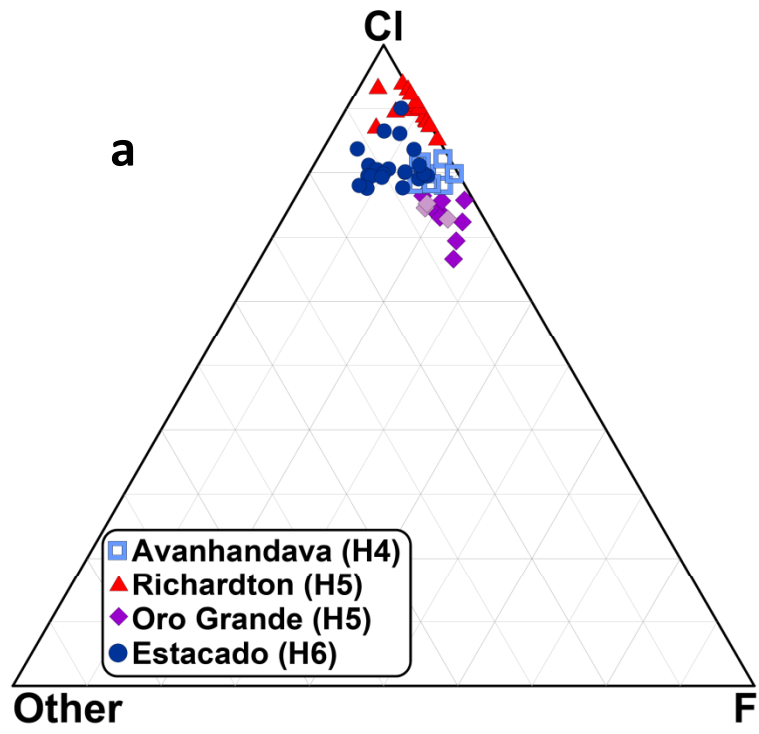


Fig. 6

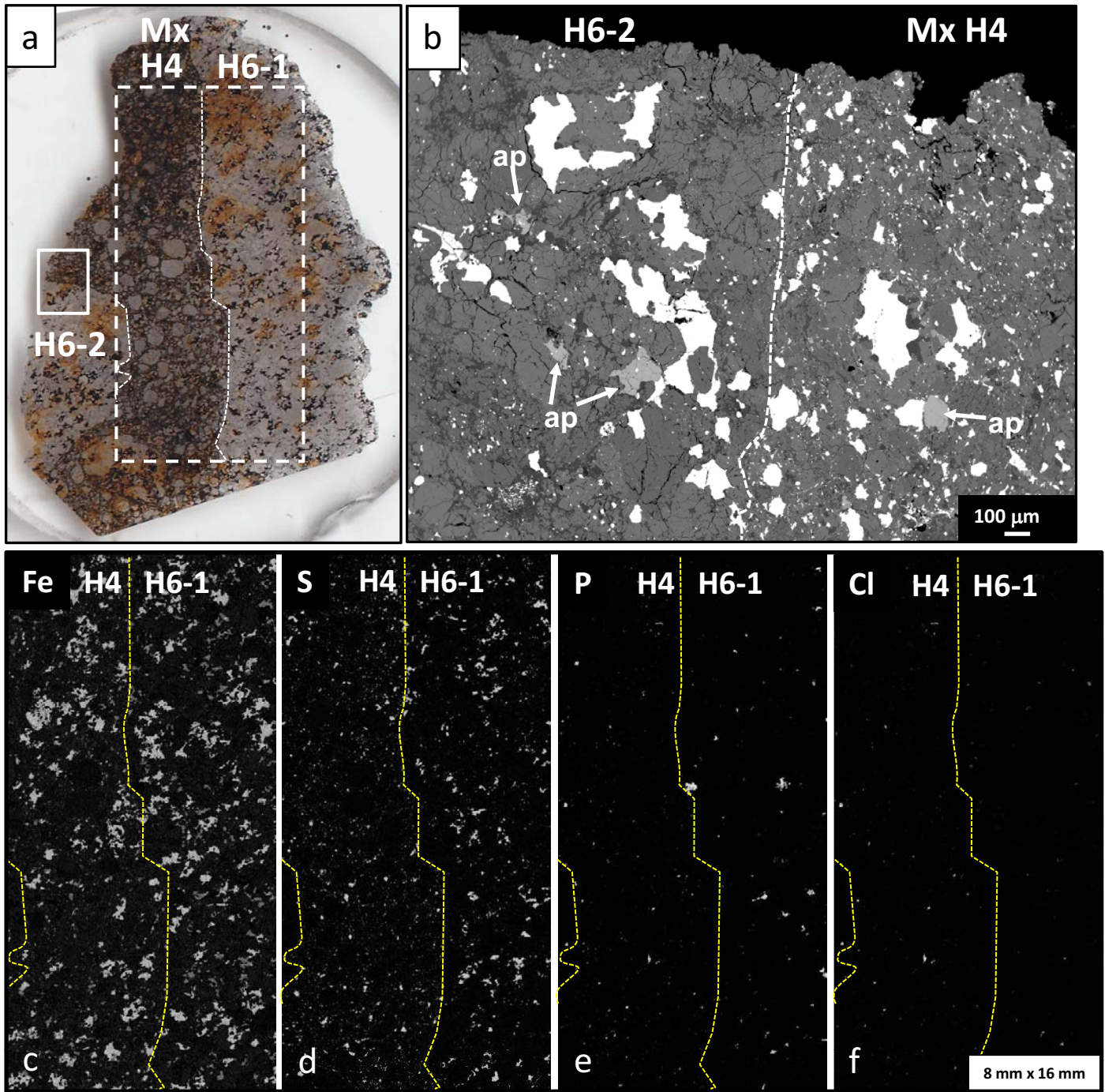


Fig. 7

Zag



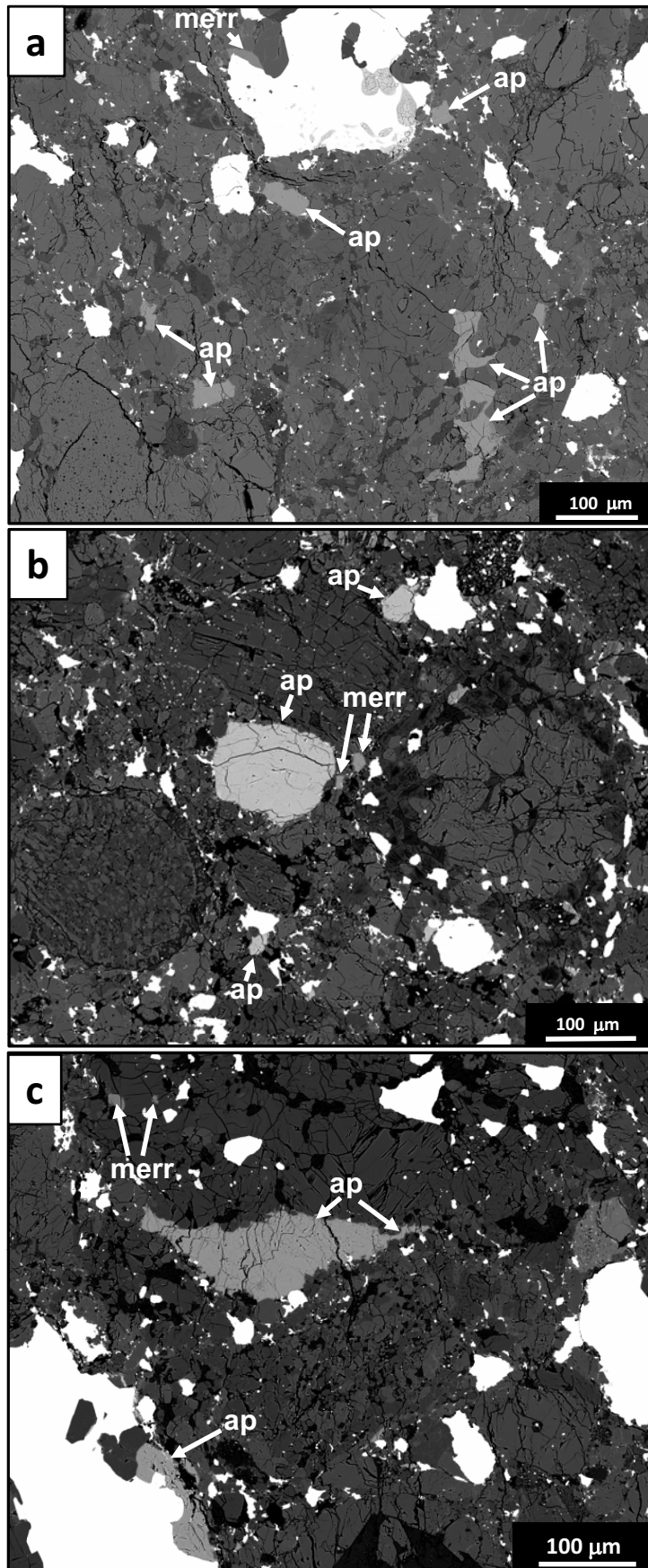


Fig. 8  
Zag: H4 matrix



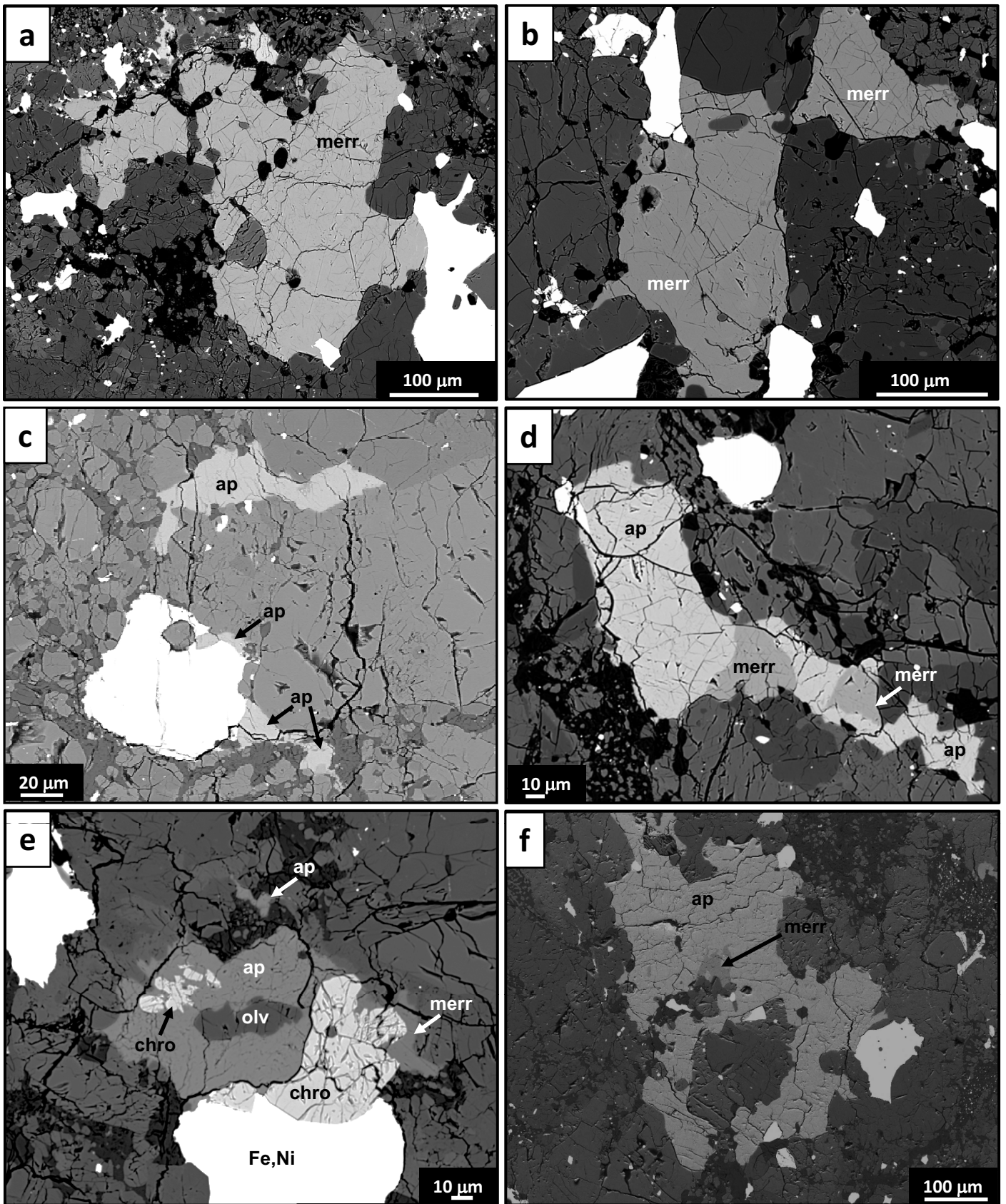


Fig. 9  
Zag: a-e) H6-1; f) H6-2

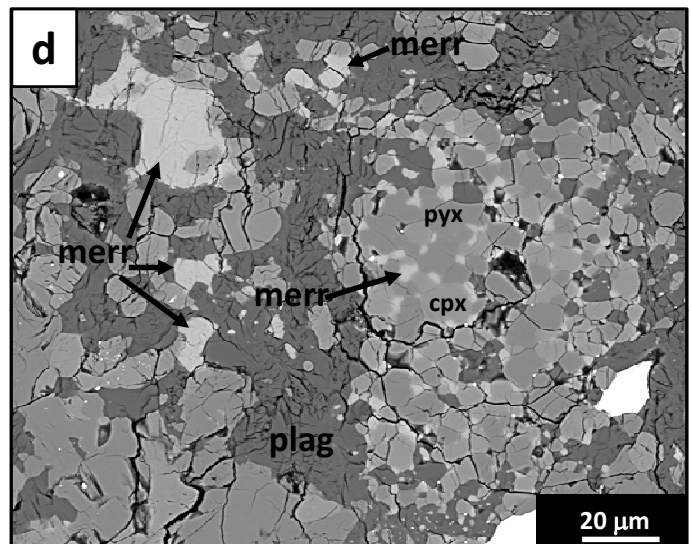
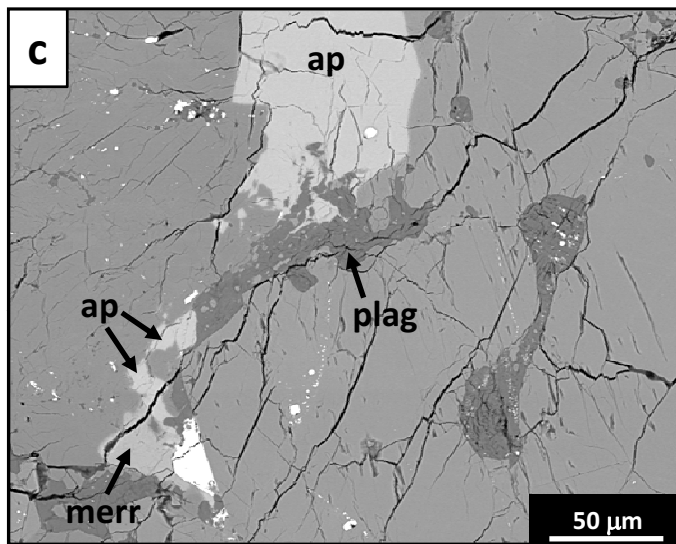
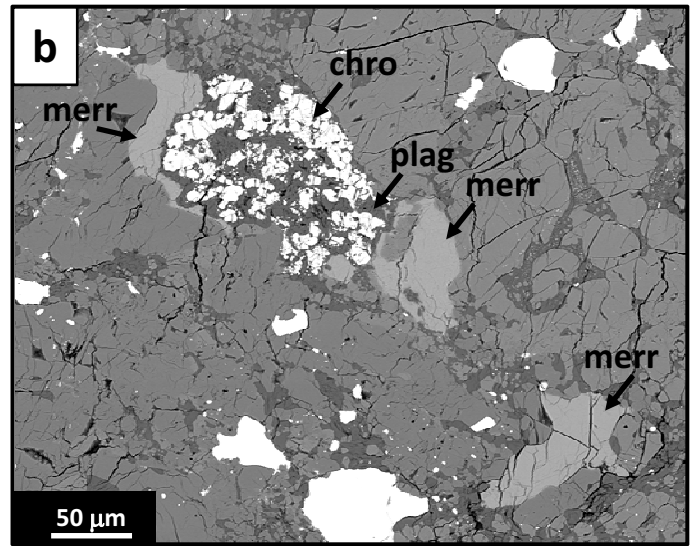
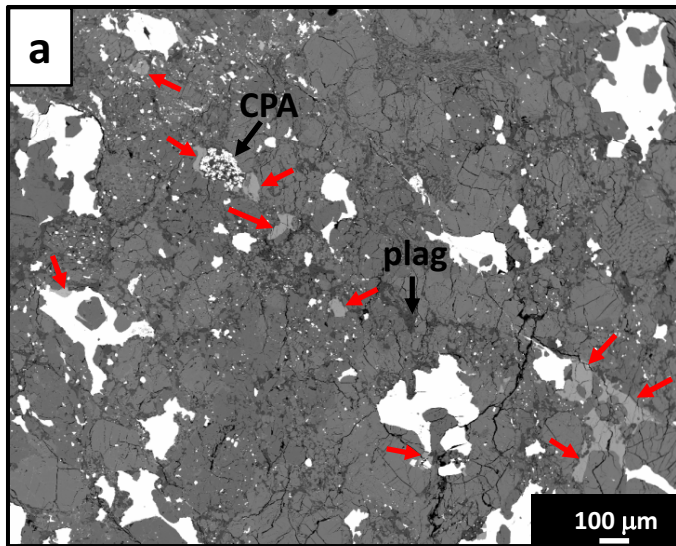


Fig. 10  
Zag: H6-1