Fe,Mg,Mn-bearing phosphates in the GRA 95209 meteorite: Occurrences and mineral chemistry

CHRISTINE FLOSS*

McDonnell Center for the Space Sciences and the Department of Earth and Planetary Sciences, Washington University, St. Louis, Missouri 63130, U.S.A.

ABSTRACT

Two large regions of Fe,Mg,Mn-bearing phosphates, together with metal and various silicate phases, have been observed in the GRA 95209 meteorite (a primitive achondrite belonging to the acapulcoite–lodranite group). Numerous grains of an orthophosphate intermediate in composition between farringtonite and graftonite/sarcopside are found in association with Fe- and Mn-rich chladniite. The chladniite occurs as rims around the Ca-free phosphate (termed Mg-graftonite here) and along boundaries between Fe,Ni metal and silicate grains. Relict metal grains are included within both phosphates. Textures, as well as mineral compositions, suggest formation of the Mg-graftonite by reaction of Fe,Ni metal with surrounding silicates (olivine and orthopyroxene). Chladniite probably formed both through replacement of Mg-graftonite and directly by reaction of metal with silicates, including plagioclase. Apatite appears to have played only a minor role in the formation of these phosphates.

INTRODUCTION

GRA 95209 belongs to a small group of unusual meteorites with primitive compositions but highly equilibrated textures, known as acapulcoites–lodranites. Petrographic and geochemical evidence indicates that these meteorites formed on a common parent body that underwent variable degrees of local partial melting, ranging from low degrees of Fe,Ni metal–FeS cotectic melting in acapulcoites to the formation and removal of silicate partial melts in lodranites (McCoy et al. 1996, 1997a, 1997b). In addition to typical silicate minerals (olivine, ortho- and clino-pyroxene, plagioclase), these meteorites generally contain Fe,Ni metal, troilite, chromite, schreibersite, and the Ca-phosphates, apatite, and merrillite. However, McCoy and Carlson (1998) noted the presence of chladniite in GRA 95209, a mineral that had been observed previously only as a single grain in the Carlton IIICD iron meteorite (McCoy et al. 1994). This paper reports on the occurrence of two distinct Fe,Mg,Mn-bearing phosphates in GRA 95209: (1) an Fe- and Mn-rich form of chladniite and (2) an orthophosphate compositionally intermediate between farringtonite and graftonite/sarcopside (Buchwald 1984; Rubin 1997).

PHOSPHATE OCCURRENCES

GRA 95209 appears to consist of three lithologies, described by McCoy and Carlson (1998): relatively metal-rich matrix, metal-poor regions, and a metal-rich sheet on the surface of the meteorite that extends into the interior (Carlson and McCoy 1998). The thin section analyzed here (,39) is representative of the matrix and consists of equigranular olivine and orthopyroxene, with abundant metal and minor clinopyroxene, plagioclase, and troilite. Rare chromite grains are present, but Ca-phosphates are not observed in this section, although they have been reported in this meteorite (McCoy and Carlson 1998). Of particular interest in the section studied are two large regions of Fe,Mg,Mn-bearing phosphate grains associated with the metal. These areas, termed I (600 × 1100 µm) and II (500 × 700 µm), are shown in Figure 1. Energy dispersive X-ray analyses revealed that each region consists of two distinct phosphates: chladniite, and an Fe,Mg,Mn-rich, Ca-free phosphate, that is compositionally intermediate between farringtonite and graftonite/sarcopside and is hereafter referred to as Mg-graftonite. It should be noted, however, that these designations are based only on mineral chemistry; structural determinations have not been made in this study.

Both areas are associated with silicate minerals (primarily olivine and orthopyroxene, but also minor plagioclase) as well as Fe,Ni metal. Contacts between the minerals are typically smooth and rounded, with many of the silicate grains partially or entirely surrounded by metal and/or phosphate. In addition, many of the silicates contain veins or regions of alteration products together with minor Fe,Ni metal and troilite. Compositionally, these alteration phases resemble orthopyroxene and olivine, but are enriched in FeO and depleted in MgO compared to their counterparts in the meteorite. Many of the alteration phases, especially those associated with olivine, also contain excess Si above that required for stoichiometric mineral compositions. Textures within the phosphates are complex (Fig. 1). Mg-graftonite is found in both regions as individual grains up to ~200 µm in size. Chladniite occurs primarily as thin rims partially surrounding Mg-graftonite or along boundaries between metal and silicate grains. It is commonly,
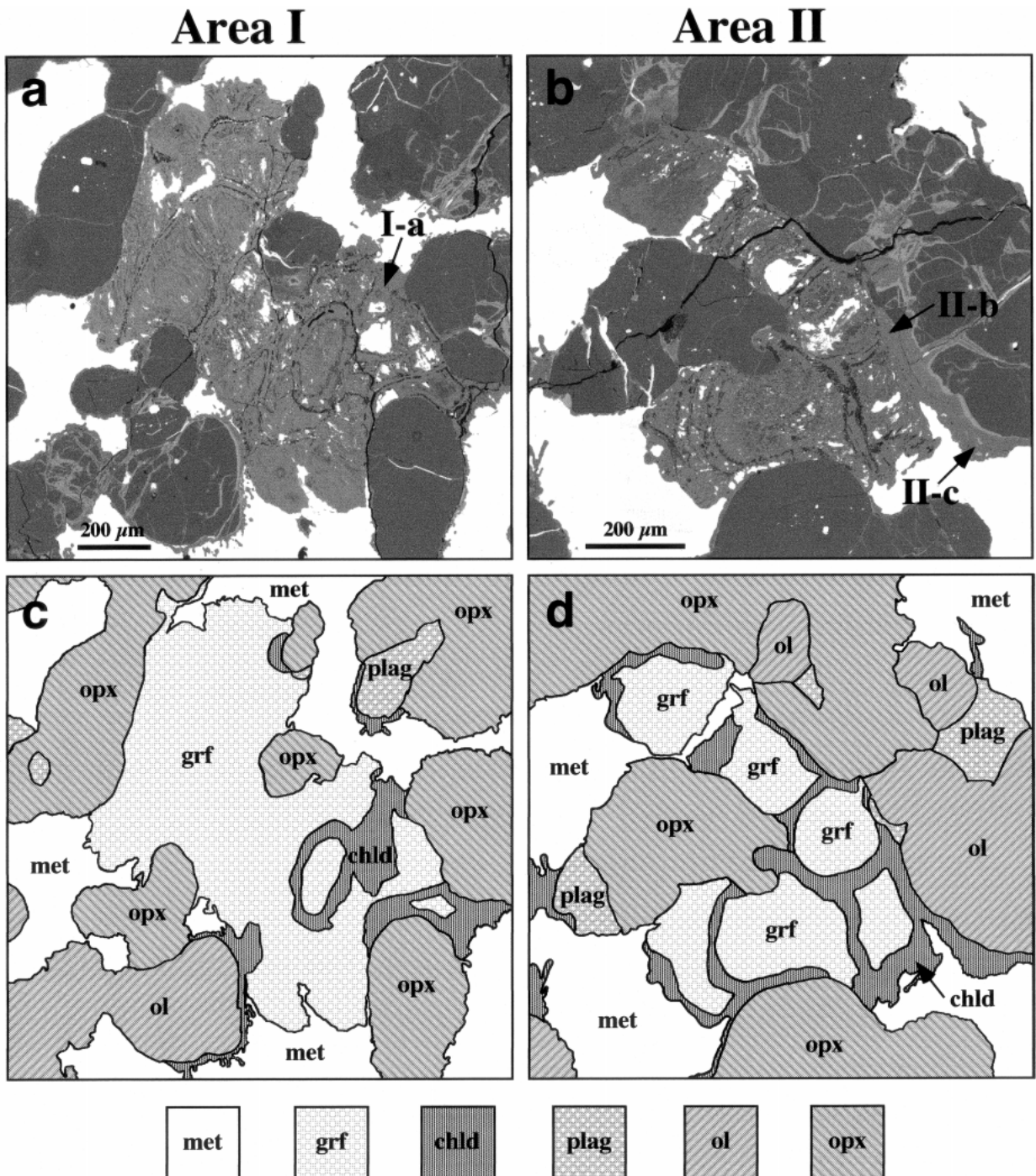

FIGURE 1. BSE images of (**a**) area I and (**b**) area II from GRA 95209,39, showing Fe,Mg,Mn-bearing phosphates (light gray). Each region contains two distinct phosphates: a Ca-free phosphate and chladniite, both with abundant included metal grains. Rounded silicate grains (dark gray) are intersected by veins filled with alteration products and remnant metal and troilite. Simplified cartoons are also shown, (**c**) for area I, and (**d**) for area II, indicating the spatial relationships among the different phases. Captions are as follows: grf: Mg-graftonite; chld: chladniite; opx: orthopyroxene; ol: olivine; met: metal; plag: plagioclase. The designations "I-a", "II-b", and "II-c" indicate the locations of ion microprobe analyses and correspond to the REE abundances in Table 3 and Figure 4.

but not always, associated with nearby or adjacent plagioclase grains. Minor chladniite also is found in the veins intersecting silicate phases, adjacent to remnant metal or troilite. Numerous small metal grains are interspersed throughout the Mg-graftonite and larger chladniite grains, and both phosphates have an uneven, corroded appearance.

MAJOR AND TRACE ELEMENT COMPOSITIONS

Major-element compositions were determined using the Washington University JEOL-733 electron microprobe. Measurements were made at 15 kV accelerating voltage, 20 nA beam current, and a beam diameter of 5 μm. The data were reduced using a modified Armstrong (1988) CITZAF routine. Detection limits are 0.03 wt% for K_2O, Na_2O, CaO, Al_2O_3, and SiO_2; 0.05 wt% for NiO; and 0.09 wt% for TiO_2. The average compositions of chladniite and Mg-graftonite from each region are given in Table 1.

Mg-graftonites in both areas have CaO and Na_2O contents below detection limits; some analyses contain minor amounts of NiO. Calculated mineral formulae on the basis of eight oxygen atoms are listed in Table 2, and correspond to an ideal formula of $(Fe,Mg,Mn)_3(PO_4)_2$. The compositions are intermediate between those of farringtonite, with an ideal formula of $Mg_3(PO_4)_2$, and graftonite/sarcopside [which are compositionally similar but differ in their structures (Olsen and Fredriksson 1966)], with an ideal end-member formula of $Fe_3(PO_4)_2$ (Fig. 2). Chladniite compositions in the two regions (Fig. 3) are distinctly more Fe- and Mn-rich than the chladniite found in the Carlton (IIICD) iron meteorite (McCoy et al. 1994). However, CaO contents are lower than those reported for Carlton chladniite. Calculated mineral formulae are shown in Table 2 and approach the compositions of johnsomervilleite (Fig. 3) reported by Araki and Moore (1981). The phosphates from area I each have higher MnO and FeO contents and lower MgO contents than those from area II. Furthermore, numerous quantitative energy dispersive X-ray analyses indicate that both types of phosphate have uniform compositions within each region; no compositions intermediate between chladniite and Mg-graftonite were observed in either area.

Rare earth element (REE) compositions of the phosphates were measured using a modified Cameca IMS 3f at Washington University. Experimental procedures are similar to those

TABLE 1. Major element compositions (wt%) of phosphates from GRA 95209

| | Area I | | Area II | |
	chladniite	Fe,Mg, Mn-phosphate	chladniite	Fe,Mg, Mn-phosphate
K_2O	b.d.	b.d.	b.d.	0.05 ± 0.04
Na_2O	6.56 ± 0.05	b.d.	6.75 ± 0.10	b.d.
CaO	3.33 ± 0.15	b.d.	3.87 ± 0.09	b.d.
MnO	11.7 ± 0.6	6.81 ± 0.43	8.61 ± 0.60	4.66 ± 0.27
MgO	15.3 ± 1.0	14.9 ± 0.8	19.8 ± 1.1	21.5 ± 1.1
FeO	17.6 ± 0.9	34.1 ± 0.9	14.4 ± 0.8	27.6 ± 1.1
P_2O_5	45.2 ± 0.2	43.8 ± 0.7	46.4 ± 0.4	45.5 ± 1.0
NiO	0.09 ± 0.05	0.26 ± 0.22	0.06 ± 0.07	0.37 ± 0.35
Sum	99.78	99.91	99.89	99.79
N	4	4	4	5

Note: Errors are 1σ standard deviation of the mean; b.d. = below detection; N = no. of analyses. Al_2O_3, SiO_2, and TiO_2 are below detection in all phosphate analyses.
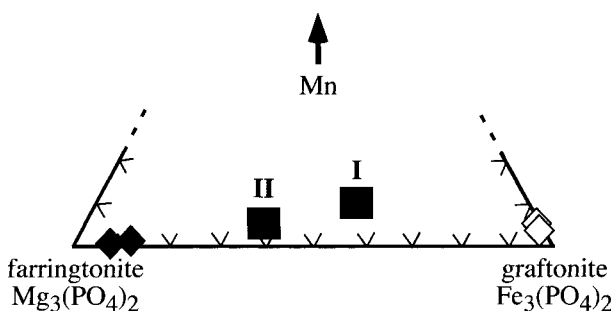

FIGURE 2. Mg,Fe-rich portion of the Mg-Fe-Mn ternary plot showing Ca-free phosphate compositions from areas I and II (squares). Solid and open diamonds depict compositions of farringtonite (Bild 1974; Buseck and Holdsworth 1977) and graftonite/sarcopside (Olsen and Fredriksson 1966), respectively.

used by Floss et al. (1998). REE concentrations were determined using sensitivity factors, relative to Ca, determined from phosphate standards with known REE concentrations (Zinner and Crozaz 1986) and the CaO concentrations listed in Table 1. REE abundances are below detection in the Mg-graftonite, but concentrations and patterns are variable in three chladniite analyses (Table 3, Fig. 4). An analysis from area I is

TABLE 2. Chemical formulae for phosphates from GRA 95209*

magnesian graftonite	this work, area I	$(Fe_{1.53}Mg_{1.19}Mn_{0.31})_{\Sigma=3.03}(P_{0.99}O_4)_2$
	this work, area II	$(Fe_{1.18}Mg_{1.65}Mn_{0.2})_{\Sigma=3.03}(P_{0.99}O_4)_2$
farringtonite	Bild (1974)	$(Fe_{0.32}Mg_{2.55}Mn_{0.04})_{\Sigma=2.91}(P_{1.02}O_4)_2$
	Buseck and Holdsworth (1977)	$(Fe_{0.21}Mg_{2.76}Mn_{0.01})_{\Sigma=2.98}(P_{1.00}O_4)_2$
graftonite	Olsen and Fredriksson (1966)	$(Fe_{2.9}Mg_{0.0}Mn_{0.2})_{\Sigma=3.1}(P_{1.15}O_4)_2$
chladniite	this work, area I	$Na_{1.99}Ca_{0.56}(Fe_{2.31}Mg_{3.57}Mn_{1.55})_{\Sigma=7.43}(P_{0.99}O_4)_6$
	this work, area II	$Na_{1.99}Ca_{0.63}(Fe_{1.83}Mg_{4.49}Mn_{1.11})_{\Sigma=7.43}(P_{0.99}O_4)_6$
	McCoy et al. (1994)	$Na_{1.77}Ca_{0.98}(Fe_{0.26}Mg_{6.96}Mn_{0.04})_{\Sigma=7.26}(P_{0.98}O_4)_6$
johnsomervilleite	Araki and Moore (1981)	$Na_{1.47}Ca_{1.05}(Fe_{3.54}Mg_{3.04}Mn_{0.68})_{\Sigma=7.26}(P_{0.99}O_4)_6$
		$Na_{1.89}Ca_{0.86}(Fe_{2.64}Mg_{2.48}Mn_{1.73})_{\Sigma=6.85}(P_{0.99}O_4)_6$

*Chladniite and johnsomervilleite on the basis of 24 oxygen atoms; graftonite and farringtonite on the basis of 8 oxygen atoms.
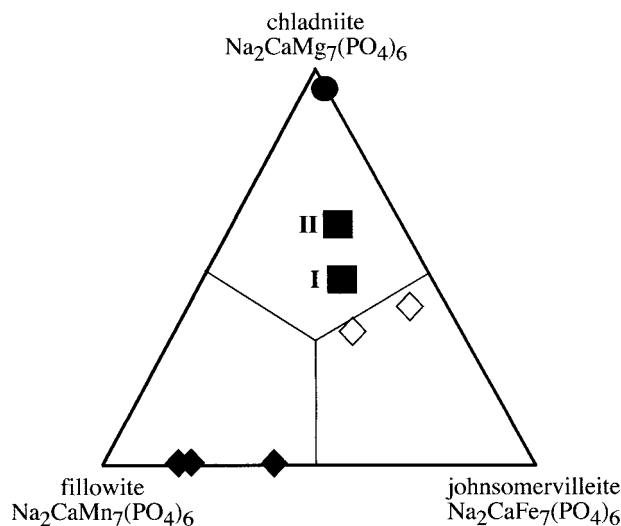
FIGURE 3. Ternary plot showing chladniite compositions from areas I and II (squares). Chladniite from the Carlton iron meteorite (circle) is more Mg-rich (McCoy et al. 1994). Solid and open diamonds show fillowite and johnsomervilleite compositions, respectively, from Araki and Moore (1981).

FIGURE 4. CI chondrite-normalized REE patterns in chladniite. Letters refer to the locations of analyses shown in Figure 1 and the concentrations listed in Table 3.

L(light)REE-enriched (La ~2× CI), with a positive Eu anomaly and H(heavy)REE abundances below detection. Two analyses from area II also differ. One pattern is HREE-enriched, with a Lu abundance of ~100× CI and a chondrite-normalized Lu/La ratio of 5, and has a negative Eu anomaly. The other is relatively flat at ~2× CI for the LREE (La–Eu), but exhibits an offset of the HREE (Gd–Lu), which are present at ~0.5× CI.

DISCUSSION

As noted above, the only occurrence of chladniite previously reported is a single nearly pure $Na_2CaMg_7(PO_4)_6$ grain in a complex silicate-bearing inclusion from the Carlton iron meteorite (McCoy et al. 1994). In contrast, reported analyses of both fillowite and johnsomervilleite, the respective Mn- and Fe-bearing analogues of chladniite, contain significant amounts of Fe and/or Mg (Fig. 3). The occurrence of chladniite in GRA 95209 with significant proportions of Fe and Mn suggests that all three minerals exhibit extensive solid solution. McCoy et al. (1994) noted that both chladniite and johnsomervilleite show excesses of divalent Fe, Mg, and Mn (over 7 per 24 O atoms), and suggested that these cations substitute for monovalent Na, which is depleted relative to the ideal formula. The analyses of chladniite presented here also have excess Fe, Mg, and Mn, but show near stoichiometric abundances of Na. Instead, these cations appear to be substituting for divalent Ca, which is depleted relative to the ideal formula (Table 2). The analyses of fillowite reported by Araki and Moore (1981) suggest that divalent Fe and Mn are substituting for Ca in this mineral as well.

The orthophosphates graftonite/sarcopside and farringtonite (both Ca-free, unlike Ca-bearing terrestrial graftonite) have been reported in iron and pallasite meteorites (Olsen and Fredrikson 1966; Bild 1974; Buchwald 1977; Buseck and Holdsworth 1977) and generally have end-member compositions (Fig. 2).
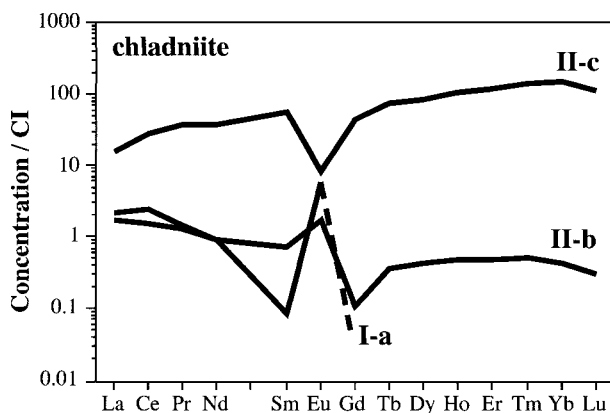
In contrast, the Ca-free phosphates in GRA 95209 are compositionally intermediate between farringtonite and graftonite/sarcopside. This is the first reported occurrence of meteoritic phosphates with these compositions.

GRA 95209 appears to have undergone extensive thermal metamorphism at temperatures that allowed significant melting of Fe,Ni metal and troilite (McCoy and Carlson 1998). Trace-element evidence suggests, furthermore, that some silicate partial melting also may have occurred (Floss 1998). The rounded contacts of silicate–metal grain boundaries, and the presence of silicate inclusions in the metal and between metal and phosphate boundaries, are consistent with this melting scenario. Both textural and compositional evidence suggests growth of the phosphates by reaction and replacement processes, which probably took place during the thermal metamorphic event affecting GRA 95209.

Small metal grains occur throughout both phosphates and small amounts of NiO are present in the analyses of both chladniite and Mg-graftonite, suggesting that they may have formed through replacement of Fe,Ni metal by reaction with surrounding silicate phases. One possible scenario for the formation of the phosphates is suggested by the fact that olivine and orthopyroxene in GRA 95209 have highly magnesian compositions, but associated alteration products in veins intruding the silicates and along phosphate–silicate boundaries are enriched in Fe. As noted above, in some areas these phases also contain excess Si above that required for stoichiometric mineral compositions. Thus, Mg-graftonite may have formed primarily by exchange of Fe for Mg in olivine/orthopyroxene via reactions such as (ignoring Mn and Ni for purposes of simplification):
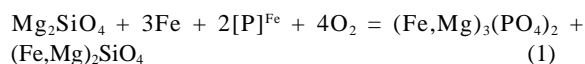
$$Mg_2SiO_4 + 3Fe + 2[P]^{Fe} + 4O_2 = (Fe,Mg)_3(PO_4)_2 + (Fe,Mg)_2SiO_4 \qquad (1)$$

TABLE 3. REE concentrations in chladniite from GRA 95209

	Area I			Area II					
	a (ppb)			b (ppb)			c (ppm)		
La	501	±	29	405	±	30	3.5	±	0.2
Ce	1455	±	93	949	±	65	17	±	1
Pr	127	±	13	116	±	12	3.3	±	0.2
Nd	416	±	22	423	±	23	16.8	±	0.6
Sm	13	±	7	107	±	18	8.0	±	0.5
Eu	324	±	20	96	±	14	0.46	±	0.06
Gd		b.d.		21	±	20	8.9	±	0.7
Tb		b.d.		13	±	5	2.7	±	0.2
Dy		b.d.		104	±	13	20.5	±	0.8
Ho		b.d.		27	±	5	5.8	±	0.4
Er		b.d.		75	±	11	19.1	±	0.7
Tm		b.d.		13	±	4	3.4	±	0.2
Yb		b.d.		68	±	12	24.3	±	1.1
Lu		b.d.		7	±	4	2.7	±	0.3

Note: Errors are 1σ from counting statistics only; b.d. = below detection.

$$(Mg,Ca)_2Si_2O_6 + 3Fe + 2[P]^{Fe} + 4O_2 = (Fe,Mg)_3(PO_4)_2 + (Fe,Mg,Ca)_2Si_2O_6 \qquad (2)$$
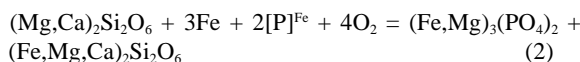
where $[P]^{Fe}$ represents phosphorus dissolved in the Fe,Ni metal. Alternatively, P may come from schreibersite that was oxidized during the heating event. Olsen and Fredriksson (1966) have suggested similar reactions for the formation of farringtonite in iron meteorites. Relict metal grains attest to the fact that this process did not go to completion; the availability of P may well have been the limiting factor. The Mn in these phosphates undoubtedly comes both from Fe,Ni metal and from the silicates, although it is not clear that these sources can fully account for the high Mn abundances observed. Some Mn may also have been available from the oxidation of sulfides, such as troilite, during the heating event.

Chladniite may have formed from Mg-graftonite with addition of Na and Ca from associated plagioclase. Although the presence of relict metal grains in the two phosphates appears to indicate that both formed from Fe,Ni metal, the textural relationship between them suggests that chladniite may have formed after Mg-graftonite. Chladniite commonly occurs as thin rims around Mg-graftonite grains or along the boundaries between metal and Mg-graftonite (Fig. 1). Furthermore, phosphate compositions vary sympathetically: both chladniite and magnesian graftonite from area I are more Fe-rich than their counterparts from area II, implying a common origin. One possible reaction by which chladniite forms from Mg-graftonite is:

$$3(Fe,Mg)_3(PO_4)_2 + 4(Na,Ca)AlSi_3O_8 + 2O_2 = Na_2Ca(Fe,Mg)_7$$
$$(PO_4)_6 + 2CaAl_2Si_2O_8 + (Fe,Mg)_2SiO_4 + 8SiO_2 \qquad (3)$$
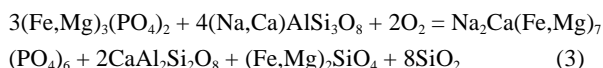
where the SiO_2 is present in the form of excess Si in the alteration products associated with olivine grains, as noted above. Alternatively, the presence of chladniite rims along boundaries between metal and silicates where no Mg-graftonite is present (see Fig. 1), suggests that chladniite may also have formed directly from reaction of Fe,Ni metal with olivine/orthopyroxene and plagioclase, via a combination of reactions 1 and 2 with 3.

REE patterns in the phosphates provide additional clues as to how these phases formed. Mg-graftonites contain virtually no detectable REE, suggesting that their formation probably did not involve the presence of large amounts of REE-bearing phases, such as Ca-phosphates. In contrast, REE patterns and abundances in chladniite are highly variable (Table 3, Fig. 4). Pattern "c" from chladniite in phosphate area II resembles a typical apatite pattern, with the HREE being enriched relative to the LREE and abundances up to ~100× CI for Lu. Although Ca-phosphates have not been observed in this section of GRA 95209, a small amount of apatite may have originally been present in this area and reacted with the silicates and metal to form chladniite. However, the amount of apatite reacting to form chladniite must be limited because other analyses of chladniite exhibit different REE patterns. Pattern "a" from phosphate area I is LREE-enriched with a large positive Eu anomaly, reminiscent of REE patterns typically seen in plagioclase. It is likely that REE were incorporated together with Na and Ca from nearby plagioclase during the formation of this chladniite. Finally, pattern "b" from phosphate region II has approximately chondritic LREE abundances, a small positive Eu anomaly, and HREE abundances that are a factor of 2–3 lower than those of the LREE. Both plagioclase and orthopyroxene may be contributing REE together with Na and Ca in this instance.

Thus, Mg-graftonite seems to have formed in a relatively simple manner from the reaction of metal and/or schreibersite with olivine and orthopyroxene. Chladniite formation is more complex, and may have included formation through replacement of Mg-graftonite or direct formation through reaction of metal and/or schreibersite with silicate phases. Although Ca-phosphate may have been involved in the formation of some chladniite, the REE data suggest it was not a major source of P for the phosphates in these areas.

REFERENCES CITED

Araki, T. and Moore, P.B. (1981) Fillowite, Na$_2$Ca(Mn,Fe)$_7$(PO$_4$)$_6$: its crystal structure. American Mineralogist, 66, 827–842.

Armstrong, J.T. (1988) Quantitative analysis of silicate and oxide minerals: comparison of Monte Carlo, ZAF and Phi-Rho-Z procedures. In D.E. Newbury, Ed., Analysis Microbeam, 239–246 p. San Francisco Press, California.

Bild, R.W. (1974) New occurrences of phosphates in iron meteorites. Contributions to Mineralogy and Petrology, 45, 91–98.

Buchwald, V.F. (1977) The mineralogy of iron meteorites. Philosophical Transactions of the Royal Society of London, A286, 453–491.

———(1984) Phosphate minerals in meteorites and lunar rocks. In J.O. Nriagu and P.B. Moore, Eds., Phosphate Minerals 199–214 p. Springer Verlag, Berlin.

Buseck, P.R. and Holdsworth, E. (1977) Phosphate minerals in pallasite meteorites. Mineralogical Magazine, 41, 91–102.

Carlson, W.D. and McCoy, T.J. (1998) High-resolution x-ray computed tomography of lodranite GRA95209. In Lunar and Planetary Science XXIX, Abstract no. 1541. Lunar and Planetary Institute, Houston (CD-ROM).

Floss, C. (1998) Complexities on the acapulcoite-lodranite parent body. Meteoritics and Planetary Science, 33, A49.

Floss, C., James, O.B., McGee, J.J., and Crozaz, G. (1998) Lunar ferroan anorthosite petrogenesis: clues from trace element distributions in FAN subgroups. Geochimica et Cosmochimica Acta, 62, 1255–1283.

McCoy, T.J. and Carlson, W.D. (1998) Opaque minerals in the GRA 95209 lodranite: a snapshot of metal segregation. In Lunar and Planetary Science XXIX, Abstract no. 1675, Lunar and Planetary Institute, Houston (CD-ROM).

McCoy, T.J., Steele, I.M., Keil, K., Leonard, B.F., and Endress, M. (1994) Chladniite, Na$_2$CaMg$_7$(PO$_4$)$_6$: a new mineral from the Carlton (IIICD) iron meteorite. American Mineralogist, 79, 375–380.

McCoy, T.J., Keil, K., Clayton, R.N., Mayeda, T.K., Bogard, D.D., Garrison, D.H., Huss, G.R., Hutcheon, I.D., and Wieler, R. (1996) A petrologic, chemical, and

isotopic study of Monument Draw and comparison with other acapulcoites: evidence for formation by incipient partial melting. Geochimica et Cosmochimica Acta, 60, 2681–2708.

McCoy, T.J., Keil, K., Clayton, R.N., Mayeda, T.K., Bogard, D.D., Garrison, D.H., and Wieler, R. (1997a) A petrologic and isotopic study of lodranites: evidence for early formation as partial melt residues from heterogeneous precursors. Geochimica et Cosmochimica Acta, 61, 623–637.

McCoy, T.J., Keil, K., Muenow, D.W., and Wilson, L. (1997b) Partial melting and melt migration in the acapulcoite-lodranite parent body. Geochimica et Cosmochimica Acta, 61, 639–650.

Olsen, E. and Fredricksson, K. (1966) Phosphates in iron and pallasite meteorites.

Geochimica et Cosmochimica Acta, 30, 459–470.

Rubin, A.E. (1997) Mineralogy of meteorite groups. Meteoritics and Planetary Science, 32, 231–247.

Zinner, E. and Crozaz, G. (1986) A method for the quantitative measurement of rare earth elements in the ion microprobe. International Journal of Mass Spectrometry and Ionization Processes, 69, 17–38.