Chladniite, Na₂CaMg₇(PO₄)₆: A new mineral from the Carlton (IIICD) iron meteorite

Тімотну Ј. МсСоу

Planetary Geosciences, Department of Geology and Geophysics, School of Ocean and Earth Science and Technology, University of Hawaii at Manoa, Honolulu, Hawaii 96822, U.S.A.

IAN M. STEELE

Department of the Geophysical Sciences, University of Chicago, 5734 S. Ellis Ave., Chicago, Illinois 60637, U.S.A.

KLAUS KEIL

Planetary Geosciences, Hawaii Center for Volcanology, Department of Geology and Geophysics, School of Ocean and Earth Science and Technology, University of Hawaii at Manoa, Honolulu, Hawaii 96822, U.S.A.

B. F. LEONARD

U.S. Geological Survey, Box 25046, M.S. 905, Denver Federal Center, Denver, Colorado 80225, U.S.A.

MAGNUS ENDREB

Institut für Planetologie, Westfälische Wilhelms-Universität, D-4400 Münster, Germany

ABSTRACT

A new mineral, chladniite, $Na_2CaMg_7(PO_4)_6$, occurs as a single grain within a silicatebearing inclusion in the Carlton (IIICD) iron meteorite. It is hexagonal, R_3 , a = 14.967, c = 42.595 Å. It is named for E.F.F. Chladni (1756–1827), who is widely regarded as the founder of the science of meteoritics. Chladniite is colorless and transparent when powdered. In polished section, the mineral is gray, dark, weakly bireflecting, and weakly anisotropic. Cleavage, rarely visible, is rhomboidal in plan. Polishing hardness is less than low-calcium orthopyroxene, but greater than Fe,Ni metal. Reflectance measurements at 589 nm give $R_1 = 5.3\%$, $R_2 = 5.6\%$. Assuming an absorption coefficient k = 0, the calculated refractive indices are $n_1 = 1.60$, $n_2 = 1.62$. Stronger reflections on Gandolfi X-ray film of chladniite are d = 3.694 (0,1,11; 306) s, 3.558 (0,2,10; 0,0,12) m, 2.960 (0,1,14) s, 2.753 (1,3,10) s, 2.500 (3,3,0) m, 2.126 (2,4,10; 2,3,14; 0,2,19) m, and 1.851 (701; 1,5,14; 6,0,12) m. Microprobe analysis gives, in weight percent, Na₂O 6.57, CaO 6.59, MgO 33.5, FeO 2.23, MnO 0.30, SiO₂ 0.59, P₂O₅ 49.9, total 99.68, leading to the empirical formula $Na_{1.77}Ca_{0.98}Si_{0.08}(Mg_{6.96}Fe_{0.26}Mn_{0.04})_{\Sigma=7,26}(P_{0.98}O_4)_6$. Chladniite is the Mg analogue of fillowite and johnsomervilleite, which are Mn- and Fe-dominated end-members, respectively. Chladniite occurs with chlorapatite, olivine, orthopyroxene, plagioclase, schreibersite, Fe,Ni metal, and troilite.

INTRODUCTION

The IIICD iron meteorites are a small group (20 in total; see Wasson et al., 1980, for the definition and membership of group IIICD), three of which contain silicatebearing inclusions rich in troilite, graphite, schreibersite, and phosphates. These inclusions have yielded a number of new and unusual phosphates, and the Na, Ca-, and Mg-rich phosphates brianite and panethite were first described from the IIICD iron meteorite Dayton (Fuchs et al., 1967). During a study of silicate-bearing inclusions in IIICD iron meteorites (McCoy et al., 1993), we have discovered a new naturally occurring phosphate, Na₂CaMg₇(PO₄)₆, which we have named chladniite.

OCCURRENCE

A single grain of chladniite was identified in polished section USNM 2707 (Fig. 1) of the Carlton (IIICD) iron

meteorite, which was found in 1887 near Carlton, Hamilton County, Texas. This section is the holotype for chladniite and is in the meteorite collection of the National Museum of Natural History, Smithsonian Institution, Washington, DC. Chladniite occurs within and near the edge of a silicate-bearing inclusion that is approximately 5×5 mm in size. Chlorapatite is the dominant mineral in the inclusion (69.8 vol%). Olivine, pyroxene, and plagioclase (12.8 vol% total silicates) occur as monoor polymineralic clusters within chlorapatite and along the distal portions of the inclusion. Average compositions of inclusion minerals are $Fa_{7.0\pm0.5}$ (N = 8) for olivine, $Fs_{9.6\pm0.4}$ and $Wo_{1.6\pm0.2}$ (N = 9) for low-calcium orthopyroxene, and An_{5.1±3.0} and Or_{3.7±0.9} (N = 9) for plagioclase (deviations are 1σ of compositional variability, and N values are number of analyses). Schreibersite (3.9 vol%) occurs as millimeter-sized grains, and an intergrowth of



Fig. 1. Reflected light photomicrograph of chladniite and adjacent phases in the Carlton (IIICD) iron meteorite. Chladniite (Ch) occurs as an irregularly shaped grain at the edge of a silicatebearing inclusion. Silicates are olivine (Ol), pyroxene (Px), and plagioclase (Pl). Chlorapatite (Ca) is the dominant phase within the inclusion. Schreibersite (Sc) is in contact with chladniite. Fe,Ni metal (M) encloses the entire assemblage. Scale bar = $200 \ \mu m$.

micrometer-sized Fe,Ni and FeS occurs as millimetersized pockets (12.7 vol%) at the edges of the inclusion. The entire inclusion is rimmed by swathing kamacite. Complete descriptions of other inclusions in Carlton are given by McCoy et al. (1993).

APPEARANCE AND PHYSICAL PROPERTIES

Chladniite occurs as a single grain, which measures $175 \times 975 \ \mu m$ (Fig. 1). The small size of the grain prevented the measurement of many physical properties, such as streak, hardness, and density. Some physical properties were observed in reflected light using a Nikon binocular microscope. The luster is vitreous to resinous. Irregular fractures are filled with hydrated iron oxides of terrestrial origin. These veins give the mineral an orange-brown ap-

pearance; however, observation of areas free of these veins suggests that chladniite is transparent and colorless.

OPTICAL PROPERTIES

The thickness of polished section USNM 2707 prevented the observation of the optical properties of chladniite in transmitted light. The possibility of measuring the optical properties in transmitted light on the small piece extracted for X-ray studies was rejected because of the precious nature of the material, its minute size, and the substantial risk of losing this piece. Optical properties were determined by observations in reflected light on the polished thick section. Experimental conditions for the measurements in vertically incident, vertically reflected plane-polarized light were mineral surface cleaned with methanol; reflectance standard Zeiss NG1, no. 064, R (589 nm) = 4.42%; the effective numeric aperture of objective 0.35, reflector of Smith type; running interference filter Veril S200, band width 12 nm; photomultiplier RCA 1 P28.

Chladniite in polished section is gray, dark (slightly darker than the adjacent orthopyroxene), weakly bireflecting, and weakly anisotropic without polarization colors. Internal reflection is orange-brown and pervasive, the color probably an effect of the associated alteration products. Cleavage, outlined by alteration products in one minute area, is rhomboidal in plan and thus very likely rhombohedral in three dimensions. Polishing hardness is less than that of pyroxene, but greater than that of Fe,Ni metal. Examination of the grain after drilling reveals numerous domains 10-20 µm in diameter that have different optical orientations. At 589 nm, $R_1 = 5.3\%$, $R_2 =$ 5.4% on one area, 5.5 and 5.6% on another. If k = 0(complete transparency), $n_1 = 1.60$ and $n_2 = 1.60$ for the first area; $n_1 = 1.61$ and $n_2 = 1.62$ for the second. The relation is $n = (1 + \sqrt{R})/(1 - \sqrt{R})$, where R is a decimal value. This is a transposition of the familiar Fresnel equation, $R = (n - 1)^2/(n + 1)^2$ (see, for example, Galopin and Henry, 1972, p. 92). Very low bireflectance, com-

TABLE 1. Microprobe analyses (wt%) of phosphates from the IIICD iron meteorites Dayton and Carlton

		Dayton		Carl	ton
	Panethite	Brianite	Whitlockite	Chlorapatite	Chladniite
Na ₂ O	13.8(2)	20.6(3)	2.67(5)	0.23(3)	6.6(1)
MgO	25.0(2)	13.4(1)	3.67(2)	0.45(4)	33.5(2)
P ₂ O ₅	47.6(4)	46.8(3)	45.6(3)	40.5(4)	49.9(4)
CaO	6.28(8)	19.3(1)	48.0(3)	54.7(2)	6.59(2)
FeO	4.9(3)	0.38(4)	0.39(8)	0.25(9)	2.2(2)
MnO	0.48(5)	bd	bd	0.06(1)	0.30(6)
K₂O	1.19(3)	bd	0.04(1)	bd	bd
SiO ₂	0.13(3)	bd	bd	bd	0.59(8)
Cl	0.11(1)	bd	bd	4.18(8)	bd
F	bd	bd	bd	1.64(4)	bd
•	99.49	100.48	100.37	102.01	99.68
O ≡ CI,F	0.02	0.00	0.00	1.63	0.00
Total	99.47	100.48	100.37	100.38	99.68
N	5	5	5	5	5

Note: bd = below detection. Values in parentheses are uncertainties in the last digit and are equal to 1 o compositional variability. N = no. of analyzed points.

Panethite	this work	(Na _{3.92} K _{0.22}) _{z=4.14} Ca _{0.99} (Mg _{5.46} Fe _{0.60} Mn _{0.06}) _{z=6.12} (P _{0.99} O ₄) ₆ Si _{0.02} Cl _{0.03}
Brianite	Fuchs et al. (1967) this work	$Na_{4.32}Ca_{0.67}K_{0.21}(Mg_{5.10}Fe_{0.63}Mn_{0.21})_{5-5.54}(P_{0.99}O_{4})_{6}$ $Na_{5.99}Ca_{3.10}(Mg_{3.00}Fe_{0.05})_{5-3.05}(P_{0.99}O_{4})_{6}$
Whitlockite	Fuchs et al. (1967) this work	ideal, Na ₆ Ca₃Mg₃(PO₄) ₆ Na₀ ₇₉ (Ca _{7 89} Mg₀ ₈₄ Fe₀₀ ₉) _{2=8.76} (P₀₀ ₉₉ O₄) ₆
Chlorapatite	Fuchs et al. (1967) this work	Na _{0.90} (Ca _{7.65} Mg _{0.87} Fe _{0.03}) _{2=6.55} (PO ₄) ₆ Na _{0.08} (Ca _{10.09} Mg _{0.12} Fe _{0.04} Mn _{0.01}) _{2=10.26} (P _{0.99} O ₄) ₆ (Cl _{1.22} F _{0.89}) _{2=2.11}
Chladniite	ideal this work ideal	Ca ₁₀ (PO ₄) ₆ Cl ₂ Na _{1,77} Ca _{0.98} (Mg _{6.96} Fe _{0.26} Mn _{0.04}) _{2-7,26} (P _{0.98} O ₄) ₆ Si _{0.08} Na ₂ CaMg ₇ (PO ₄) ₆

TABLE 2. Chemical formulas (O = 24) for phosphates analyzed in this work compared with data in the literature

bined with the small areas free from internal reflections or alteration products, prevented measurement of the complete dispersion curves.

Absorption coefficient k could not be determined by the two-media method because immersion oil enhanced the internal reflection of the mineral and made the measurement of im R invalid. The assumption that k = 0(complete transparency) is based on the presence of white, transparent particles lining the ragged edges of the hole drilled to remove material for X-ray study. The reproducibility of R in the 5–6% range is no better than $\pm 0.1\%$ absolute. Thus, the birefringence of chladniite is not reliably given by subtracting n_1 from n_2 , the true birefringence is probably closer to 0.01 than 0.02. Imprecision in the measurement of R also leaves the optical symmetry of chladniite in doubt. It is possible that $R_1 = 5.4 \pm 0.1\%$ represents R_0 and $R_2 = 5.5 \pm 0.1\%$ represents R'_{e} , making the mineral uniaxial (+), but the sensitive conoscopic test for the uniaxiality of monoreflecting sections is unsatisfactory, owing to reflection from adjacent weathering veinlets.

There can be no gross error in the calculated values of n_1 and n_2 , for the adjacent pyroxene has at 589 nm, $R_1 = 7.2\%$, $R_2 = 7.4\%$, giving $n_1 = 1.73$, $n_2 = 1.75$. These refractive indices fall within the range 1.723-1.776, birefringence 0.017-0.023, reported in the literature for orthopyroxenes whose composition differs little from that of the pyroxene analyzed in Carlton.

COMPOSITION

The composition of chladniite was determined using a Cameca SX-50 electron microprobe. Conditions of the analyses were a beam 10 μ m in diameter, 10-nA incident current, 15-keV accelerating voltage, and 30-s counting times on peak and background positions. Data were corrected using the manufacturer-supplied PAP ZAF program. Standards used were jadeite for Na, hypersthene for Mg, Marjalahti olivine for Si and Fe, Verma garnet for Mn, orthoclase for Al and K, and apatite for Ca, P, F, and Cl. Minimum detection limits are 0.02 wt% for Cl, Na₂O, and K₂O; 0.03 wt% for MnO, SiO₂, and MgO; 0.04 wt% for FeO; and 0.05 wt% for F. All phosphates analyzed in this study, including chladniite, have Al₂O₃ contents below the detection limit of 0.02 wt%.

The average composition of chladniite, calculated from five analyses, and the 1σ compositional variabilities of

these analyses are given in Table 1. Care was taken to avoid veins of terrestrial weathering products during the analyses. The lack of natural or synthetic microprobe standards of similar composition to chladniite prompted us to analyze four other, previously analyzed phosphates (panethite, brianite, and whitlockite in the Dayton IIICD iron meteorite; chlorapatite in Carlton) to test our analytical method. Our analyses and, hence, calculated mineral formulae (Table 2) differ only slightly from previously published data, thus attesting to the reliability of our analyses.

MINERAL FORMULA

Calculated mineral formulae for all five phosphates analyzed in this work are given in Table 2. Formulae for panethite, brianite, and whitlockite from the Dayton meteorite agree well with those given by Fuchs et al. (1967). The formula for chlorapatite from Carlton agrees with the ideal formula. The ideal formula for chladniite is $Na_2CaMg_7(PO_4)_6$.

The formula of chladniite suggests that it is related to two rare minerals, fillowite and johnsomervilleite. Fillowite has the ideal formula of $Na_2Ca(Mn,Fe)_7(PO_4)_6$ (Ara-



Fig. 2. Ternary plot showing the relationship between chladniite, fillowite, and johnsomervilleite. All have the general formula $Na_2CaX_7(PO_4)_6$, where X is Fe²⁺, Mg²⁺, or Mn²⁺. Data for fillowite (triangles) and johnsomervilleite (circles) are summarized in Araki and Moore (1981).

MCCOY ET AL.: CHLADNIITE, Na₂CaMg₇(PO₄)₆

	Chladniite			Johnsomer JCPDF 33		Fillowite JCPDF 18-516	
I _{meas} (Å)	lest	d _{calc} (Å)	hkl	d (Å)	lo	d (Å)	10
				14.5	5		-
				11.2	50	11.4	35
				8.19	5	8.49	20
				7.20	5 1	7.35	5
				6.75	5		
				6.22	2	6.37	5
				5.60	2 2 2 5	5.69	10
				5.16	2	5.29	10
				4.91	5	5.16	5
				4.48	10	4.57	10
				4.30	10	4.37	5
				4.12	10	4.25	5
3.694		3.710	0,1,11	3.70	70	3.789	40
3.094	5	3.691	306			0.716	5
0.550	_	3.560	0,2,10	3.55	70	3.716 3.640	60
3.558	m	3.550	0,0,12	0.00			
				3.48	5	3.492	10
				3.326	5	3.397	10
	-			3.209	5	3.293	5
						3.234	10
3.085	w	3.095	137	3.109	5	3.172	5
0.000					-	3.029	10
2.960	S	2.962	0,1,14	2.965	70	3.017	70
	_					2.935	10
	1				—	2.896	10
	_				-	2.873	5
				2.843	10	0.014	100
2.753	S	2.747	1,3,10	2.764	100	2.814	10
				2.637	2	2.692	
	-			2.595	2	2.647	10
2.500	m	2.495	330	2.501	40	2.552	60
2.459	w	2.446	241	2.443	10	2.500	5
2.354	w	2.353	336	2.355	10	2.442	10
	· · · ·					2.408	10
				2.310	5	2.390	5
				2.269	2	2.367	10
2.226	w	2.214	0,5,10	2.221	2	2.25	0
		2.212	1,4,12			0.16	20
2.126	m	2.123	2,4,10	2.129	10	2.16	20
		2.127	2,3,14				
		2.119	0,2,19			2.10	5
				2.085	2	2.04	5
				2.045	2	2.04	5
				2.008	2	2.01	
1.973	w	1.965	609	1.971	2		
		1.962	2,4,13	1 0 1 0	0	1.94	5
1.920	w	1.916	2,3,17	1.918	2 20	1.888	40
1.851	m	1.850	701	1.852	20	1.000	
		1.849	1,5,14				
		1.845	6,0,12	1 004	10	1.853	Ę
				1.824	10	1.831	10
	-			1.796	10	1.81	
				1.790	5	1.7404	10
1.715	w			1.675		1.69	5
	: .			1.656	5	1.66	
				1.645	5 5 5 5	1.64	ł
				1.616	5	1.61	1
1.588	-			1.586	5	1.59	;
	w			1.568	5	1.57	-
				1.549	5		-
				1.496	5	1.51	1
1 400				1.490	5	-	
1.492	w			1.460	2	1.46	1
				1.442	8		
	—			1.418	2	1.41	
1.351	w			nd	-	1.39,5; 1.16,15; 1.12,10	
1.551	W			1.0			

TABLE 3. Values for d and approximate intensities of chladniite compared with johnsomervilleite and fillowite

ki and Moore, 1981) and is the Mn analogue of chladniite. Johnsomervilleite is the Fe-dominated analogue, whose formula is given as $Na_{10}Ca_6Mg_{18}(Fe,Mn)_{25}(PO_4)_{36}$ (Livingstone, 1980). All three minerals share the general, simplified formula $Na_2CaX_7(PO_4)_6$, where X is Mg^{2+} , Fe^{2+} , or Mn^{2+} . However, whereas chladniite is close to the Mg end-member, fillowite has appreciable amounts of Fe and johnsomervilleite appreciable amounts of Mg and Mn (Fig. 2). The empirical formulae of both chladniite and johnsomervilleite show excesses of divalent Mg, Fe, and Mn and depletions in Na⁺ relative to the ideal formulae. It appears that in both minerals the divalent cations sub-

X-RAY STUDIES

stitute for the monovalent Na.

Obtaining a sample for X-ray study from the unique occurrence of chladniite in a polished section presented a challenge. After optically selecting an area free from weathering veins 50 μ m in diameter, a Medenbach diamond drill affixed to a Zeiss microscope was used to scribe a shallow trench, leaving a tapered spindle about 50 μ m in diameter at the base and 30 μ m in diameter at the top. Drilling left ~80% of the mineral intact for future studies, including many areas 10–40 μ m in size free from terrestrial weathering veins. This spindle was removed from the sample using a surgical scalpel. The resulting fragment measures about 20 × 30 × 30 μ m and was attached to a glass fiber for X-ray study.

Using a Gandolfi camera 57.28 mm in diameter, Mnfiltered FeK α radiation, and a 6-d exposure, a diffraction pattern was obtained consisting of 17 measurable lines. These data, converted to d values, and their approximate intensities are given in Table 3. For comparison, calculated d values obtained from the cell constants from a single-crystal cell refinement and the diffraction patterns for johnsomervilleite and fillowite (JCPDF 33-1224 and 18-516, respectively) are included in Table 3. Although most matches between the observed and calculated spacings for chladniite are good, those for the weakest diffractions are poorer, probably because of the difficulty of accurate measurement. The apparent absence of strong diffractions with d values greater than about 4 Å in chladniite is due to the broad darkening of the film caused by scattering from the fiber and glue. Indications of many weak peaks in the range of 1.9-1.3 Å are present on the film but could not be accurately measured. The close match among the three diffraction patterns given in Table 3 strongly suggests that the structures are similar.

A four-circle single-crystal study provided both refined cell parameters and a set of diffraction intensities. The cell parameters were obtained by least-squares refinement using 20 centered diffractions, each the average of automatic centering of eight equivalent diffractions. The resulting cell parameters are $a = 14.967 \pm 0.002$, $c = 42.595 \pm 0.004$ Å, $\beta = 120^{\circ}$, cell volume = 8263.6 Å³. The calculated density is 3.01 g/cm³, with Z = 18, as for fillowite. Systematic absences of diffractions are consistent with space group R3, as for fillowite (Araki and Moore, 1981). Precession photographs confirm the symmetry, and no additional diffractions were noted on these precession photographs, indicating that the fragment is not polycrystalline. Based on these data, we suggest that chladniite is isostructural with fillowite, but, because of the small crystal size, a data set suitable for crystal structure refinement has not as yet been obtained. However, the structure determination of Na₄Ca₄Mg₂₁(PO₄)₁₈, a composition close to chladniite, is isostructural with fillowite (Domanskii et al., 1982). The small difference in composition between chladniite, Na₆Ca₃Mg₂₁(PO₄)₁₈, and this compound is considered to be within the recognized compositional uncertainty, as discussed by Araki and Moore (1981) for the case of fillowite.

MINERAL NAME

Chladniite is named for Ernst Florens Friedrich Chladni (1756-1827). Chladni (1794) published a pioneering book that, for the first time, presented strong evidence for an extraterrestrial origin of meteoritic stones and iron meteorites. Prior to that work, it was widely accepted that meteorites formed by condensation of solid matter in clouds. Chladni's work set the stage for the development of the science of meteoritics, from which we have learned much about the origin and evolution of the solar system. Chladni is widely regarded as the father of meteoritics. It is particularly appropriate that a meteoritic mineral be named in his honor, as we mark the bicentennial of the publication of his book. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

ACKNOWLEDGMENTS

This work would not have been possible without the unwavering support of R.S. Clarke, Jr., of the U.S. National Museum, Smithsonian Institution, Washington, DC. We also acknowledge helpful discussions with E.J. Olsen and P.B. Moore of the University of Chicago. Constructive reviews by E.J. Olsen and G.E. Harlow significantly improved the manuscript. This work was supported in part by NASA grants NAG 9-454 and NAGW-3281 (K.K., Principal Investigator) and NAG 9-47 (I.M.S., Principal Investigator). This is Planetary Geosciences publication no. 742 and School of Ocean and Earth Science and Technology publication no. 3063.

REFERENCES CITED

- Araki, T., and Moore, P.B. (1981) Fillowite, Na,Ca(Mn,Fe)²⁺ (PO₄)₆: Its crystal structure. American Mineralogist, 66, 827–842.
- Chladni, E.F.F. (1794) Über den Ursprung der von Pallas gefundenen und anderer ihr ähnlicher Eisenmassen, 63 p. Hartknoch, Riga, Latvia.
- Domanskii, A.I., Smolin, Yu.I., Shepelev, Yu.F., and Majling, J. (1982) Determination of crystal structure of triple magnesium calcium sodium orthophosphate Mg₂₁Ca₄Na₄(PO₄)₁₈. Soviet Physics--Crystallography, 27, 535-537.
- Fuchs, L.H., Olsen, E., and Henderson, E.P. (1967) On the occurrence of brianite and panethite, two new phosphate minerals from the Dayton meteorite. Geochimica et Cosmochimica Acta, 31, 1711–1719.
- Galopin, R., and Henry, N.F.M. (1972) Microscopic study of opaque minerals, 322 p. Heffer, Cambridge, England.

- Livingstone, A. (1980) Johnsomervilleite, a new transition-metal phosphate mineral from the Loch Quoich area, Scotland. Mineralogical Magazine, 43, 833-836.
- McCoy, T.J., Keil, K., Scott, E.R.D., and Haack, H. (1993) Genesis of the IIICD iron meteorites: Evidence from silicate-bearing inclusions. Meteoritics, 28, 552-560.
- Wasson, J.T., Willis, J., Wai, C.M., and Kracher, A. (1980) Origin of iron meteorite groups IAB and IIICD. Zeitschrift f
 ür Naturforschung, 35a, 781-795.

MANUSCRIPT RECEIVED JUNE 28, 1993 MANUSCRIPT ACCEPTED NOVEMBER 24, 1993