sical double-shock methods as were used in the studies reported, interpretations regarding a final role for the caudate are necessarily limited. Answers to such questions of function must await more extensive behavioral studies under conditions in which complex interactions of excitatory and inhibitory responses can take place and give a natural modulation of afferent information (*11*).

STEPHEN S. FOX
JAMES H. O'BRIEN
Mental Health Research Institute
and *Department of Psychology,*
University of Michigan, Ann Arbor

References and Notes

1. S. M. Peacock and R. Hodes, *J. Comp. Neurol.* **94**, 409 (1951).
2. R. G. Heath and R. Hodes, *Trans. Am. Neurol. Assoc.* **77**, 204 (1952); J. Magnes, G. Moruzzi, O. Pompeiano, *Federation Proc.* **20**, 336 (1961).
3. N. H. Buchwald and F. R. Ervin, *Electroencephalog. Clin. Neurophysiol.* **9**, 477 (1957).
4. W. Umbach, *Arch. Psychiat.* **199**, 553 (1959); C. Ajmone-Marson and M. Dillworth, *Electroencephalog. Clin. Neurophysiol.* **3**, suppl., 85 (1953); T. Shimamoto and M. Verzeano, *J. Neurophysiol.* **17**, 278 (1954).
5. J. P. Segundo and X. Machne, *ibid.* **19**, 325 (1956).
6. D. Albe-Fessard, E. Oswald-Cruz, C. E. Rocha-Miranda, *J. Physiol. Paris* **50**, 105 (1958).
7. F. A. Mettler, C. A. Hovde, H. Grundfest, *Federation Proc.* **11**, 107 (1952).
8. C. L. Li, *J. Physiol. London* **131**, 115 (1956).
9. S. S. Fox, D. P. Kimble, M. Lickey, J. O'Brien, in preparation.
10. W. R. Hess, *Diencephalon Autonomic and Extrapyramidal Functions* (Grune, New York, 1954).
11. This research was supported by NSF grant No. G16033.

26 February 1962

Occurrence of Whitlockite in Chondritic Meteorites

Abstract. The first reported occurrence of the tricalcium phosphate mineral, whitlockite, in several chondrites is described. The identification of this mineral and previously reported chlorapatite were made by x-ray diffraction; the results do not confirm the postulated existence of meteoritic merrillite. Some other remarks pertaining to the existence of merrillite are presented.

Specific identification of phosphate minerals in stony meteorites has been neglected, since they usually occur in concentrations of less than 1 percent. The names apatite, chlorapatite, and merrillite have been assigned to material having optical properties approximately characteristic of these minerals, but apparently no x-ray diffraction patterns have been reported.

The meteoritic mineral, merrillite, was reported by Shannon and Larsen to have the formula 3CaO • Na_2O • P_2O_5 (*1*). Their identification was made from chemical analyses on concentrates of the phosphate mineral obtained from kilogram amounts of the New Concord and Allegan chondrites. Since the reported optical properties of merrillite are similar to those of whitlockite, I suspected that these two minerals could be the same.

Recognition of a phosphate mineral in meteorites is ordinarily based on examination of prepared thin rock sections under the petrographic microscope; this limits any additional work on the few grains that may be present. I have found it possible to recognize phosphate grains in etched polished sections of meteorites. Powders scraped from these grains can then be identified by x-ray methods (*2*). Powder patterns of whitlockite have been obtained from the following chondrites: Pantar, Plainview, Allegan, Waconda, Harrisonville, Holbrook, Harleton, New Concord, and Arriba. Chlorapatite patterns have also been obtained from the last three stones and only chlorapatite from the Ness County chondrite.

The terrestrial occurrence of whitlockite was first described by Frondel (*3*) as a late hydrothermal mineral in granite pegmatites from the Palermo quarry in New Hampshire. The analyzed material was essentially $Ca_3(PO_4)_2$ with some magnesium and iron replacing the calcium. The x-ray pattern was distinctly different from that of apatite and was shown to be identical to the low-temperature polymorph of artificial anhydrous tricalcium phosphate, $\beta\,Ca_3(PO_4)_2$.

Powder data (Table 1) for whitlockite from the Palermo pegmatite quarry in New Hampshire (*4*) and from the Allegan chondrite are compared with synthetic $\beta\,Ca_3(PO_4)_2$. The main difference between the natural-occurring mineral and the pure compound is in the interplanar spacings, which undoubtedly reflect the substitution of sodium, magnesium, and iron for calcium. Ando has observed this effect when magnesium substitutes for calcium in synthetic preparations (*5*). A powder pattern from a preparation of composition 0.3 MgO • 2.6 CaO • 0.1 Na_2O • P_2O_5 sintered in air at 1350°C is identical to that of whitlockite. It should be noted that special x-ray techniques are required because the amount of material available from the meteorites is small. Consequently, the relative line intensities, rather than the absolute intensities, should be compared. In this respect the agreement is good, as indicated. The patterns of whitlockite from all meteorites studied are identical in spacings and relative intensities and most probably indicate a uniformity of composition. The chlorapatite patterns from all the meteorites are alike. Calculated cell constants for the New Concord chlorapatite are $a_0 = 9.55 \pm 0.02$ A, $c_0 = 6.81 \pm 0.01$ A, in agreement with results reported for a terrestrial sample (*6*).

The results of a semiquantitative spectroscopic analysis, made with the copper spark method, for microgram amounts of whitlockite from the Allegan, Waconda, and Holbrook chondrites are presented in Table 2. Although phosphorus was detected microchemically, it was not possible to detect it spectroscopically. A blank of reagent grade tricalcium phosphate

Table 1. X-ray powder diffraction data, Norelco powder camera (diameter 11.45 cm), $CuK_{\alpha_1\alpha_2}$, Ni filter. Abbreviations: I, intensity; S, strong; W, weak; F, faint; V, very; M, moderate(ly).

Whitlockite				Synthetic $\beta\,Ca_3(PO_4)_2$*	
Palermo quarry		Allegan chondrite			
d (A)	I	d (A)	I	d (A)	I
8.05	W	8.02	VVW	8.19	M
6.45	MW	6.45	VW	6.51	MS
5.155	M	5.18	W	5.25	S
4.33	VVW	4.355	F	4.40	W
4.04	MW	4.04	VVW	4.11	MS
3.505	VVW			3.83	VW
3.418	M	3.43	W	3.47	S
3.33	VW	3.34	F		
3.175	MS	3.185	W	3.22	VS
3.08	F				
2.98	W	2.99	VVW	3.03	W
2.858	S	2.852	M	2.90	VS
2.73	MW	2.732	VVW	2.83	W
2.688	F	2.688	F	2.73	
2.646	F				
2.583	MS	2.583	W	2.61	VS
2.54	VW	2.525	F	2.54	MW
2.495	VW	2.502	F		
2.383	W	2.392	F	2.42	MW
2.358	F	2.358	F		
2.24	W	2.24	F	2.27	M
2.18	VW	2.178	VVW	2.21	M
2.14	W	2.141	VW	2.17	M
2.082	F			2.09	M
2.04	F	2.048	F		
2.018	W	2.012	F	2.04	M
1.98	VW	1.996	F	2.01	M
1.916	MW	1.917	VW	1.95	S
1.88	W	1.877	dbl.	1.93	S
1.862	W		F		
1.815	F	1.813	F	1.85	M
1.795	F			1.82	M
1.78	F				
1.758	W	1.762	F	1.79	M
1.712	MW	1.710	VW	1.74	VS
1.692	VW	1.695	F	1.70	W
1.67	VW	1.67	F		
1.65	VVW				
1.622	VVW			1.65	MW
1.61	VVW	1.610	F		
1.588	VVW	1.590	F	1.61	M
1.54	MW	1.539	VVW	1.56	S

* Spacings calculated from θ values of Bredig *et al.* (*9*).

Table 2. Spectroscopic analysis of whitlockite in chondrites. In the third column heading, M stands for the metal indicated at the left of the various values.

Metal	Micrograms*	Moles M_xO in $3\ M_xO \cdot P_2O_5$
	Allegan	
Mg	0.06	0.2
Fe	.08	.2
Ca	.8	2.5
Na	.04	.1
	Waconda	
Mg	0.025	0.3
Fe	.02	.1
Ca	.35	2.5
Na	.012	.1
	Holbrook	
Mg	0.07	0.4
Fe	.05	.1
Ca	.7	2.4
Na	.028	.1

* 0.01 μg of silicon was reported in this analysis and is believed to represent a silicate contamination. The silicon, together with amounts of Mg and Fe corresponding to an olivine composition of forsterite$_{75}$, are omitted.

with a calcium content of 0.8 μg, successfully detected, was also below the limit of detection for phosphorus. Assuming the sum of the metal oxides exist in the ratio of 3 moles per mole of P_2O_5, as in isostructural $\beta\ Ca_3(PO_4)_2$, an approximate formula for whitlockite in these meteorites is $0.3\ MgO \cdot 2.5\ CaO \cdot 0.1\ FeO \cdot 0.1\ Na_2O \cdot P_2O_5$. The formula agrees fairly well for that of terrestrial whitlockite from Palermo quarry, except for the Na_2O reported by Frondel, and is consistent with some studies of binary phosphate systems made by Ando. He found that a maximum of about 0.4 mole MgO could substitute for CaO in $\beta\ Ca_3(PO_4)_2$ in the system $3\ MgO \cdot P_2O_5 - 3\ CaO \cdot P_2O_5$. The amount of MgO in substitution depends on the temperature of formation and the rate of cooling in a relatively insensitive manner. In the system $Ca_3(PO_4)_2 - CaNaPO_4$, Ando found that the $\beta\ Ca_3(PO_4)_2$ structure can accommodate 0.1 mole of Na_2O but that samples with 0.3 or 0.2 moles of Na_2O per mole of P_2O_5 yield x-ray diffraction patterns of $\beta\ CaNaPO_4$ and $\beta\ Ca_3(PO_4)_2$. The latter structure does not form when Na_2O is equal to or exceeds 0.4 mole.

In the chondrites studied, whitlockite occurs as xenomorphic grains 0.1 to 0.6 mm in diameter, and is generally found in the silicate matrix of the meteorite. It adjoins the grain edges of silicates, iron-nickel, troilite, ilmenite, magnetite, and chromite. Inclusions of these minerals are common. Only in the Plainview chondrite, was whitlockite observed inside a chondrule. Since the formation of chondrules is not well understood, the significance of this observation is not readily apparent. The optical properties for meteoritic whitlockite are similar to those found by Frondel but generally have slightly smaller refractive indices: $N = 1.624 \pm 0.002$. The birefringence is very weak, about 0.002. The grains are clear and colorless with a vitreous luster. Preliminary surveys made on etched polished sections indicate the mineral occupies from 0.1 to 0.2 percent of the volume of the stone. Harrisonville contains the highest concentration, about 1 percent of the volume.

In those chondrites where whitlockite and chlorapatite coexist, they occur as monomineralic grains dispersed throughout the matrix of the stone. This mutual association is consistent with the phase diagram of the binary system $CaCl_2–Ca_3(PO_4)_2$ (*7*). The separation suggests slow cooling of a melt accompanied by crystal fractionation. On the other hand, both phosphate minerals appear as interstitial fillings in the silicate matrix, are without crystal form, and contain inclusions of most of the other minerals present in the stone.

The evidence presented here suggests that the previously recognized meteoritic mineral merrillite is actually whitlockite. In addition, the formula for merrillite ($3\ CaO \cdot Na_2O \cdot P_2O_5$) is in disagreement with the findings of Franck, Bredig, and Frank (*8*), who report that the only ternary compound found in the system $CaO\text{-}Na_2O\text{-}P_2O_5$ is $2\ CaO \cdot Na_2O \cdot P_2O_5$, which is stable up to 1450°C even in the presence of free CaO.

The high temperature form, $\alpha\ Ca_3(PO_4)_2$, is not known to occur naturally but can exist as a metastable compound at room temperature owing to the sluggish inversion at 1185°C; however, substitution of 0.1 mole of magnesia for lime prevents the β-α transition even up to 1450°C, as shown by Ando. The presence of whitlockite in meteorites cannot be regarded as conclusive evidence for a temperature of formation of less than 1450°C. Additional studies on synthetic preparations of compositions in the neighborhood of meteoritic whitlockite are needed. The stability of the mineral phosphates in contact with the associated minerals at elevated temperatures may affect our ideas concerning the origin of stony meteorites. Phosphorus can be present in both the oxidized and reduced state; reliable identifications of the phosphates can be made with the techniques employed in this study, which yield information on the distribution and occurrence of the phosphorus present. This work will be extended to include an investigation of an extended group of chondrites as well as the achondrites.

LOUIS H. FUCHS
Argonne National Laboratory,
Argonne, Illinois

References and Notes

1. E. V. Shannon and E. S. Larsen, *Am. J. Sci.* (1925), p. 250.
2. Details of this technique are in preparation for publication elsewhere.
3. C. Frondel, *Am. Mineralogist* **26**, 145 (1941).
4. I am indebted to Dr. George Reed for supplying the samples of the meteorites, to John Faris for the spectroscopic data, to Dr. Stanley Siegel and Elizabeth Gebert for the x-ray diffraction results, and to Dr. George Montet for a critical review of the manuscript; all are employees of this laboratory. Special thanks are accorded Prof. Clifford Frondel of Harvard University for supplying a sample of whitlockite from the Palermo pegmatite. While this paper was being revised it was learned from him that studies relating to the identity of merrillite are underway at Harvard. Dr. Brian Mason kindly furnished the sample of the Waconda chondrite. This work was performed under the auspices of the U.S. Atomic Energy Commission.
5. J. Ando, *Bull. Chem. Soc. Japan* **31**, 201 (1958).
6. S. B. Hendricks, M. E. Jefferson, V. M. Mosley, *Z. Krist.* **81**, 355 (1932).
7. R. Nacken, *Zentr. Mineral. Geol.* (1912), p. 545.
8. H. H. Franck, M. A. Bredig, R. Frank, *Z. Anorg. Allgem. Chem.* **230**, 1 (1936).
9. M. A. Bredig, H. H. Franck, H. Füldner, *Z. Elektrochem.* **38**, 160 (1932).

18 April 1962

Electron-Microscope Studies of Braarudosphaera bigelowi and Some Related Coccolithophorids

The Coccolithophoridae are planktonic marine flagellates which produce complex calcite skeletal elements called coccoliths. Fossil coccoliths are currently receiving much study, and have been shown to have great value as index fossils. In many instances the forms are distinctive and large enough to be readily identified in the light microscope. However, study of the smaller species and of detailed structure of the larger forms is best made on carbon replicas of their surfaces in the electron microscope.

Genera of the family Coccolithophoridae having coccoliths made of five calcite units, each a single crystal, are placed in the subfamily Braarudosphae-