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Caryopilite—a member of the friedelite rather than the serpentine group[1]

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Abstract

Electron microprobe analyses of caryopilite show that the octahedral cation to silicon ratio is close to 8:6, consistent with a friedelite structure type, rather than the 9:6 ratio expected for a serpentine type. The powder X-ray diffraction patterns are very similar to those of friedelite but somewhat different from those of serpentine. We propose that caryopilite is friedelite-like rather than a member of the serpentine group as is generally assumed.

Introduction

During a general investigation of the mineralogy and petrology of the metamorphosed manganese deposit at Bald Knob, North Carolina, we have undertaken a study of the sheet silicates. We have previously published an account of a new member of the serpentine group, kellyite, $Mn_4Al_2Si_2Al_2O_{10}(OH)_8$, and have shown that grovesite, which coexists with kellyite, is a member of the chlorite group (Peacor *et al.*, 1974). Two other manganese sheet silicates occur at Bald Knob, manganoan stilpnomelane and a phase having a principal *d* value of 7.2A and resembling descriptions of caryopilite. This note is concerned with the latter phase, which has been considered in the past to have the serpentine structure and a formula approaching $Mn_6Si_4O_{10}(OH)_8$.

There has been considerable confusion regarding the relation between the manganese silicates caryopilite, ectropite, and bementite. Pardee *et al.* (1921) claimed that caryopilite and bementite are the same mineral, whereas Larsen (1925) noted that ectropite and bementite are the same species and that bementite is a member of the serpentine group. Frondel (1955) showed that ectropite and caryopilite give identical powder patterns, and he concluded that they are the same mineral. He noted that the bementite powder pattern is similar to these. In addition, he reported that the caryopilite and ectropite powder patterns "are similar to, but not quite identical with, that of antigorite." Kato (1963) subsequently showed on the basis of electron diffraction studies that bementite consists of two different phases. The first constitutes the bulk of the type Franklin, New Jersey, material and is related to the friedelite group, which consists of the polytypically related phases friedelite, schallerite, and pyrosmalite (Frondel and Bauer, 1953; Takéuchi *et al.*, 1969). The remainder of the Franklin material, and all other bementite, caryopilite, and ectropite, were considered to be identical and to have the serpentine structure. Read and Reay (1971) noted that least-squares refinement of reported lattice parameters for bementite and caryopilite from powder diffraction data resulted in inconsistencies. Huebner (1967) obtained powder diffraction patterns of a number of layered manganese silicates from the Buckeye Mine, California. Several gave patterns characterized by a strong 7A peak and with general features similar to those of either septechlorites or friedelite and manganpyrosmalite. He concluded that "some Buckeye layered silicates, probably the bementites of previous investigators, are closely allied with chlorite, septechlorite, and pyrosmalite mineral groups." It has been generally accepted, however, that caryopilite, ectropite, and most bementite are a single mineral to be referred to as caryopilite and that this material has a serpentine-like crystal structure. Only the bementite from Franklin and some of that from the Buckeye Mine are recognized to perhaps possess a friedelite-like crystal structure.

While examining manganese silicates from Bald Knob, we obtained preliminary microprobe analyses

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of caryopilites giving a formula with Mn to Si ratio of about 5:4, far less than the 6:4 required by the ideal serpentine formula. Our material gave a typical caryopilite powder diffraction pattern (Table 1). Kato (1963) had previously noted a deficiency of Mn in some caryopilites, but we could not understand how such large deficiencies as we observed could be consistent with a serpentine structure. We therefore obtained a number of caryopilites including material from the type locality from Pajsberg, Sweden, as well as bementites from Franklin. We present data which indicates that most of this material has a friedelite-like structure type.

Specimen descriptions

The Bald Knob material occurs in a thin, discontinuous vein consisting of manganoan calcite, tirodite, rhodonite, jacobsite, and caryopilite, cutting across a gneissic rock composed of manganoan calcite, manganese equivalents of humites, and pyroxenoids. Other mineral assemblages from this deposit have been described by Simmons *et al.* (1974), Peacor *et al.* (1974), and Winter *et al.* (in preparation). The Bald Knob caryopilite consists of tan, 3 to 4 mm rosettes and has a barely detectable micaceous cleavage. Caryopilite from Långban, Sweden, coexists with gonyerite (a Mn-chlorite) in a type specimen of the latter. In a specimen from Pajsberg, the caryopilite type locality, caryopilite occurs with calcite as a replacement of bladed rhodonite crystals. The Franklin bementite is from NMNH sample number R4897. It has a distinctly layered appearance with layers up to about 5 mm thick consisting principally of a cream-colored foliated phase.

Table 1. Powder diffraction data for caryopilite and friedelite

Caryopilite[1]		Caryopilite[2]		Friedelite[3]		Friedelite[4]		Friedelite[5]	
d	I	d	I	d	I	d	I	d	I
				11.4	10	11.3	5		
7.24	90	7.17	100	7.17	90	7.2	100	7.08	100
3.64	80	3.61	45	3.60	70	3.60	75	3.57	40
2.78	70	2.76	20	3.88	60	2.88	30	2.85	17
2.49	100	2.48	40	2.56	100	2.55	50	2.53	31
2.35	10	2.35	5	2.408	30	2.41	10	2.39	8
2.08	50	2.08	6	2.115	50	2.12	20	2.10	13
1.954	30	1.951	5	1.974	20	1.98	5	1.96	4
1.724	10	1.722	6	1.731	30	1.73	10	1.72	6
				1.676	60	1.68	10	1.67	9
1.617	20	1.618	9	1.632	20	1.64	10	1.62	7
				1.625	10	1.63	10		
1.578	10	1.565	8						
				1.620	10			1.51	2

[1] Caryopilite from Långban. Debye-Scherrer pattern. Specimen LB-1 from University of Michigan Collection, labelled as "ectropite".

[2] Caryopilite from Pajsberg. Diffractometer pattern. Specimen PB-1 collected and donated by P. B. Moore.

[3] Friedelite from Franklin, N.J. Debye-Scherrer pattern. Data from Frondel and Bauer, 1953.

[4] Friedelite from Franklin, N.J. Diffractometer pattern. Data from Huebner, 1967.

[5] Friedelite from Franklin, N.J. Diffractometer pattern. Specimen from University of Michigan Collection.

Chemical analyses

Electron microprobe analyses were obtained on the three caryopilites, one gonyerite, and three Franklin bementites described above, using standards and procedures as described in Brown *et al.* (1978). Results are reported in Table 2. The totals for the caryopilite analyses are near 98%, but we associate the low total with difficulty in obtaining well-polished surfaces. In our experience poor polish leads to somewhat low totals but does not change the stoichiometry significantly. The analyses were normalized to six (Si + Al) and ten (OH,Cl,F) in order to compare the compositions with that of an ideal friedelite, $Mn_8Si_6O_{15}(OH)_{10}$. The valence of Mn and Fe is assumed to be 2+ in accordance with ordinary friedelites and serpentines; the mol % OH and wt % H_2O are calculated from assumed stoichiometry. Bulk analyses reported in Larsen (1925) show little Fe^{3+} when the oxidation state of caryopilite was directly measured. While some variation on the order of ±4% from the ideal octahedral occupancy for friedelite is found, the friedelite formula fits the data for caryopilite far better than a serpentine formula would. Only the Franklin bementite deviates substantially from the 8:6 ratio, deviating even further from the serpentine ratio and approaching 7:6. The significance of the chemistry of Franklin bementite is uncertain. The analyses could possibly represent a multiphase mixture, although the analyzed areas appear optically to be single phase. Alternatively, the structure of the Franklin bementite may well be different from that of either friedelites or serpentines.

The chemistry of caryopilite and gonyerite show some consistent similarities and differences. All analyses show little Al, F, or Cl. Caryopilites show 75–90% Mn occupancy in the octahedral sites whereas

Table 2. Electron microprobe analytical data for caryopilite, bementite, and gonyerite

	LB-1a Långban Caryopilite	BK-1 Bald Knob Caryopilite	PB-1 Pajsberg Caryopilite	R4897a Franklin Bementite	R4897b Franklin Bementite	R4897c Franklin Bementite	LB-1b Långban Gonyerite
SiO_2	35.94	36.35	36.13	38.87	38.32	38.24	32.35
Al_2O_3	0.13	0.21	<.02	0.10	1.38	1.10	0.57
FeO	0.81	1.09	11.21	5.21	6.77	6.36	7.30
MnO	49.07	42.39	38.56	39.78	25.34	33.24	35.50
MgO	2.79	8.01	2.82	3.80	13.09	8.76	10.26
CaO	0.10	0.03	0.03	<.03	0.05	<.03	0.08
ZnO	0.13	<.03	<.03	2.54	5.00	4.79	0.47
H_2O*	9.01	9.22	9.00	9.67	9.90	9.80	9.89
F_2	<.05	<.05	<.05	<.05	0.11	0.11	<.05
Cl_2	0.03	0.14	0.12	0.09	0.14	0.14	0.05
sum**	98.01	97.44	98.08	100.06	100.10	102.44	96.47
Si	5.98	5.96	6.00	5.98	5.76	5.80	3.92
Al	0.02	0.04	<.01	0.02	0.24	0.20	0.08
Fe	0.11	0.15	1.58	0.67	0.86	0.81	0.74
Mn	6.91	5.89	5.42	5.18	3.23	4.26	3.64
Mg	0.69	1.96	0.70	0.87	2.93	1.98	1.85
Ca	0.02	<.01	<.01	<.01	0.01	<.01	0.01
Zn	0.02	<.01	<.01	0.29	0.56	0.54	0.04
OH*	9.99	9.96	9.96	9.96	9.92	9.91	7.99
F	<.01	<.01	0.01	<.01	0.05	0.04	<.01
Cl	0.01	0.04	0.03	0.03	0.03	0.05	0.01
sum R^{2+}	7.75	8.00	7.70	7.01	7.59	7.59	6.28

* Calculated from assumed stoichiometry
** Total corrected for O = F, Cl

gonyerites have less than 60% Mn occupancy with significant Mg. The Franklin bementites have significant Zn, averaging about 5% of the total R^{2+}. This compares well with levels of Zn in bementites reported by Larsen (1925). The Mn in gonyerite may well be restricted to <60% of the octahedral sites unless substantial Al^{IV} and Al^{VI} can relieve some of the mismatch between brucite and talc layers as in idealized grovesite—$Mn_5Al_2Si_3O_{10}(OH)_8$.

X-ray diffraction analysis

Diffractometer or Debye-Scherrer patterns were obtained on several samples identified as caryopilite. They were all very similar and matched patterns given in the literature (*e.g.* Read and Reay, 1971). The samples were those described above plus a sample labeled ectropite from Långban, obtained from the University of Michigan collections. Table 1 contains data from two of the patterns. These patterns are characterized by two intense reflections with *d* values of approximately 7.2 and 3.6A. These are presumably first- and second-order reflections from planes parallel to the silicate layers of the crystal structure. Because serpentine patterns are characterized by similar reflections, they previously provided evidence for the conclusion that the serpentine and caryopilite crystal structures are similar, and that caryopilite is a septechlorite.

Friedelite also is a layer silicate, however, with a powder pattern which also is characterized by two prominent basal reflections having *d* values of approximately 7.2 and 3.6A. The friedelite structure is characterized by alternating octahedral and tetrahedral layers, as is true for septechlorites, but with tetrahedral layers in which tetrahedron vertices of alternate six-rings are directed up and down (Takéuchi *et al.*, 1969). Data from powder patterns of three friedelites are listed in Table 1. It is clear that the friedelite patterns are all very similar, differing principally in relative peak intensities. Such variations are in part due to preferred orientation differences caused by the perfect cleavage, especially with respect to diffractometer *vs.* Debye-Scherrer patterns.

The most striking feature of the data of Table 1 is the marked similarity in the caryopilite and friedelite patterns. The principal differences are in the common occurrence of a weak 11.3A peak in friedelite, and in a series of peaks with *d* values of approximately 1.6A. In addition, the peaks of caryopilite are significantly broadened. These differences are repeated in all patterns of these two phases, including those of Franklin friedelites made available by Mr. Pete Dunn of the Smithsonian Institution. Friedelite is one of a series of three polytypically-related phases, the others being schallerite and pyrosmalite (Frondel and Bauer, 1953; Takéuchi *et al.*, 1969). Differences in the powder patterns of caryopilite and friedelite could be expected on the basis of differences in stacking sequences. The breadth of diffractions of caryopilite and the distorted and clay-like single-crystal size of crystallites suggest that it is a phase in the friedelite group with a disordered layer sequence, equivalent perhaps to a $1M_d$ mica.

One unusual sample from the University of Michigan Mineralogical Collection was labelled friedelite from Franklin, New Jersey. It was massive with a reddish-yellow color and closely resembled some friedelite. The diffraction pattern was clearly that of a serpentine-like mineral with a third-order basal reflection which is typically broad and asymmetric, and several other features in contrast to the patterns of caryopilite. The identification was confirmed with an electron microprobe analysis, which gave a Mg/Si ratio of approximately 3/2 typical of serpentine, and a minor amount of Mn replacing Mg. This provides further evidence for the differences in diffraction patterns of caryopilite and serpentine.

The bementite from Franklin gave powder patterns which were somewhat variable, but always characterized by a doublet at approximately 3.5A. The material is quite heterogeneous when viewed with a binocular microscope, and consists of a predominant cream-colored foliated phase resembling pyrophyllite with smaller amounts of a finely intergrown yellow crystalline phase. X-ray patterns of very small amounts of material of slightly different appearance showed that they consist of manganoan calcite, a chlorite, and a 7A phase. Microprobe analyses revealed a phase with a 7:6 octahedral cation to Si ratio as well as a 7.6:6 phase resembling caryopilite chemically although it also had higher Mg similar to gonyerite. Local intergrowths and veins of calcite were also identified on the microprobe. Bulk analyses of this bementite are thus certainly subject to contamination by more than one additional phase. Some grains seemed suitable for single-crystal diffraction, and a few poorly-resolved, weak and diffuse reflections were observed by the Weissenberg method. The best of these showed a sequence of 001 reflections with only two other strong peaks, symmetrical with respect to 002. This explains the presence of the doublet at that position in the powder pattern, but we are unable to further interpret the single-crystal results with any certainty. Because we have no positive identification of the analyzed phases in the Franklin bementite sample, we have continued to identify them simply as bementite.

Conclusions

Wicks and Whittaker (1974), in a survey of the crystal chemistry of the serpentine minerals, noted that the amount of Mn in the octahedral layers should be limited, because its substitution would create strain involving the mismatch in dimensions of the octahedral and tetrahedral layers. The mismatch in the serpentine-group mineral kellyite is compensated by substitution of Al, but there is negligible Al in caryopilites. We believe that the data which we have presented here show conclusively that caryopilite is not a member of the serpentine group. There are no data to suggest that a pure manganese analogue [$Mn_6Si_4O_{10}(OH)_8$] of serpentine exists, and crystal-chemical arguments suggest that such a phase would be relatively unstable and should not occur under equilibrium conditions. All chemical and structural data indicate that caryopilite belongs to the friedelite group and may be represented as a member with a disordered stacking sequence. Caryopilite samples which yield materials suitable for single-crystal X-ray diffraction are necessary for more complete structural studies.

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References

Brown, P., E. J. Essene and D. R. Peacor (1978) The mineralogy and petrology of manganese-rich rocks from St. Marcel, Piedmont, Italy. *Contrib. Mineral. Petrol., 67*, 227–232.

Frondel, C. (1955) Two chlorites: gonyerite and melanolite. *Am. Mineral., 40*, 1090–1094.

——— and L. H. Bauer (1953) Manganpyrosmalite and its polymorphic relation to friedelite and schallerite. *Am. Mineral., 38*, 755–760.

Huebner, J. S. (1967) *Stability Relations of Minerals in the System Mn-Si-C-O.* Ph.D. Thesis, Geology Department, The Johns Hopkins University, Baltimore, Maryland.

Kato, T. (1963) New data on the so-called bementite. *J. Japan Assoc. Mineral. Petrol. Econ. Geol., 49,* 93–103.

Larsen, E. S. (1925) The identity of ectropite and bementite. *Am. Mineral., 10,* 418–421.

Pardee, J. T., E. S. Larsen and G. Steiger (1921) Bementite and neotocite from western Washington, with conclusions as to the identity of bementite and caryopilite. *J. Wash. Acad. Sci., 11,* 25–32.

Peacor, D. R., E. J. Essene and W. B. Simmons (1974) Mineralogy of the manganese silicate deposit at Bald Knob, Alleghany Co., N.C. *Geol. Soc. Am. Abstracts with Programs, 6*:4, 386.

——— and W. C. Bigelow (1974) Kellyite, a new Mn–Al member of the serpentine group from Bald Knob, North Carolina, and new data on grovesite. *Am. Mineral., 59,* 1153–1156.

Read, P. B. and A. Reay (1971) Akatoreite, a new manganese silicate from eastern Otago, New Zealand. *Am. Mineral., 56,* 416–426.

Takéuchi, Y., I. Kawada, S. Irimaziri and R. Sadanaga (1969) The crystal structure and polytypism of manganpyrosmalite. *Mineral. J. (Japan), 5,* 450–467.

Wicks, F. J. and E. J. W. Whittaker (1975) A reappraisal of the structures of the serpentine minerals. *Can. Mineral., 13,* 227–243.

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