Brianite, Na$_2$CaMg[PO$_4$]$_2$: A Phosphate Analog of Merwinite, Ca$_2$CaMg[SiO$_4$]$_2$

PAUL BRIAN MOORE

Department of the Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637

Abstract

Brianite, Na$_2$CaMg[PO$_4$]$_2$, a 13.36(5)Å, b 5.23(2)Å, c 9.13(3)Å, β 91.2(0.2)°, space group P2$_1$/a, is structurally isomorphic to merwinite, Ca$_2$CaMg[SiO$_4$]$_2$.

Fuchs, Olsen, and Henderson (1967) described a new species, brianite, which occurs as a rare constituent in small pockets in the Dayton octahedrite from Montgomery County, Ohio. Brianite was observed to possess fine lamellar structure with extinction angles between adjacent lamellae of 2–3°. The authors concluded that the compound is almost ideally Na$_2$CaMg[PO$_4$]$_2$ on the basis of detailed electron microprobe study.

Rotation and Weissenberg photographs led Fuchs *et al* to conclude that brianite is orthorhombic, and their results are presented in Table 1. A marked spatial similarity between brianite and bredigite, (Ca,Ba)Ca$_{13}$Mg$_2$[SiO$_4$]$_8$, was noted by these authors, having been suggested by Dr. A. Kato as a private communication in their study. For this reason, I proposed to study brianite in greater detail as part of a broad program on the structure systematics of slag-related phases.

A single crystal was kindly donated by Dr. Louis Fuchs of Argonne National Laboratory. Although the crystallographic axes were located and the axial dimensions matched those of the earlier study, it was observed that the intensity distributions violated each of the three reflection planes expected for an orthorhombic crystal. Accordingly, the photographs which constituted the original study were requested and these were presented by Dr. Fuchs. These photographs, too, revealed the same violations in intensity distributions. More significant, however, was the observation that the "*a*"-axis and "*c*"-axis rotation photographs and their zero-layer Weissenberg projections almost exactly duplicated photographs about the [011]- and [100]-axes, respectively, of merwinite. Reorientation of brianite forced me to conclude that the compound is in fact structurally isomorphic with merwinite. Table 1 lists the new data on brianite, its comparison with merwinite and the

calculations along [011], [03$\bar{1}$], and [100] which are compared with the earlier study. It is instructive to note that Moore and Araki (1972) pointed out missettings of the same kind in an earlier study on merwinite. The refined cell data for brianite obtain from an indexing of the original powder data in Fuchs *et al*. The first thirty lines of these powder data have been indexed (Table 2) on the basis of a calculated powder pattern derived from merwinite crystal structure data. Brianite is polysynthetically twinned on {100}, explaining the lamellar appearance of the grains.

Moore (1973), in a topological-geometrical analysis of alkali sulfate and calcium orthosilicate structures, noted three kinds of large cation polyhedra: $X^{[12-p]}$ with ($0 \leq p < 6$) so as to define the pinwheel type; $Y^{[10]}$ polyhedra; and $M^{[6]}$, the octahedron ($p = 6$). The $Y^{[10]}$ polyhedra, owing to shared faces with the tetrahedral anionic groups, most likely receive the cations of lowest net charge. Accordingly, it is proposed that brianite is isostructurally related to merwinite as follows:

TABLE 1. Structure Cell Data for Brianite and Its Relation to Merwinite

	1	2	3	4
a(Å)	10.50	10.53	13.36(5)	13.25
b(Å)	18.16	18.15	5.23(2)	5.29
c(Å)	13.31	13.36	9.13(3)	9.33
β	90°	90.4°	91.2(0.2)°	91.90°
space group	P222$_1$		P2$_1$/a	P2$_1$/a

[1]Fuchs *et al*. (1967) for brianite.

[2]Computed from (3) with a = [011], b = [03$\bar{1}$], c = [100].

[3]Brianite (this study). Results refined from partly indexed powder data.

[4]Merwinite (Moore and Araki, 1972).

TABLE 2.   Indexed Powder Data for Brianite*

I	d(obs)	d(calc)	hkl		I	d(obs)	d(calc)	hkl
2	9.15	9.13	001		2	2.432	2.432	213
1	5.37	5.44	$\bar{2}$01		1	2.382	2.358	$\bar{2}$21
1	4.55	4.54	011		6	2.311	2.313	$\bar{5}$11
3	4.27	4.28	111		3	2.284	2.291	511
2	4.15	4.12	210		3	2.254	2.269	022
9	3.734	3.735	211		7	2.230	2.226	600
7	3.344	3.338	400		3	2.166	2.156	$\bar{2}$22
6	3.158	3.161	311		4	2.137	2.142	222
1	2.809	2.814	410		3	2.078	2.092	014
8	2.718	2.703	$\bar{4}$11		2	2.049	2.031	$\bar{3}$22
9	2.679	2.676	411		5b	2.013	2.013	322
10	2.625	2.631	013		9	1.875	1.886	$\bar{4}$22
6	2.596	2.606	020		1	1.783	1.771	$\bar{2}$05
1	2.553	2.567	120		2	1.760	1.757	414
2	2.452	2.436	220		3	1.731	1.739	$\bar{5}$22

*The first thirty lines reported by Fuchs et al. (1967).

Brianite	Na(1)	Na(2)	Ca	Mg	$[PO_4]_2$
Merwinite	Ca(2)	Ca(3)	Ca(1)	Mg	$[SiO_4]_2$
Polyhedra (ideal)	$Y^{[10]}$	$Y^{[10]}$	$X^{[12]}$	$M^{[6]}$	$[T^{[4]}O_4]_2$

It seems reasonable that brianite, like merwinite, is a well-ordered and stoichiometric compound. In addition it is tempting to suggest that other alkali-alkaline earth phosphate analogs of silicates may exist, such as the analogs of larnite, bredigite, and the "T-silicate" phase. Such compounds would have compositions $NaCa[PO_4]$, $Na_4BaCa_2Mg[PO_4]_4$, and $Na_4Ca_3Mg[PO_4]_4$, respectively.

References

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