

two minerals. All d-spacings (permitted by the space group) down to  $d=1.340 \text{ \AA}$  were calculated using the cell parameters of Zemann and Zemann (1960) for teineite and those of Gattow (1958) for chalcomenite.

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## NEW DATA ON BARYSILITE

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Chemical analyses of barysilite have been generally interpreted as indicating the composition  $\text{Pb}_3\text{Si}_2\text{O}_7$ , although Hey (1955) suggests a relation between barysilite and the synthetic phase  $\text{K}_2\text{O} \cdot 2\text{PbO} \cdot 2\text{SiO}_2$ .

Single crystals of barysilite have been examined. These were from a sample labelled U.S.N.M. C-6389, Franklin, N. J. X-ray oscillation and rotation photographs confirm that the rhombohedral symmetry deduced from the crystal morphology is correct, and give the following cell dimensions (referred to hexagonal axes).

$$a = 8.46 \pm 0.02 \text{ \AA}, \quad c = 38.3 \pm 0.2 \text{ \AA}$$

$$V_{\text{hex.}} = 2380 \text{ \AA}^3$$

Powder x-ray data are shown in Table I. Because of the very long  $c$  spacing no attempt has been made to index these data; however, single crystal photographs were compared with powder photographs taken on the same camera. All stronger reflections match powder arcs perfectly.

Unit cell contents have been calculated in Table II. Complete data—chemical analysis, unit cell volume and density—are not available for any one specimen. However, all three chemical analyses are similar; the sample used in the present study is probably very similar to anal. 3,

Table II. The general similarity of the analyses suggests that Flink's (1917) density values can be used with confidence. Flink reports observed densities between 6.55 and 6.706; the present calculations use  $G=6.70$ . The chemical analyses have been recalculated to 100% making certain assumptions.  $H_2O$  has been ruled out as an essential constitu-

TABLE I. X-RAY POWDER DATA FOR BARYSILITE

Diffractometer		Film		Diffractometer		Film		Diffractometer		Film	
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
8.72	12	7.2	m	2.344	8	2.34	mw	1.595	10	1.58	w
5.11	10	5.7	vw	2.307	4	2.29	mw	1.586	2		
4.71	35	4.6	m	2.267	5			1.557 <sub>d</sub>	6	1.54	mw
4.58	40	4.3	w	2.177 <sub>d</sub>	10			1.523	2		
4.349	5			2.108	10	2.10	vw	1.498	2	1.50	vw
3.146	5			2.086	4						
3.885	30			2.064	6	2.06	vw	1.474 <sub>d</sub>	8	1.46	m
3.501	10			2.002 <sub>d</sub>	15			1.454	5	1.45	vw
3.307	80			1.973	10	1.98	m			1.37	mw
3.198	100	3.24	s	1.945	20	1.93	ms			1.34	vw
3.163	60	3.18	vs	1.908	6					1.32	w
3.039	3			1.886	10	=1.87	vw	1.293	4	1.30	w
2.960	80	2.92	ms	1.853	20					1.240	mw
2.905	30			1.846	18	1.84	s	1.210	4	1.20	m
2.826	35			1.834	15					1.17 <sub>d</sub>	w
										1.14 <sub>f</sub>	
2.767	70	2.74	m	1.821 <sub>d</sub>	15	1.80	s				
2.678	35	2.61 <sub>d</sub>	ms	1.779 <sub>d</sub>	4	1.76	vw				
2.637 <sub>d</sub>	30			1.706	7	1.69	mw				
2.581	4			1.678	4	1.66	w				
2.415	7	2.42	vw	1.644	3	1.63	w				

Radiation:  $CuK_{\alpha, \alpha_2}$ , Ni Filter. Diffractometer data were obtained on a Philips PW 1010 diffractometer at a scanning speed of  $\frac{1}{2}^\circ 2\theta/\text{min}$ . The scanning range was  $80^\circ-4^\circ 2\theta$ . Observed d-spacings were corrected by an external silicon standard. Intensities were measured relative to the strongest line  $d=3.198$ , which was arbitrarily taken as  $I=100$ . Film data were taken on a 6 cm. diameter camera. Thus the observed d-spacings are not particularly accurate. Intensities were estimated visually by comparison with the strongest line ( $d=3.163$ ). Comparison of the two sets of intensity data indicate a considerable degree of preferred orientation in the diffractometer sample. Additional power lines were recorded on film at  $d=1.12$  (mw) and  $1.08$  (m).

d=diffuse; s=strong; m=medium; w=weak; v=very.

ent. A 257 mg sample of barysilite, hand picked from sample C-6389, lost 0.0 mg after heating in dry nitrogen at  $700^\circ\text{C}$ . for 24 hrs. Table II gives other details of the recalculation.

Barysilite inverts to an apparently new phase upon heating. The inversion temperature is  $730 \pm 30^\circ\text{C}$ . in dry  $N_2$ ; the reverse reaction has not been observed in runs of 24 hr duration. X-ray data for the high temperature form are shown in Table III. Cleavage flakes of barysilite apparently convert topotactically to the high temperature phase, which has a large monoclinic cell. Rotation and Weissenberg photographs taken

about a symmetrical 9.75 Å axis give  $a=25.7$ ,  $c=16.9$  Å,  $\beta=90^\circ$ . No attempt has been made to study the orientation relationships.

The higher temperature phase persists to at least 960° C. in dry N<sub>2</sub>. Cleavage flakes, formerly barysilite, heated several hours at 960° retain their shape except for a slight rounding of the edges. Microscopic examination did not show any signs of liquid formation. This phase is much more refractory than the pure lead silicates; for example, both PbSiO<sub>3</sub> and Pb<sub>2</sub>SiO<sub>4</sub> melt at temperatures below 800° C.

TABLE II. CHEMICAL ANALYSES AND UNIT CELL CONTENTS OF BARYSILITE

	Recalculated in wt. %				4	5	6	7
	1	2	3					
SiO <sub>2</sub>	16.68	16.66	17.05	Si	8.8	8.8	9.0	9.0
PbO	78.00	78.53	78.05	Pb	11.2	11.2	11.2	12.0
FeO	0.10	—	0.23	Fe	0.0	0.0	0.1	
MnO	3.06	2.86	3.37	Mn	1.4	1.3	1.5	
ZnO	—	0.92	0.30	Zn	0.0	0.4	0.1	
CaO	1.75	0.53	0.21	Ca	1.0	0.3	0.1	3.0
MgO	0.41	—	0.79	Mg	0.3	0.0	0.6	
K <sub>2</sub> O	—	0.09	—	K	0.0	0.1	0.0	
Na <sub>2</sub> O	—	0.07	—	Na	0.0	0.1	0.0	
	100.00	100.00	100.00	O	31.5	31.0	31.6	33.0

1. Recalculated to 100% from Flink Type 2, ignoring 0.40% H<sub>2</sub>O.

2. Recalculated to 100% from Flink Type 3, ignoring 0.63% SO<sub>3</sub>, 0.08% H<sub>2</sub>O and 0.12% Cl.

3. Recalculated to 100% from Bauer and Berman ignoring 0.59% Al<sub>2</sub>O<sub>3</sub> and 0.07% H<sub>2</sub>O.

4, 5, 6. Atomic cell contents calculated from analyses 1, 2, and 3 respectively.

7. Theoretical atomic cell contents for 3[Pb<sub>4</sub> (Mn, etc.)<sub>1</sub> Si<sub>3</sub>O<sub>11</sub>].

Efforts to synthesize barysilite have not been successful. Dry heating of a 4:1:3 PbO-MnCO<sub>3</sub>-SiO<sub>2</sub> mixture in N<sub>2</sub> gave mostly unreacted starting materials after 2-3 days at 600°-650° C. Above 700° C. an apparently homogeneous preparation was obtained which gave an x-ray powder pattern similar to, but not identical with, the high temperature phase obtained from heating barysilite. It is thus probable, but not certain, that the two products are the same. Unfortunately, heating experiments did not yield any crystals suitable for single crystal x-ray diffraction.

Combining the chemical analyses and x-ray data it is shown that barysilite is a valid mineral species containing essential divalent manganese. It is not related to any known lead silicate, nor to the hexagonal K<sub>2</sub>O·2PbO·2SiO<sub>2</sub> phase ( $a=5.62$  Å,  $c=7.57$  Å; McMurdie, 1941).

TABLE III. X-RAY DATA FOR HIGH TEMPERATURE PHASE  
OBTAINED BY HEATING BARYSILITE

Cu2θ	I	Cu2θ	I
17.65	m	41.40	w
18.80	s	45.30	w
19.40	m	45.60	w
20.05	vw	46.10	w
20.40	w		
		46.60	m
21.40	w	49.15	w
22.90	m	49.80	w
23.50	vw	50.20	m
25.50	w	53.65	vw
27.00	vs		
		56.0 <sub>b</sub>	vw
28.00	vs	56.5 <sub>b</sub>	vw
29.00	vs	57.70	w
30.10	vs	59.0 <sub>b</sub>	vw
30.70	w	59.5 <sub>b</sub>	vw
31.55	s		
32.20	s		
33.45	m		
34.05	ms		
37.25	vw		
38.5 <sub>b</sub>	vw		

Sample heated 760° C. in N<sub>2</sub>, 24 hrs. Other samples heated between 760°-960° C. for varying time (2-48 hrs.) gave identical patterns. d-spacing values were obtained from a diffractometer trace (CuK<sub>α</sub> radiation); intensities were obtained from film measurements. b=broad.

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