## Roeblingite: new chemical data

PETE J. DUNN AND JULIE A. NORBERG

Department of Mineral Sciences, Smithsonian Institution, Washington, DC 20560, USA

AND

## PETER B. LEAVENS

Department of Geology, University of Delaware, Newark, Delaware 19711, USA

ABSTRACT. New chemical analyses of roeblingite from Franklin, New Jersey, and Långban, Sweden, are presented. The average composition of Franklin roeblingite is SiO<sub>2</sub> 24.9, CaO 23.8, SrO 2.4, MnO 2.4, PbO 30.2, SO<sub>3</sub> 10.4, H<sub>2</sub>O 6.13%, Sum = 100.23%. The data support space group C2/m and suggest the formula is (Ca,Sr)<sub>12</sub> (Mn,Ca)<sub>2</sub>Pb<sub>4</sub>(SO<sub>4</sub>)<sub>4</sub>Si<sub>12</sub>O<sub>28</sub>(OH)<sub>20</sub>, if there is ordering on the site of rank 2.

ROEBLINGITE was first described from Franklin, New Jersey, by Penfield and Foote (1897). It was among the first of the lead silicate minerals found at Franklin, many of which are known only from there and from Långban, Varmland, Sweden.

The chemical composition of roeblingite has long been the subject of some confusion. The original analysis of Penfield and Foote (1897) reported the presence of sulphite in roeblingite, but a later analysis by Blix (1931) demonstrated that the S in roeblingite is present as sulphate. His procedures are well detailed and the reader is referred to his paper for details. The original formula proposed by Penfield and Foote was H<sub>10</sub>Ca<sub>7</sub>Pb<sub>2</sub>Si<sub>5</sub>S<sub>2</sub>O<sub>28</sub>; Blix (1931) proposed  $2PbSO_4R_7H_{10}Si_6O_{24}$  where R = Ca, Sr, and Mn. Subsequent study by Foit (1966) established the unit cell parameters for roeblingite and presented a tentative formula of  $(Pb_4S_4O_{16})R_{16}Si_{12}O_{44}H_{20}$ with R = Ca, Mn, Sr, Na, and K. Our results, given here, indicate eighteen divalent cations instead of the twenty proposed by Foit (1966), and confirm the data of Blix (1931).

Optical properties. The Franklin roeblingite occurs as nodular masses, usually not exceeding 10 cm in diameter, and composed of very finegrained aggregates of lath-like crystals. Unlike this massive Franklin material, Långban roeblingite occurs as colourless prismatic crystals in parallel growth and suitable for the measurement of optical properties. Crystals from analysed sample no. B17051 are biaxial (+) with refractive indices  $\alpha = 1.654(1)$ ,  $\beta = 1.660(1)$ , and  $\gamma = 1.678(1)$ . The optic axial angle was measured directly using a spindle stage and is  $2V_{\gamma} = 61(2)^{\circ}$ , in good agreement with the calculated value of 61°. The plane of the cleavage contains  $\alpha$  and  $\beta$ . Dispersion of the optic axes is slight with r < v. There is no pleochroism. Calculation of specific refractive energy for roeblingite using the constants of Mandarino (1976) yield  $K_C = 0.189$  and  $K_P = 0.190$ , providing excellent compatibility of the data using the compatibility index of Mandarino (1979).

Chemistry. All samples studied herein are from the Smithsonian collection and were chemically analysed using an ARL-SEM electron microprobe with an operating voltage of 15 kV and a beam current of 0.15  $\mu$ A. The standards used for analysis were PbO for Pb, manganite for Mn, hornblende for Ca and Si, and celestine for Sr and S. The data were corrected using a modified version of the *MAGIC-4* computer program. Total water was determined using the Penfield method; H<sub>2</sub>O<sup>-</sup> was determined as loss at 110 °C. Additional water analyses of otherwise unanalysed samples yielded 6.01 H<sub>2</sub>O<sup>+</sup>, 0.44 H<sub>2</sub>O<sup>-</sup>%, and 5.96 H<sub>2</sub>O<sup>+</sup>, 0.37 H<sub>2</sub>O<sup>-</sup>%, confirming the given water content of sample R18452 in Table I.

The analysis by Blix (1931) agrees closely with those of this study. The Franklin roeblingites are slightly enriched in strontium, but Sr is much lower in the Långban sample. Penfield and Foote (1897) reported the presence of sodium and potassium, but these were not found by Blix (1931) and are not present in the samples we studied. Ba, P, and Zn were sought but not found.

Discussion. Calculation of unit cell contents for Långban rocblingite (analysis 5) using the unit cell

|    | $SiO_2$ | CaO   | SrO  | MnO  | РЬО   | $SO_3$ | $H_2O^+$ | $H_2O^-$ | Total     | NMNH no.                   | Locality        |
|----|---------|-------|------|------|-------|--------|----------|----------|-----------|----------------------------|-----------------|
| A. | 23.58   | 25.95 | 1.40 | 2.48 | 31.03 | 9.00*  | 6.35     |          | 100.32**  |                            | Franklin, NJ    |
| B. | 23.57   | 23.12 | 2.79 | 2.49 | 30.04 | 10.81  | 6.15     | 0.45     | 100.03*** |                            | Franklin, NJ    |
| 1. | 25.2    | 23.7  | 2.3  | 2.8  | 30.2  | 10.5   | 6.04†    | 0.18     | 100.92    | R124-1                     | Franklin, NJ    |
| 2. | 24.7    | 24.5  | 2.6  | 1.5  | 30.7  | 10.5   | 6.13††   |          | 100.63    | C6402                      | Franklin, NJ    |
| 3. | 24.6    | 22.9  | 2.4  | 3.4  | 30.4  | 10.4   | 6.13††   |          | 100.23    | R3996                      | Franklin, NJ    |
| 4. | 25.0    | 24.2  | 2.2  | 2.0  | 29.6  | 10.2   | 6.13++   |          | 99.33     | R18452                     | Franklin, NJ    |
| 5. | 24.6    | 22.6  | 0.7  | 44   | 30.7  | 10.6   | 6.13††   |          | 99.73     | B17051                     | Långban, Sweden |
|    | 24.9    | 23.8  | 2.4  | 2.4  | 30.2  | 10.4   | 6.13††   |          | 100.23    | Average of<br>analyses 1-4 | 0               |
|    | 24.63   | 22.98 | ·    | 4.84 | 30.48 | 10.94  | 6.13     |          | 100.00    | Theory ††                  |                 |

TABLE I. Chemical analyses of roeblingite

\* Originally given as SO<sub>2</sub>. \*\* Included 0.40% Na<sub>2</sub>O, 0.13% K<sub>2</sub>O. \*\*\* Included 0.61% CO<sub>2</sub>. † Water determined by Penfield method. †† Water taken from theoretical composition. ††† Theory for  $Mn_2Ca_{12}Pb_4$  (SO<sub>4</sub>)<sub>4</sub>Si<sub>12</sub>O<sub>28</sub>(OH)<sub>20</sub>. A- analysis from Penfield and Foote (1897). B -analysis from Blix (1931). Accuracy of data:  $\pm 3\%$  of the amount present.

parameters of Foit (1966) (a = 13.27, b = 8.38, b = 8.38) $c = 13.09 \text{ Å}, \beta = 103.86(10)^{\circ}$  and a newly determined density of 3.50 g/cm<sup>3</sup> yields: (Ca<sub>12.00</sub>Sr<sub>0.20</sub>  $Mn_{1.84}Pb_{4.09})_{\Sigma 18.13}(SO_4)_{3.94}Si_{12.19}O_{28.57}(OH)_{20}$ The sum of divalent cations approximates eighteen which, although inconsistent with the space groups Cc or C2/c (Foit, 1966), which require equipoint ranks of four and eight, is consistent with the space group C2/m reported by Welin (1968) from an unpublished study by Moore (1967). The near constancy of Pb in all analyses suggests little or no solid solution of other ions with Pb. Mn is present in all roeblingite analyses and approximates two atoms in Långban material, which suggests that Mn may be essential to roeblingite and ordered in the site of rank 2. Comparison of the average of the Franklin analyses with the Långban analysis (Table I) shows inverse variation of Mn and Sr, but the substitution of these two is unlikely because of the substantial difference in their atomic radii. Based on these considerations, we suggest that roeblingite has the formula  $(Ca,Sr)_{12}(Mn,Ca)_2$  $Pb_4(SO_4)_4Si_{12}O_{28}(OH)_{20}$  with space group C2/m, and Z = 1, but this can be proven only by a complete crystal structure determination. In addition, it is noteworthy that both Franklin and Långban have barysilite among the lead silicates, indicating that conditions were conducive to the formation of compound silicates of Pb and Mn.

Acknowledgements. The authors are indebted to Mr Richard Johnson and Mr Frank Walkup for the preparation of polished sections. This project was supported, in part, by a grant from Mrs E. Hadley Stuart, Jr.

## REFERENCES

- Blix, R. (1931) Am. Mineral. 16, 455-60.
- Foit, F. F. (1966) Ibid. 51, 504-8.
- Mandarino, J. A. (1976) Can. Mineral. 14, 498-502.
- ------ (1979) Ibid. 17, 71-6.
- Palache, C. (1935) U.S. Geol. Surv. Prof. Pap. 180, 113.
- Penfield, S. L., and Foote, H. W. (1897) Am. J. Sci., Ser. 4, 3, 413 15.
- Welin, E. (1968) Arkiv Mineral. Geol. 4, 499 541.

[Manuscript received 3 August 1981]