MINERALOGICAL MAGAZINE, DECEMBER 1985, VOL. 49, PP. 756-8

Roeblingite: a revised formula from infra-red and thermal analysis data

WHEN roeblingite was first described, it was considered to be the first sulphite-containing mineral (Penfield and Foote, 1897). This distinction has now fallen to scotlandite (Paar *et al.*, 1984), Blix (1931) having re-analysed roeblingite and shown chemically that sulphite is absent. Further revisions to the formula were proposed by Foit (1966) and recently, from a number of consistent analyses, by Dunn *et al.* (1982) to $(Ca,Sr)_{12}(Mn,Ca)_2Pb_4(SO_4)_4Si_{12}O_{28}(OH)_{20}$. The late Dr M. H. Hey suggested to the author that the infra-red spectrum of roeblingite should be studied as an additional means of confirming the absence of sulphite and the presence of sulphate, as these anions are readily distinguished from one another by infra-red spectroscopy.

The infra-red spectra of two samples of roeblingite from Franklin, New Jersey (BM 83806, and one from the W. H. Paar collection) were measured under similar conditions, in the 400-4000 cm^{-1} range, and gave similar spectra (fig. 1).

In the region of O-H stretching vibrations, the spectrum of roeblingite displays a strong sharp absorption at 3560 cm^{-1} assigned to ν_{O-H} of hydroxyl other than that which is part of H_2O. Broader absorptions at 3480 cm^{-1} and 3250 cm^{-1}, and a shoulder near 3300 cm^{-1}, are due to O-H stretching vibrations which are more restricted, as in H_2O or by hydrogen bonding. An important feature of the spectrum is the very distinctive absorption at 1665 cm^{-1} due to the H-O-H 'scissor' deformation vibration of H_2O, which is too strong and sharp to be due to contamination with moisture. It is of the same relative strength, within experimental error, in the spectra of the two samples of roeblingite from different sources, so is not likely to be due to impurity [such as, for example, charlesite, a water-rich mineral closely associated with roeblingite from Franklin, New Jersey (Dunn *et al.*, 1983)].

The strong absorption at 1103 cm^{-1} is assigned to the ν_3 asymmetric stretching mode of the sulphate anion, and the band at 627 cm^{-1} is probably due to its ν_4 asymmetric deformation vibration. The ν_1 symmetrical stretching and ν_2 symmetrical deformation modes of sulphate are usually found near 1000 cm^{-1} and 450-500 cm^{-1} respectively. These symmetrical vibrations are forbidden, but appear when distortion of the anion lowers its symmetry. For roeblingite, the ν_1 band, which is always weak, would be buried under Si-O stretching absorptions; the ν_2 band may be part of, or buried under, the absorption complex 460-510 cm^{-1}, or it may be absent if the sulphate anion has full T_d symmetry within the roeblingite lattice.

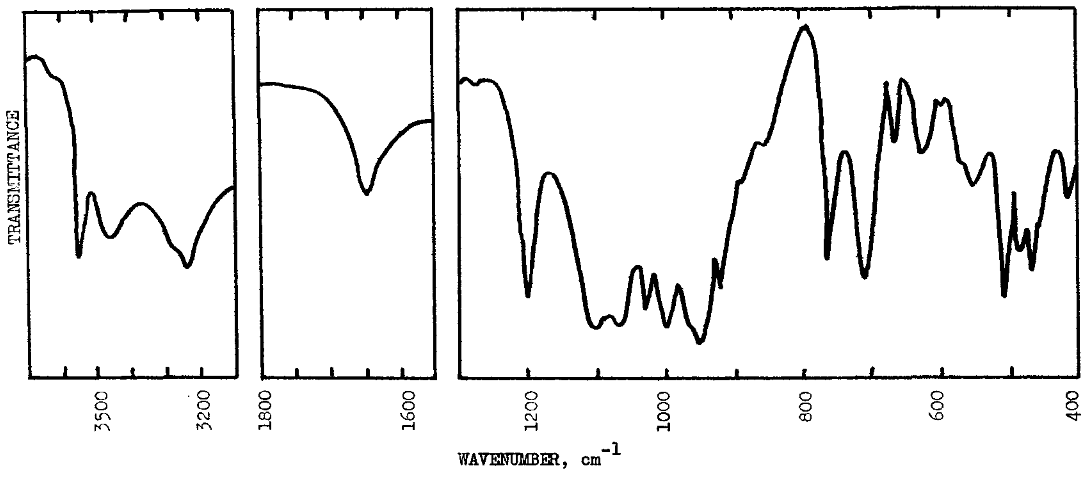

FIG. 1. Infra-red spectrum of roeblingite from Franklin, New Jersey (BM 83806) measured in 'Nujol' mull, between KBr plates, using a Perkin-Elmer 397 precision grating spectrophotometer.

The very strong sharp absorption near 1200 cm^{-1} is in the same position and of the same strength and profile as the distinctive absorption band in xonotlite ascribed by Ryskin *et al.* (1969) to a stretching vibration of linear Si-O-Si bonds linking between chains. A number of other silicates of various structure types (e.g. babingtonite, beryl, sillimanite) also show absorptions in this region, though usually less sharp, but so also do some sulphates (e.g. jarosite, antlerite) in which the normally rather broad ν_3 asymmetric stretch near 1100 cm^{-1} is split by degeneracy loss into up to three sharper absorptions, one of which usually lies between 1150 and 1200 cm^{-1}. The sulphate ν_3 absorption at 1103 cm^{-1} in the spectrum of roeblingite is sharp enough to be a part of a multiplet of this nature, any third absorption being camouflaged among the silicate absorptions. Queitite, like roeblingite, is a lead-containing silicate and sulphate, and a very sharp absorption in its spectrum at 1168 cm^{-1} has been ascribed to a sulphate ν_3 vibration (Povarennykh *et al.*, 1982). The evidence for the assignment of the 1200 cm^{-1} absorption of roeblingite is therefore not conclusive, but it is probably due to either an S-O or Si-O stretching vibration.

The silicate absorption pattern is complex, with Si-O stretching bands in the 900-1100 cm^{-1} region, possible Si-O-Si bending or ring deformation vibrations at 710 and 760 cm^{-1}, and other Si-O vibrations in the 450-510 cm^{-1} region. This pattern shows general similarities with those of foshagite and margarosanite.

The strong sulphite ν_3 asymmetric stretching bands of scotlandite and of orthorhombic lead sulphite lie near 900 cm^{-1} (Paar *et al.*, 1984), where roeblingite has relatively weak absorption, although the presence of lighter cations in roeblingite might be expected to shift it to slightly higher wavenumbers, where roeblingite absorbs increasingly strongly. The ν_2 absorption of sulphite lies near 600 cm^{-1}, in the same region as the sulphate ν_2 band, and cannot be used to distinguish between them. The ν_4 absorption of lead sulphites lies near 470-495 cm^{-1}, in the same region as the ν_2 band of sulphate and Si-O-Si bending vibrations, and so is also of no diagnostic value in this case. Thus although the infra-red spectrum of roeblingite affords reasonable evidence for the presence of sulphate, it is insufficient evidence for the absence of sulphite.

The presence of the H-O-H deformation vibration is strong evidence for the presence of H_2O in the roeblingite structure, not allowed for in previous formulations, indicating that the formula should be revised to include H_2O as well as hydroxide.

The implied accuracy from the good consistency of the analyses of roeblingite reported by Dunn *et al.* (1982) leaves little leeway for removing cations in order to restore charge balance when transforming hydroxyl ions into water molecules, the removal of any one cation appreciably upsetting agreement with the analytical results. The empirical formula, and hence the fit of the analyses, remain unchanged if, for every hydroxyl transformed into water, another hydroxyl oxygen becomes an oxygen of the silicate system. The formula of roeblingite would thus become $(Ca,Sr)_{12}(Mn,Ca)_2Pb_4(SO_4)_4Si_{12}O_{28+n}(OH)_{20-2n}\cdot nH_2O$.

In order to determine the value of n, 7.3 mg of powdered Franklin roeblingite from BM 83806 was submitted to thermogravimetric analysis by Mr Roy Adams in the Metallurgy Department, UMIST, at a heating rate of 10 °C per minute, in a Pt holder in a static air atmosphere, using a Stanton Redcroft TG 770 thermogravimetric balance fitted with a Pt-Rh thermocouple.

No weight loss was detected below about 250 °C, followed by a steady weight loss to $5.0\pm0.2\%$ by 410 °C (4.91% would be due to 8 H_2O; loss for 7 H_2O would be 4.3% and for 9 H_2O 5.5%), after which the slope changes sharply to a steady slower loss to $6.0\pm0.2\%$ at 600 °C, corresponding to the values for total water loss of 6.04% (measured), 6.13% (theoretical) given by Dunn *et al.* (1982). Above about 700 °C weight was slowly gained, presumably by oxidation. The 250-410 °C weight loss is probably loss from 8 H_2O, whereas the 410-600 °C loss is more likely to be hydroxide loss, and closely fits 2 H_2O from 4 hydroxide ions. The value of n is therefore 8, and the formula of roeblingite is $(Ca,Sr)_{12}(Mn,Ca)_2Pb_4(SO_4)_4Si_{12}O_{36}(OH)_4\cdot 8H_2O$.

Acknowledgements. The author is indebted to the late Dr M. H. Hey, whose suggestion initiated the study; to the Trustees of the British Museum (Natural History) and to Professor Dr W. H. Paar of Salzburg for samples of roeblingite; to Mr Roy Adams of the Metallurgy Department, UMIST for the thermal analysis work, and to Dr G. Ryback for his critical appraisal of the manuscript.

REFERENCES

Blix, R. (1931) *Am. Mineral.* **16,** 455-60.

Dunn, P. J., Norberg, J. A., and Leavens, P. B. (1982) *Mineral. Mag.* **46,** 341-2.

—— Peacor, D. R., Leavens, P. B., and Baum, J. L. (1983) *Am. Mineral.* **68,** 1033-7.

Foit, F. F. (1966) Ibid. **51,** 504-8.

Paar, W. H., Braithwaite, R. S. W., Chen, T. T., and Keller, P. (1984) *Mineral. Mag.* **48,** 283-8.

Penfield, S. L., and Foote, H. W. (1897) *Am. J. Sci.*, Ser. 4, **3,** 413-15.

Povarennykh, A. S., Keller, P., and Kristiansen, R. (1982) *Can. Mineral.* **20,** 601-3.

Ryskin, Ya. I., Stavitskaya, G. P., and Mitropol'skii, N. A. (1969) *Izv. Akad. Nauk SSSR, Neorg. Mater.* **5**, 577–81.

ADDENDUM

Since submission of this paper, Moore and Shen (1984) have published the crystal structure of roeblingite from Långban, Sweden, using X-ray diffraction data. The silicate portion of the structure was found to be based on $[Si_3O_9]^{6-}$ rings related to those in margarosanite, from which a formula $Pb_2Ca_6(SO_4)_2(OH)_2(H_2O)_4[Mn(Si_3O_9)_2]$ was derived without using any additional analytical data. This formula is similar to that proposed in this paper, but halved and idealized, and with the manganese linked with the silicate units.

It is owing to their structural similarity that the silicate portion of the infra-red spectrum of roeblingite is related to that of margarosanite.

REFERENCE

Moore, P. B., and Shen, J. (1984) *Am. Mineral.* **69**, 1173–9.

[*Manuscript received 18 October 1984;*
revised 18 January 1985]

KEYWORDS: roeblingite, infra-red spectra, thermal analysis.

Department of Chemistry, The University of Manchester
Institute of Science and Technology, Manchester M60 1QD

R. S. W. BRAITHWAITE

MINERALOGICAL MAGAZINE, DECEMBER 1985, VOL. 49, PP. 758–9

Petalite and spodumene in the Meldon Aplite, Devon

ASPECTS of the mineralogy of the Meldon aplite have been reported in detail in the series of studies listed by Chaudhry and Mahmood (1979) but none of these recent investigations deal specifically with petalite and spodumene. Petalite here was first described by McLintock (1923) as moulded on, enclosing and filling spaces between quartz and feldspar in the coarser portions of the aplite and more commonly in pegmatite veins in the aplite. Similarly, Edmonds *et al.* (1968) described petalite in some of the sporadic coarser pegmatitic veins and forming disseminations in the surrounding aplite. Chaudhry and Mahmood (1979) noted the petalite is of extremely irregular occurrence, although tending to be most abundant in the pegmatite-rich areas, and primary orthoclase may have been replaced by petalite. Spodumene at Meldon receives only two notices; the description by Kingsbury (1966) is cited by Edmonds *et al.* (1968). Kingsbury described in the dyke coarse complex pegmatite lenses which show evidence of several stages of mineralization and notes that, in one or two of these pegmatites, amblygonite, spodumene, montebrasite, pollucite, and beryllium minerals are found. Edmonds *et al.* (1968) record among the coarser pegmatitic veins some that carry petalite and traces of columbite and the minerals—including spodumene—listed by Kingsbury.

Petalite and spodumene from Meldon in the A. W. G. Kingsbury Collection, British Museum (Natural History) were examined. The petalite is massive glassy greyish white petalite. No evidence was found of the isochemical breakdown of petalite to spodumene and quartz or of replacement of spodumene by petalite. Spodumene and petalite are never associated together. This petalite is similar in composition (Table I) to the petalites from Bikita, Tanco, Hirvikallio, Piaui, and Rubicon

TABLE I. *Composition of petalite and spodumene from the Meldon aplite*

	Petalite (BM 1968, 112)		Spodumene (BM 1968, 105)
SiO_2	78.1	±0.3	64.8
Al_2O_3	16.7	±0.2	27.4
FeO (total Fe)	0.03	±0.03	0.06
MnO	0.00	±0.02	0.17
MgO	0.08	±0.01	0.02
CaO	0.02	±0.01	0.02
Na_2O	0.14	±0.09	0.02
K_2O	0.04	±0.01	0.25
			0.04
Li_2O	about 4.0		about 7.0
Total	99.0±		99.0±

Analysis by electron microprobe; Li_2O estimate only by A.A. because of very small sample available.