

compositions of the Broken Hill ferroan tephroites from this study, gives a predicted  $\beta$  refractive index close to  $\beta = 1.820$ . Refractive indices determined by Dr J. McAndrew on the Broken Hill type specimen (cited in Stillwell's report) were  $\alpha = 1.791$ ,  $\beta = 1.819$ ,  $\gamma = 1.829$ , with errors of  $\pm 0.002$ . Thus, the measured  $\beta$  agrees with that predicted by the Mossman-Pawson grid.

The terms knebelite, tephroite, and roepperite have all been used for what appears to be essentially the same mineral at Broken Hill. Their use, however, has been arbitrary in the absence of sufficient data to establish natural compositional limits. The results of this study indicate that most (if not all) of the Broken Hill occurrences are ferroan tephroite, with a compositional range defined by Fe/Mn between 0.61 and 0.30. However, more data are needed to determine whether there are any compositional variations related to either position in the lode horizon or the nature of the tephroite-bearing assemblage.

The term knebelite, now defined as a synonym for manganoean fayalite (Fleischer, 1980) is not generally applicable to any Broken Hill mineral and roepperite, on the basis of this study, is not a valid mineral at Broken Hill (Birch *et al.*, 1982).

The nature of the original roepperite specimen from Sterling Hill is unknown. However, there may be some doubt cast on its validity, since Hurlbut (1961) demonstrated that the solid solubility of Zn in tephroite is limited and, of the four Franklin roepperite specimens available for Hurlbut's study, three proved to be black willemite and the fourth to be ferroan tephroite with exsolved willemite.

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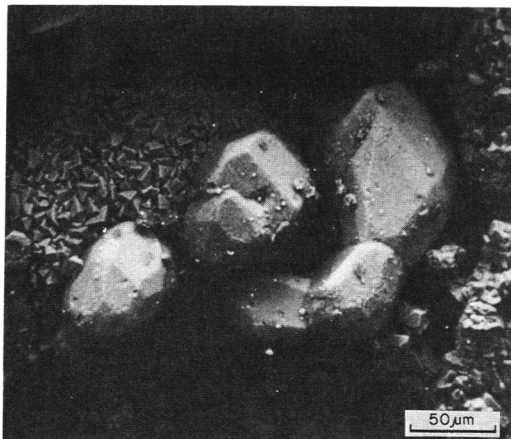
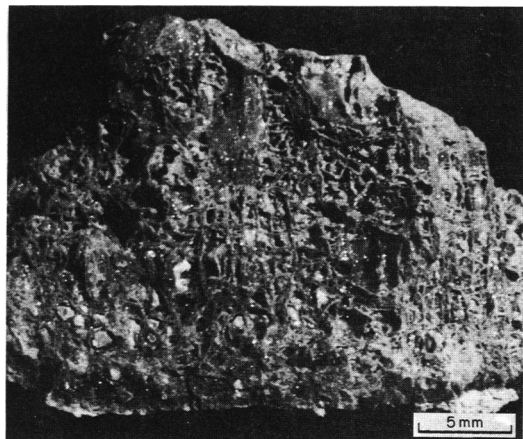
W. D. BIRCH

MINERALOGICAL MAGAZINE, MARCH 1984, VOL. 48, PP. 139-42

## An unusual pyrite-sulphur-jarosite assemblage from Arkaroola, South Australia

AN occurrence of co-existing pyrite, elemental sulphur, and jarosite ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ) has recently been discovered in South Australia. Although jarosite is a common alteration product of pyrite (e.g. Furbish, 1963; Bladh, 1982), this is apparently the first time that native sulphur has been reported in association with the two.

The occurrence was discovered by Mr Edward Madden of Echunga, South Australia, in a metamorphic formation known as the Woodnamoka Phyllite, which is in the lower part of the Proterozoic Adelaidean system in the Mount Painter Province of South Australia. A description of the regional geology is provided by Coats and Blissett



FIGS. 1 and 2. FIG. 1 (*left*). Photograph of broken surface, showing jarosite boxwork containing sulphur and pyrite. FIG. 2. (*right*). SEM micrograph of sulphur crystals on a bed of finer-grained jarosite crystals.

(1971). The site of the discovery is about 2 km north-west of Wywyana Park (Lat. 30° 18' S, Long. 139° 19'), on the Arkaroola pastoral lease, in the Flinders Range of South Australia.

The pyrite-sulphur-jarosite assemblage occurs at and near the surface of the weathered rock in the form of fist-sized pseudomorphs of pyrite crystals which, when broken open, are seen to consist of cellular jarosite boxworks (fig. 1) with small crystals of elemental sulphur in many of the cells, and pyrite remnants in a few of the larger ones. The pseudomorphs under consideration contain virtually no goethite, although some small goethitic pseudomorphs of pyrite have been recovered from the same weathered rock.

The jarosite comprising the external surfaces of the pseudomorphs has an earthy, yellow-brown appearance, with the darker shades being due to traces of goethite. The cell walls of the internal boxwork consist of finely crystalline jarosite (fig. 2). The jarosite is yellow to light brown in colour. In some places the boxwork has a rectilinear pattern, but mostly it is quite irregular (fig. 1).

The sulphur crystals are quite small, generally less than 0.1 mm in diameter, and are multi-faceted (fig. 2). They are transparent, pale yellow, and have a vitreous lustre; X-ray diffraction patterns show that the sulphur is in the orthorhombic ( $\alpha$ ) modification.

The pyrite grains in the boxwork cells are corroded in appearance (fig. 3), and many of them have clear, splendant surfaces; others are lightly coated by jarosite. It is obvious that the pyrite grains are unoxidized remnants of the original pyrite crystals that resulted in the pyrite-sulphur-jarosite assemblage.

Thermodynamic calculations indicate that these three minerals do not form a stable assemblage. This is illustrated by fig. 4, an Eh-pH diagram constructed from data published by Brown (1971), and adopting Brown's assumptions about the activities of the various species involved, which approximate the activities found in naturally occurring acid waters (Hem, 1959).

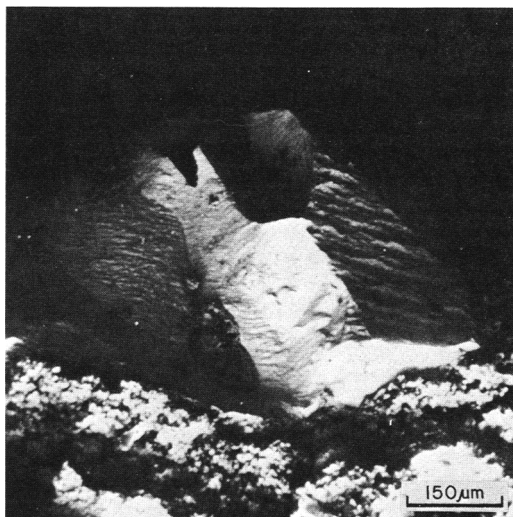


FIG. 3. SEM micrograph of corroded pyrite remnant in jarosite.

Fig. 4 shows that the jarosite predominance field is widely separated from those of pyrite and sulphur by an area where  $\text{Fe}^{2+}$  remains in solution; the

separation approximates about 0.4 V. The predominance field of elemental sulphur is very small, and indicates a stable existence for this phase only at a pH below 1, which is probably unrealistic for normal weathering conditions. Therefore, to explain the pyrite-sulphur-jarosite assemblage, it is necessary to look beyond the theoretical thermodynamic framework and to consider the possible mechanisms involved.

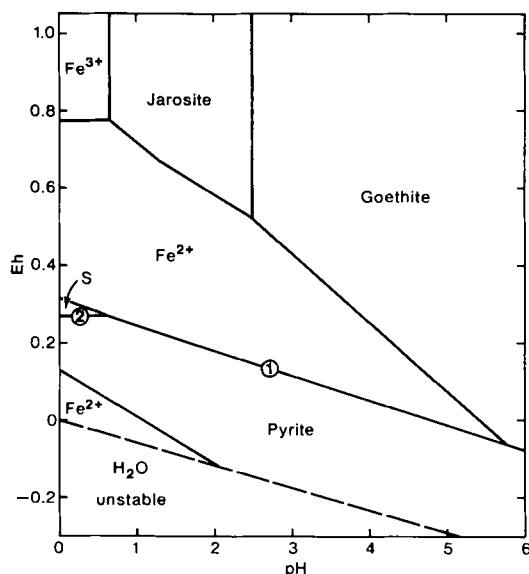
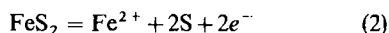
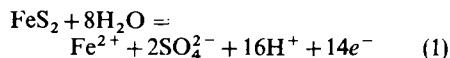


FIG. 4. An Eh pH diagram constructed to show the predominance fields of pyrite, sulphur, jarosite, and goethite. Numbered lines correspond to numbered equations in the text. Activities of dissolved species are as follows:  $\text{Fe} = 10^{-4}$ ,  $\text{K}^+ = 10^{-3}$ , and total  $\text{S} = 10^{-2}$ .

Theoretically, as shown in fig. 4, the oxidation of pyrite can produce either sulphate ions (equation 1) or elemental sulphur (equation 2), reactions which are shown as numbered lines 1 and 2 on fig. 4.



However, in practice,  $\text{SO}_4^{2-}$  forms only with difficulty, and elemental sulphur precipitates over a much larger area, i.e. at higher pH and Eh than those indicated by fig. 4 (Garrels and Naeser, 1958; Peters, 1976; Hamilton and Woods, 1981). Furthermore, there is also a likelihood of metastable sulphur species being produced (Garrels and Naeser, 1958).

The initial products of pyrite oxidation are thus likely to be metastable sulphur species from which

elemental sulphur crystallizes, and which react to form  $\text{SO}_4^{2-}$  only at a considerable over-potential, estimated by Hamilton and Woods (1981) to be at about 0.8 V, which is in the predominance field of jarosite (fig. 4). In the meantime, the hydrogen ions liberated by the oxidation of the sulphide component of pyrite attack the surrounding potash feldspar and/or muscovite, putting  $\text{K}^+$  ions into solution. When the activity of  $\text{K}^+$  gets sufficiently high, jarosite precipitates from the solution, which also contains abundant iron and sulphur species; in the process,  $\text{Fe}^{2+}$  is oxidized to  $\text{Fe}^{3+}$  and the metastable sulphur species are converted to  $\text{SO}_4^{2-}$ .

The jarosite apparently precipitated along fractures in the pyrite, giving rise to the cellular boxwork. Following the initial development of the boxwork, the pyrite continued to dissolve, leaving most of the cells empty except for the small sulphur crystals. The few pyrite remnants have been mostly left with clean splendiant surfaces probably because, during the dissolution process, both iron and sulphur species went into solution simultaneously. Most of the sulphur appears to have crystallized after the jarosite, which indicates that the oxidation potential must have returned to a lower level, possibly because of a rising water table.

Bladh (1982), in a computerized simulation of the oxidation of pyrite and chalcopyrite in rocks containing feldspar and muscovite, predicts that goethite should precipitate before jarosite. This has not happened in the pyrite pseudomorphs under discussion, and can probably be explained by the pH prevailing at the time of oxidation. In Bladh's simulation, the pH is maintained at a relatively high level, presumably by silicate buffering reactions, whereas in the case of the pyrite pseudomorphs, the pH probably remained at a locally low level throughout the oxidation process because of the large size of the original pyrite crystals and possibly by the lack of effective water circulation. The smaller pyrite crystals, on the other hand, were converted to goethite because of the relatively stronger influence of the buffering wall-rock reactions.

In conclusion, it is evident that a purely thermodynamic approach is inadequate to explain the unusual pyrite-sulphur-jarosite assemblage, and that kinetic factors must be taken into consideration.

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## Triplite from East Kemptville, Nova Scotia

THE manganese fluor-phosphate, triplite, has been found for the first time in Canada, in the East Kemptville greisen-hosted tin deposit near East Kemptville, Yarmouth County, Nova Scotia, where it occurs with apatite and sulphides in glassy quartz veins.

The geology of the East Kemptville tin deposit has been summarized by Richardson *et al.* (1982). It is an example of a large tonnage, low grade, greisen-hosted tin deposit in an endocontact zone of a granite pluton. The mineralized zone occurs within an extension of the south-west end of the 300 × 60 km South Mountain Batholith, which has been termed the Davis Lake monzogranite by Shell Canada Resources Limited who discovered the deposit in 1978. The property was subsequently acquired by RioCanex Incorporated in October 1982. The deposit is located near East Kemptville, Yarmouth County, Nova Scotia at latitude 44° 16' N and longitude 65° 41' W. The tin mineralization occurs in pods of massive greisen and zoned greisen selvages flanking thin (0.5 to 2.5 cm) hydrothermal veins. Cassiterite is associated with topaz, white mica, quartz, pyrite, pyrrhotine, sphalerite, chalcopyrite, arsenopyrite, columbite-tantalite, and minor amounts of a member of the wolframite group, probably ferberite.

The triplite occurs in quartz-sulphide-phosphate veins and is also present in quartz-phosphate veins. Both these vein types cross-cut the greisen-bordered veins and massive greisen zones. A complex sequence of carbonates, phosphates, and silicates was precipitated later in open spaces, on regional joint surfaces, and within shear zones. Among the

mineralogically interesting species that occur in this sequence is a member of the childrenite-eosphorite series, stilbite, siderite, pyrite, and fluorite. For a summary of the paragenetic sequence, see Table 4.1 of Richardson *et al.* (1982). This is the second occurrence of a member of the childrenite-eosphorite series in Canada, childrenite having been recorded from the Big Fish River area, Yukon Territory, by Mandarino and Sturman (1976).

*Triplite* occurs as creamy-pink, anhedral grains, 3 to 10 mm in diameter. The main associated minerals are apatite, quartz, pyrite, and sphalerite. An X-ray powder diffraction pattern was prepared in a Debye-Scherrer camera of 114.6 mm diameter using Cu-K $\alpha$  X-radiation. Because the powder data for East Kemptville triplite do not differ significantly from those of other triplites, they are not given here. The cell parameters refined from the powder data are  $a$  12.134,  $b$  6.546,  $c$  9.939 Å,  $\beta$  106.08°,  $V$  = 758.56 Å<sup>3</sup> and  $Z$  = 8.

An electron microprobe analysis yielded the data given in Table I. The analysis was performed using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a sample current of 0.025  $\mu$ A, measured on brass. The standards used were hornblende (for Fe, Mg, and Ca), fluorite (for F), manganite (for Mn), and maricite (for P). The data were corrected using standard Bence-Albee factors.

A thermogravimetric analysis of 41.6 mg was carried out in a Mettler Thermoanalyzer equipped with a high-vacuum system and a quadrupole mass spectrometer to determine if the mineral contained hydroxyl. No quantitative data could be obtained