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# End-member triploidite from Cornwall

TRIPLOIDITE $(Mn,Fe)_2PO_4(OH)$, found recently on an old specimen from Wheal Owles, St. Just, Cornwall, in the British Museum (Natural History), is a rather rare mineral, occurring generally as a secondary product in a small number of granitic pegmatites. Following its original description from Branchville, Connecticut, by Brush and Dana (1878), the mineral has been recorded from Wien, Moravia (Kovář and Slavík, 1900) and from the Hunnakko pegmatite, Finland (Haapala, 1966). It has a monoclinic crystal structure with space group $P2_1/a$ and is isostructural with wolfeite $(Fe,Mn)_2PO_4(OH)$ and with the arsenate analogue sarkinite $Mn_2AsO_4(OH)$. Triploidite and wolfeite form an isomorphous series, and although occurrences of the latter have been reported by Frondel (1949), Mason (1940), and Kovář and Slavík (1900), no mineral with a composition close to the Mn- or Fe-end member has hitherto been recorded. The reported Fe:Mn ratios range from 1:3.30 for triploidite (with 14.88 % FeO) to 3.39:1 for wolfeite (Frondel, 1949). No isomorphous series between triploidite and sarkinite has been recorded.

Closely related to the triploidite group are the fluoride analogues triplite $(Mn,Fe)_2PO_4F$, zwieselite $(Fe,Mn)_2PO_4F$, and wagnerite $Mg_2PO_4F$. A comparison of the triploidite and triplite structures by Waldrop (1970) showed a general similarity but with small shifts in the atomic positions. The difference lies in the complete disorder of the F atoms between two possible sites in triplite and the complete ordering of the OH sites in triploidite, leading to a doubling in the triploidite cell volume. The X-ray powder patterns of the two are distinct (Mason, 1940), and the refractive indices are noticeably different.

In this investigation the new find of triploidite has been compared with that from the type locality and with a specimen of wolfeite from Hagendorf, Bavaria.

*Triploidite from Wheal Owles, Cornwall.* Triploidite has been found on a specimen of neotocite (penwithite) from Wheal Owles, St. Just, Cornwall (Collins, 1878, 1879; Clark *et al.*, 1978). In the specimen examined, the mineral occurs as several dozen small globular aggregates with a radial structure (fig. 1) deposited in a cavity on the botryoidal surface of neotocite. The size and colour of the triploidite globules range from 0.1 mm and pale orange-pink to 1 mm and orange-red. The specimen, BM 52182, was purchased by the British Museum (Natural History) in 1878 from Mr A. K. Barnett of Penzance and is accompanied by a label in his handwriting '"Penwithite" of Mr. J. H. Collins. From Wheal Owles, St. Just'. The mineral, representing the first occurrence of triploidite in the British Isles, has been distinguished from triplite by its optical characteristics and X-ray powder pattern. The latter shows the characteristic differences in line spacing and intensities for the five strongest lines of triploidite when compared with the triplite pattern.

*Chemical composition.* The three specimens used in the investigation have been analysed by electron-probe microanalysis using a Geoscan instrument. The results, shown in Table I after correction for matrix effects, were obtained using standards of pure Mn, Fe, and As, with schreibersite for P, and wollastonite for Ca and Si. The water values have been obtained by difference.

The Wheal Owles triploidite is virtually iron-free as the 0.03 % FeO reported in analyses 1 and 2 could well result from a failure to eliminate all the Mn-$K\beta$ counts from the adjacent Fe-$K\alpha$ peak. This occurrence is the first iron-free triploidite and, on account of its arsenic content, the first to show any evidence of solid-solution with sarkinite.

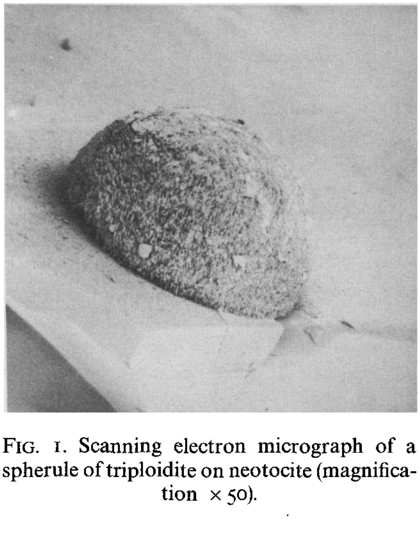

FIG. 1. Scanning electron micrograph of a spherule of triploidite on neotocite (magnification × 50).

TABLE I. *Electron-probe analyses and optical data for triploidite and wolfeite*

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| MnO | 59.16% | 59.84% | 41.54% | 38.38% | 12.35% |
| FeO | 0.03 | 0.03 | 21.49 | 24.78 | 50.09 |
| $P_2O_5$ | 28.54 | 28.58 | 32.05 | 32.17 | 32.04 |
| $As_2O_5$ | 3.64 | 3.83 | 0.02 | — | 0.04 |
| CaO | 0.34 | 0.35 | 0.04 | 0.04 | 0.01 |
| $SiO_2$ | 0.68 | 0.66 | — | — | 0.03 |
| $H_2O$* | 7.61 | 6.71 | 4.86 | 4.63 | 5.44 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

* By difference.

Molecular ratios based on 3 (Mn,P,...)

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Mn | 1.947 | 1.952 | 1.314 | 1.211 | 0.395 |
| Fe | 0.001 | 0.001 | 0.671 | 0.772 | 1.580 |
| Ca | 0.014 | 0.014 | 0.002 | 0.002 | — |
| Si | 0.025 | 0.024 | — | — | 0.001 |
| Σ Mn,Fe,... | 1.987 | 1.991 | 1.987 | 1.985 | 1.976 |
| P | 0.939 | 0.932 | 1.013 | 1.015 | 1.023 |
| As | 0.074 | 0.077 | — | — | 0.001 |
| Σ P,As | 1.013 | 1.009 | 1.013 | 1.015 | 1.024 |
| OH | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| $H_2O$ | 0.486 | 0.362 | 0.105 | 0.075 | 0.184 |

| | 1, 2 | 3, 4 | 5 |
|---|---|---|---|
| α | 1.709 | 1.735 | 1.749 |
| β | — | 1.736 | 1.750 |
| γ | 1.714 | 1.740 | 1.754 |
| γ:[001] | 5° for *v*<br>7° for *r* | 12° for *v*<br>14° for *r* | 33° for *v*<br>35° for *r* |
| | | 2V ~ 50° (est.) | ~ 50° (est.) |
| | | *r* > *v* v. strong | *r* > *v* v. strong |

1, 2. BM 52182 Triploidite. Wheal Owles, St. Just, Cornwall.
3, 4. BM 51863 Triploidite. Branchville, Connecticut, USA.
5. BM 1922, 990 Wolfeite. Hagendorf, Bavaria, Germany.

The specimens from all three localities have very close (Mn,Fe):P ratios, although the water content of the Wheal Owles specimen is higher than that to be expected from the presence of a single (OH) group in the formula. Evidently, additional water is present in the mineral and this may result from the fibrous nature of the triploidite globules and the hydrous environment in which they have formed (Clark *et al.*, 1978).

*Optical properties.* In transmitted light crushed fragments appear as either very small individual fibres or, more usually, sub-parallel fibrous aggregates. No pleochroism was observed and only α and γ were measured. The fibres are length slow and show dispersed extinction with γ:[001] greater for red light than blue light. The optical data are included in Table I.

Re-examination of Branchville triploidite and Hagendorf wolfeite gave results similar to those published in Frondel (1949). Grains from both specimens showed very strong dispersed extinction, which produced abnormal blue and pink interference colours in grains close to, or at, extinction for red and blue light respectively. γ:[001] was greatest in grains viewed along the obtuse bisectrix. There was also very strong dispersion of the optic axes with *r* > *v*. Some interference figures showed both a red and a blue fringe on the same side, but at different ends of an isogyre, consistent with horizontal dispersion.

The refractive indices of the Wheal Owles triploidite are slightly lower than the values obtained by linear extrapolation of the graph of iron content against refractive indices for the Branchville and Hagendorf specimens. Similarly, they are a little lower than the values for iron-free triploidite from the graph (fig. 1) in Frondel (1949).

*Conclusions.* The Wheal Owles triploidite represents a new occurrence of this mineral but its radiating spherulitic habit is very different from previous occurrences. Whereas triploidite and wolfeite are generally found as alteration products of lithiophilite or triphylite, or as inclusions in alluaudite, on the Wheal Owles specimen it is the sole phosphate present and was clearly deposited from residual phosphatic solutions after the precipitation of neotocite.

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