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Pharmacosiderite and unusual samples of scorodite from Peninsular Malaysia

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INTRODUCTION

Primarily this note serves two purposes. The first is to record the discovery of pharmacosiderite [$Fe_3(AsO_4)_2(OH)\cdot5H_2O$] at Pelepah Kanan tin mine (Johore), earlier this year, and at Sungei Besi mine (Selangor) in 1970. As far as the writers are aware this species has not hitherto been recorded from Peninsular Malaysia. The second is to record and describe some unusual scorodites that were collected from Sungei Besi mine a few years ago.

PHARMACOSIDERITE

At bench number F of Pelepah Kanan mine a thin detached plate was found consisting of a mass of crystals whose emerald-green colour and habit immediately indicated that they were pharmacosiderite: these encrust an aggregate of fractured quartz and loellingite cemented by iron oxide. Individual crystals occur as cubes replaced by a vicinal trapezohedron and so display the habit of the Cornish specimen figured by Palache et al. (1966, p. 996). The edge of the largest crystal is c. 1 mm.

At the time in question loellingite is the sole primary arsenic-bearing species and so the arsenate component of the pharmacosiderite must have been derived from it by oxidation.

Whilst crusts, etc., of scorodite are not uncommon at Pelepah Kanan, the specimen of pharmacosiderite is the only one that the writers have found there during the course of several visits. Indeed, the fairly common occurrences of scorodite and the rareness of pharmacosiderite in Peninsular Malaysia, and, indeed, in other mining areas where arsenopyrite and/or loellingite have been subject to oxidation lead, one to the conclusion that a rather special chemical environment is necessary for the development of pharmacosiderite.

X-ray diffraction data for the pharmacosiderite appear later in this note.

In the granitic eastern side of No. 2 opencast of Sungei Besi Tin Mines, Selangor, a number of highly stanniferous and originally sulphidic replacement bodies were discovered some 5 or 6 years ago, Fig. 1. These bodies, which have a maximum dip-length of c. 100 ft, and had probably developed more-or-less immediately beneath an impounding marble roof, which has since been removed by denudation, are all strongly oxidised throughout.

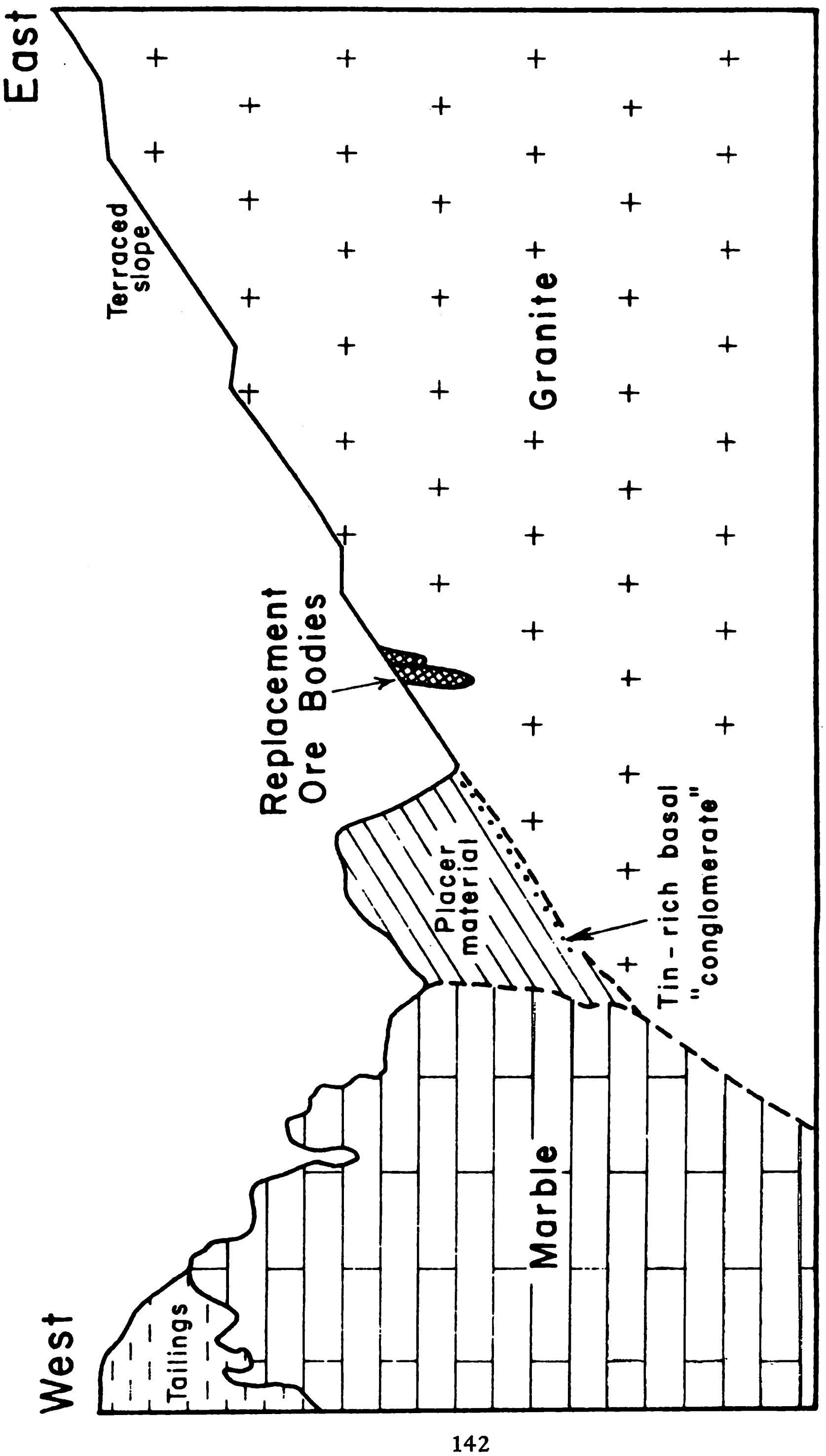

Fig. 1. Schematic section through the No. 2 opencast Sg. Besi Mines showing the approximate location of the replacement ore bodies in the granite. Looking north.

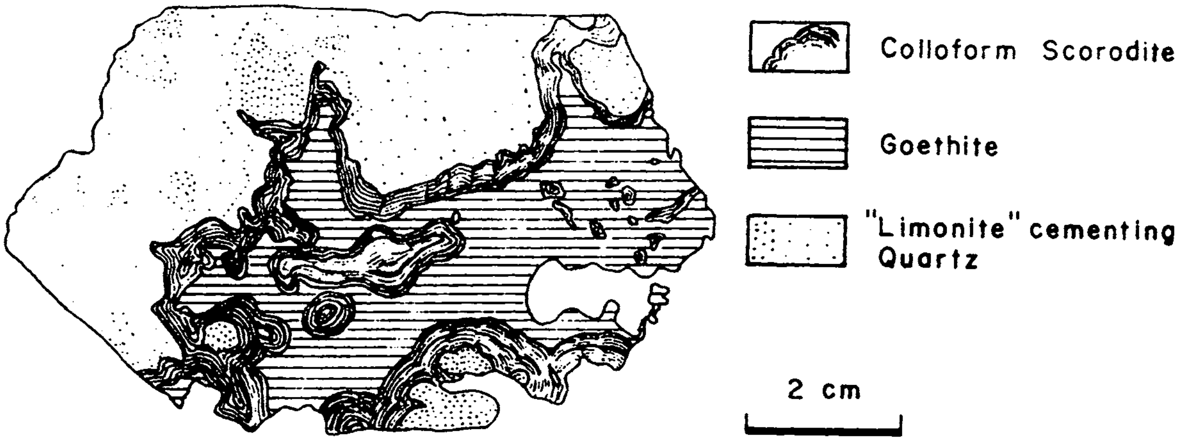

Fig. 2 Colloform "scorodite" from Lode 4, No. 2 Opencast, Sungei Besi Mines. Diagram traced from a cut and polished specimen.

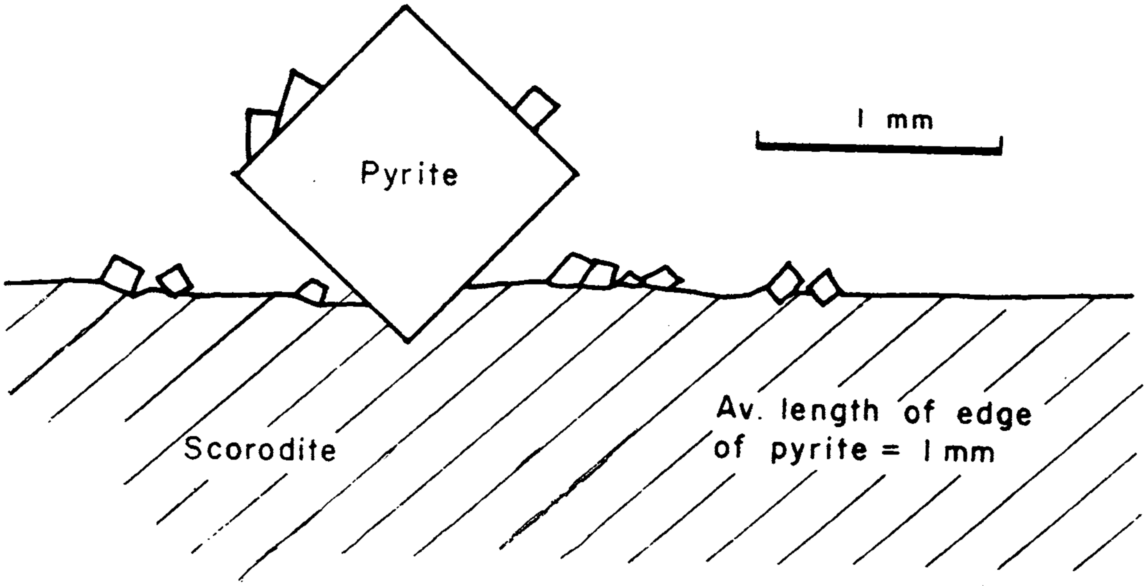

Fig. 3. Diagramatic section through a scorodite crystal from the Lee Gosan, No. 2 Opencast, Sungei Besi Mines, showing the common orientation of the larger pyrite crystals and the distribution of the minor ones.

One of these bodies, known as the Lee Gossan, provided both the pharmacosiderite and the crystalline scorodite described below.

This body originally consisted predominantly of massive quartz enclosing pockets of cassiterite and locally pyrite, arsenopyrite and pale-green fluorite. Although the quartz has protected some of the unstable minerals from oxidation a considerable proportion of the metallics has been converted to iron oxides whilst the arseno-pyrite has locally broken down yielding the arsenate and some, or all, of the iron ions necessary for the generation of both pharmacosiderite and scorodite.

The pharmacosiderite present is in very small amount by comparison with that of the scorodite, and such as has been found occurs as smallish crystals of the same colour and habit as that of Pelepah Kanan. It occupies small voids in limonite in specimens that for the most part consist of scorodite and in one instance scorodite has been deposited immediately on the pharmacosiderite. Not enough pharmacosiderite was found to justify its destruction in order to obtain X-ray diffraction data relating to it.

SCORODITE

In the Lee Gossan scorodite occurs, for the most part, as prismatic crystals displaying the habit figured by Dana (1932, p. 732), and reaching lengths of one cm or more. They may occur in isolation, but more usually they are found as dense aggregates on partially decomposed, cellular and blackened arsenopyrite, or within negative pseudomorphs of quartz after the sulpharsenide, or coating the walls of druses within masses of brown or orange iron oxides. In the last case the scorodite crystals sometimes display a palisade texture and on some occasions those parts of the crystal which are near the iron-oxide support are brownish, whilst the upper portions are greenish or bluish. Possibly, therefore, these crystals are in the process of being decomposed and yielding, as one product, iron oxide. However, as brown scorodite is known (Palache et al., 1966, p. 764) the brown hue of the crystals noted above may not be due to partial decomposition. Most of the scorodite crystals collected at Sungei Besi are of a rather dull, dark-green colour, but others that are paler green or pale greenish-blue are not uncommon. In addition, on rare occasions sky-blue and violet scorodites are of rare occurrence in the mineral kingdom, and have not been recorded before from Malaysia, they are known from extra-Malaysian areas, and the fact that such coloured ones exist is noted by Palache et al (1966, pp. 764–65).

It is also of interest to record that some of the scorodite is encrusted with small cubes of pyrite.

In addition, the neighbouring No. 4 Lode, that is highly oxidised, has provided some beautiful specimens of what in the field might be reasonably called colloform scorodite, but which, as will be apparent from the X-ray diffraction data provided later, is not scorodite ($FeAsO_4.2H_2O$) but Iron (III) Arsenate Hydrate ($FeAsO_4.xH_2O$).

This colloform arsenate (Fig. 2) locally encrusts the walls of what were originally druses in ore-body material consisting essentially of quartz cemented by light-brown iron oxides. In addition, spherulitic masses, singly or in close association, of the arsenate occur suspended in rather dark-brown iron-oxide, that in the hand-specimen displays a rather ill-defined colloform texture, and fills most of the centre of the original druse. Whilst the wall-encrusting arsenate may well have preceeded the disposition of the dark-brown oxide noted above, it is possible that the spherulitic masses of arsenate may have developed within the oxide when it was in gel state. In the hand-specimen the colloform arsenate is seen to be composed of many thin concentric shells that vary in colour from near-white, through pale olive-green, to dark olive-green. Judging by the distribution of the variously coloured bands, and by the fact that the spherulites now consists of radially disposed crystals that do *not* extend from the centre to the perimeter, but are confined to a limited number of colour bands, it seems likely that the arsenate developed by the successive deposition of a number of layers of gel, each of which developed Liesegang bands, and each layer subsequently crystallised in such a way that the long axes of the resulting crystals were about normal to the surface of the parent gel layer.

FURTHER OBSERVATIONS ON THE OXIDATION OF THE SUNGEI BESI ORE BODIES

The Lee Gossan and associated ore bodies of Sungei Besi mine, have, as noted earlier, been subject to oxidation from their tops to their bottoms. Only in the more quartzose ones have the primary sulphides and sulpharsenides been locally reasonably well-preserved. In some instances, however, as in the No. 4 Lode, masses of pyritic ore are seen surrounded by completely oxidised ore. There are relict sulphide masses owe their preservation sometimes to the early development of an impermeable iron oxide layer around them, and sometimes to the fact that they occur at points near the hanging wall which were roofed by a dome of locally highly-kaolinised and impermeable granite. The occurrence of these stranded sulphide masses also suggests that during the period of oxidation the water-table must have been lowered rapidly in response to the rapid down-cutting of the river along the granite/marble contact. This event was probably associated with the development of the low sea-level in Pleistocene times. Later, when the sea-level rose, and the Sungei Besi valley became infilled with sediments, and the drainage became very slugghish, the oxidised in situ ore bodies were in part covered by sediments that were locally accumulating in a reducing environment. It was at this stage that the cubes of pyrite locally investing the scorodite, and noted above, were deposited. However, examination of this pyrite/scorodite association under a binocular microscope provides the following data for which a unique answer cannot be offered. Briefly, the pyrite cubes on contact with the scorodites are generally anchored in the outer parts of the scorodite cyrstals and they are commonly so orientated that they (the pyrite crystals) rest on a cube edge, rather than on a face (Fig. 3). Satellite pyrite crystals have grown on these anchored ones. How then can one explain these observations? One might consider the possibility of pyrite crystals being developed in a near by reducing environment. and then being transported and deposited and anchored on the scorodite crystals which were still developing in an oxidising environment. Were this the correct explanation one would expect each pyrite crystal to be resting on one of its faces, that is, in the position of maximum stability, and not, as one often observes, on an edge of a cube. To suggest that the pyrite cyrstals were rotated into their present position by the force of crystallisation of the scorodite does not provide a very convincing solution. So this explanation of the phenomena is not acceptable.

An alternative, and somewhat more acceptable explanation, postulates that at some time after the scorodite had completed its development, the environment, for reasons noted earlier, changed to a reducing one. Biogenically derived sulphide ions and native sulphur entered the system and reacted initially with some of the in situ ferric ions (that would need to be converted at the outset to ferrous ones) of the scorodite, thus initiating the development of pyrite by replacement. What happened to the released arsenate ions is unknown, but some of them may have been reduced and some of the resulting arsenide ions may have been incorporated into the pyrite lattice. (If this did happen then this pyrite would be likely to be quite anisotropic even when polished by mechanical means. Unfortunately this has not yet been investigated). The further development of the pyrite crystals beyond the scorodite surface may have been effected by all the ingredients necessary for the development of the sulphide being transported to the site of pyrite deposition but in concentrations which were such that the solubility product of the sulphide was not exceeded except at the surfaces of the already established pyrite centres.

Perhaps the most important lesson to be learned from this portion of the note is that crystal development phenomena, similar to the one described above, which are quite frequently encountered in mineral deposits, are by no means well understood by most of us who are concerned with the study of ore-genesis!

X-RAY DIFFRACTION DATA

X-ray diffraction data for pharmacosiderite from Pelepah Kanan, and for scorodite and colloform 'scorodite' from Sungei Besi Mines, were obtained by means of a Phillips X-ray generator (PW1011) with the detector coupled to a scintillation counter. X-rays were generated using a copper target, a nickel filter, a voltage of 50 KV and a current of 30 ma. A pulse-height analyser, with the following readings, was set on the scintillation counter:— EHT, 0.7KV; lower level, 260 mV; window, 1.3V; attenuation, 2. Silicon was used as an internal standard. The scan and chart rates were 0.5 degree/minute and 10 mm/minute. Each sample was run from low to high angle and then from high to low angle having first slightly tilted the slide carrying the sample smear (which was deposited from acetone).

The necessary corrections, obtained by using the CuK_α lines of silicon, and ranging from 0.01^0 to 0.03^0 of the 2θ values, were made.

The 2θ values were averaged and the d-spacings were read to two places of decimals, from the appropriate charts.

The resulting d-spacings and intensities data, together with relevant d-spacings and other data from the JCPDS file, are tabulated below. It must be noted that for each mineral a number of peaks that might be expected from the d-spacings recorded in the JCPDS file were *not* detected: usually those that were missing have recorded intensities in the file of 10 or less.

REFERENCES

DANA, E.S., 1932. A textbook of mineralogy (revised by W.E. Ford), 4th edn., Wiley and Sons, Inc., N. York. 851 pages.

PALACHE, C., BERMAN, H. and FRONDEL C., 1966. A system of Mineralogy, vol. 2 (7th edn., 5th printing), Wiley and Sons, Inc., N. York. 1124 pages.

Pharmacosiderite (Pelepah Kanan, Johore)		Pharmacosiderite JCPDS File No. 17–466		
I/I_1	d-spacing	d-spacing	I/I_1	hK1
100	7.95	7.98	100	100
35	4.63	4.60	40	111
30	4.00	3.99	30	200
50	3.26	2.25	50	211
30	2.83	2.816	50	220
15	2.65	2.653	16	300, 221
30	2.53	2.529	30	310
20	2.41	2.404	30	311
15	1.89	1.877	16	411, 330
10	1.79	1.782	20	420
5	1.60	1.594	16	500, 430
5	1.54	1.533	14	511. 333

Scorodite (Lee Gossan, Sg. Besi Mines)		Scorodite JCPDS File No. 18–645 $FeAsO_4.2H_2O$		
I/I	d-spacing	d-spacing	I/I_1	hk1
65	5.62	5.65	80	111
10	5.16	5.21	5	200
25	5.03	5.05	40	020
100	4.48	4.50	100	002
30	4.11	4.11	40	211
30	3.82	3.82	40	112[
10	3.34	3.35	5	211, 022
80	3.18	3.20	80	122
40	3.06	3.70	60	311
50	3.00	3.01	60	131
10	2.76	2.769	5	113
15	2.68	2.695	40	032
35	2.60	2.601	60	400
30	2.51	2.511	40	040
10	2.32	2.324	20	331
5	2.18	2.190	5	412
5	2.12	2.118	5	322
10	2.01	2.011	5	
5	1.95	1.954	5	
5	1.80	1.805	5	

Colloform 'Scorodite' Lode No. 4, Sg. Besi Mines		Iron (III) Arsenate Hydrate JCPDS File No. 19–603 $FeAsO_4.xH_2O$	
I/I_1	d-spacing	d-spacing	I/I_1
50	5.59	5.61	70
10	5.16	5.17	5
15	5.02	5.02	30
100	4.46	4.48	100
20	4.09	4.08	30
15	3.80	3.80	15
10	3.38	3.38	5
10	3.34	3.34	15
40	3.18	3.18	90
50	3.06	3.06	75
10	3.00	3.00	45
10	2.68	2.679	40
40	2.58	2.584	60
10	1.64	1.649	5