Sampleite from Jingemia Cave, Western Australia

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SUMMARY. Sampleite from Jingemia Cave, Watheroo (30° 16' S. 116° 00' E.), 190 km north of Perth, Western Australia is derived from the alteration of copper sulphides in contact with guano deposits. Associated minerals are atacamite, weddellite, and gypsum on goethite and manganese-oxide-coated friable quartz rock. Birnessite, halite, dolomite, taranakite, todorokite, apatite, and malachite are also present.

The sampleite occurs as platy spheroidal aggregates to 0.3 mm with $D 3.20 \pm 0.01$, $\alpha 1.625 \parallel [010]$, β and $\gamma 1.674$, all ± 0.002 , α Turquoise Green 41d to Light Blue-Green 39d, β and γ Benzol Green 41 to Venice Green 41b, absorption $\alpha < \beta = \gamma$, $2V_{\alpha} 5-10^{\circ}$. Chemical analyses are given.

 $Cu_3(PO_4)_2.3H_2O$, a corrosion product reported on artifacts, is believed to be sampleite. A further occurrence of sampleite has been recorded from Brookton, 120 km ESE. of Perth. The structurally related mineral lavendulan has been reported from five Western Australian localities.

DURING an investigation of cave minerals at the Western Australian Government Chemical Laboratories, specimens from the collection of Dr. E. S. Simpson were re-examined. A specimen marked '?tagilite' from Jingemia Cave, 6 km north-west of Watheroo (30° 16' S. 116° 00' E.), 190 km north of Perth, was found to be sampleite. In Simpson (1951) this specimen was reported as an undetermined species and in Simpson (1952) as tagilite. The specimen was collected in 1907-8 by Mr. A. Monger, probably during guano mining.

The cave has been described by Montgomery (1908) and Woodward (1912) and is situated, together with several smaller tunnels to the north, at the base of a 26 m cliff in the 61 m diameter collapse doline. The country rock is a partially silicified Proterozoic dolomite intruded by dolerite dykes. A small chalcopyrite vein found in the cave wall by R. Adams of Electrolytic Zinc Co. of Australia has been altered by phosphatic solutions from the avian and chiropterean guano deposits, resulting in crusts of atacamite with weddellite and minor sampleite coating the cliff face near the tunnel entrances.

In Simpson's specimen, the sampleite occurs as platy spheroidal aggregates up to 0.3 mm with

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minor atacamite and gypsum encrusting a friable, cavernous, goethite- and manganese-oxide-coated quartz rock. The *in situ* position of this specimen was not recorded. Other minerals identified from the quartz cavities or as crusts are birnessite, halite, dolomite, taranakite, todorokite, apatite, and malachite, which were collected by the senior author on several trips.

Sampleite was originally described from Chuquicamata, Chile by Hurlbut (1942) associated with gypsum, atacamite, jarosite, and limonite. It is also reported from Mantos Blancos, Chile, with atacamite, chrysocolla, copper carbonate, gypsum, calcite, and halite by Knobler and Joseph (1962).

In May 1977, G. Blackburn of Otter Exploration N.L. forwarded a specimen from an outcrop in the north-west corner of Land Location 3323, Brookton $(32^{\circ} 25' S. 117^{\circ} O' E.)$, 120 km ESE. of Perth. This contained sampleite with quartz and iron oxides in a cordierite gneiss of Archaean age. The copper is derived from sulphides and the phosphate possibly from biological activity or superphosphate used on the wheat paddock. No apatite was observed in a number of thin sections of the gneiss and associated chert.

The structurally related mineral, lavendulan, has been identified from the Alice Mary Copper Mine at Kundip, High Range on Lyndon Station, Bali Low Copper Mine in the Capricorn Range, Bulldog Gold Mine at Ravensthorpe, and the Frances Furness Gold Mine at Marvel Loch in Western Australia. No phosphate analyses are available for these occurrences to compare with the phosphorian lavendulan of Kleeman and Milnes (1973).

Physical properties. The specific gravity of Jingemia sampleite is $3\cdot 20 \pm 0\cdot 01$ by sink-float, and the colour is Ridgway Peacock Blue 43i to Italian Blue 43.

Optical properties. Refractive indices (all ± 0.002): α 1.625||[010] β and γ 1.674 (orientation indeterminate). Colour (Ridgway, 1912): α Turquoise Green 41d to Light Blue-Green 39d; β and γ Benzol Green 41 to Venice Green 41b, absorption: $\alpha < \beta = \gamma$, $2V_{\alpha}$ 5-10°. The determinations were

made on wedge-shaped aggregates of subparallel [010] plates approximately $0.2 \times 0.2 \times 0.02$ mm in size. Except that the pleochroic scheme given by Hurlbut is α deep blue, β light blue, γ colourless, the optical data are similar. The pleochroic scheme of Chuquicamata sampleite examined by the authors agreed closely with that of the Jingemia specimen.

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The X-ray data of Jingemia sampleite generally agree with the published data of Guillemin (1956) and Hurlbut (1942). Guinier patterns of Western Australian sampleite showed more weak lines and intensity variations but are similar to PDF 11.349. Weissenberg films are composed of symmetrically oriented streaks indicating considerable disorder. The respective zero layers could not be identified or indexed.

The similarity between sampleite and the artificial compound Cu₃(PO₄)₂.3H₂O, (PDF 1.0054 and 22.548), indicates a close structural relationship. Otto (1959, 1961, 1963) reports the occurrence of $Cu_3(PO_4)_2$. $3H_2O$ as a corrosion product on ancient bronzes. The original X-ray powder data was published by Hanawalt et al. (1938). Otto (pers. comm., 1973) supplied the following X-ray powder data on his corrosion product (Cu- K_{a} , 114:4 mm diameter camera): 9.7 (100), 6.8 (10), 4.3 (10 wide), 3.01 (60), 2.88 (?), 2.65 (10), 2.56 (10), 2.41 (10), 2.16 (5), 1.70 (30), 1.61 (5), 1.51 (5), 1.36 (wide). This shows good agreement with Cu₃(PO₄)₂.3H₂O, PDF 1.0054, though there is some variation in intensities. The materials of Hanawalt and Otto both show a similar agreement with sampleite (PDF 11.349) and the Jingemia sampleite but again the intensities are a little variable. The corrosion product is considered to be sampleite and was not previously recognized because the PDF card for sampleite was published after the work of Otto.

Chemistry. Because the micaceous habit of the sampleite resulted in a gradual loss of the meagre material during separation from intergrown atacamite and iron and manganese oxides, analysis I had to be performed on slightly impure material.

Three analyses of sampleite are presented in Table I. A 'wet' analysis and an electron probe microanalysis of the Jingemia sampleite and an electron probe microanalysis of a Chilean sampleite specimen obtained from Minerals Unlimited, U.S.A. The analyses and unit cell content calculations in Table I show that the Jingemia sampleite is relatively high in calcium, which may be derived from associated weddellite. However, with atacamite and iron and manganese oxide impurities this would indicate a larger percentage of impurities than were actually observed to be present.

It would further appear from a comparison of available data that the structures of sampleite and lavendulan are easily distorted by variations in

TABLE I. Analyses of sampleite

| | I | 2 | 3 | 4 |
|--------------------------------|-------------------|-------|-------|--------|
| CuO | 44 | 43.91 | 37.76 | 44.12 |
| P_2O_5 | 29 | 36.66 | 35.88 | 32.10 |
| CaO | 8.8 | 5.81 | 5.99 | 5.83 |
| MgO | 0.12 | _ | | 0.52 |
| K ₂ O | 1.2 | | | 1.49 |
| Na ₂ O | 2.7 | 4.39 | 11.12 | 3.11 |
| Cl | 3.8 | 1.20 | 1.40 | 4.00 |
| H ₂ O | 9 [.] 4* | _ | _ | 9.74 |
| MnO | 0.28 | | — | |
| Fe ₂ O ₃ | 0.02 | | | _ |
| Insol. | I·2 | — | | _ |
| Fotal | 100.0 | | | 100.01 |
| $O \equiv Cl$ | 0.9 | | | 0.91 |
| | 100.0 | | | 100.00 |
| | | | | |

* Water by difference.

I. Sampleite, Jingemia. Analysis by M. B. Costello. Unit cell content:

(Na,K)_{1.07}(Ca,Mg)_{1.49}Cu_{5.00} (PO₄)_{3.70}Cl_{0.97}.4.72H₂O. 2. Sampleite, Jingemia. EPM analysis by R. B. W. Vigers, C.S.I.R.O.

3. Sampleite, Chile. EPM analysis by R. B. W. Vigers, C.S.I.R.O.

4. Sampleite, Chile. Analysis by Gonyer in Hurlbut (1942). Unit cell content:

 $(Na,K)_{1\cdot15}(Ca,Mg)_{1\cdot02}Cu_{4\cdot84}(PO_4)_{3\cdot94}Cl_{0\cdot98}.4.71H_2O.$

chemical composition resulting in disparities of intensity and spacing of the X-ray powder data patterns.

The electron probe microanalyses by R. B. W. Vigers were done on the M.A.C. instrument at the C.S.I.R.O., Floreat, Western Australia and the data corrected for atomic number, fluorescence, and matrix effects by the MAGIC-4 program of Colby (1968). Standards of analysed apatite, pyromorphite, muscovite, calcite, and nepheline were used. The analysis of Jingemia sampleite by M. B. Costello was done by atomic absorption and spectrophotometric methods.

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