Notes on Some Additional Minerals from the Oxidized Portion of the Broken Hill Lode, N.S.W., with Observations on Crystals of Coronadite

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Abstract—Six additional secondary minerals: chalcophane, hydrozincite, aurichalce, olivenite, acanthite and goslarite are recorded from the Broken Hill lode N.S.W., and some crystallographic data on single crystals of coronadite is presented.

Introduction

Recent mining operations by Broken Hill South Limited in and adjacent to the Open Cut has revealed the presence of a number of additional minerals not recorded in the previous accounts of the mineralogy of the Broken Hill lode (Smith, 1926; Stillwell, 1953). These minerals are all of a secondary nature and have formed late in the oxidation cycle insofar as they occur as overgrowths on earlier formed secondary minerals.

The identity of each mineral has been verified by X-ray diffraction measurements and, where appropriate, by optical properties either in transmitted or in reflected light.

1. Chalcophane, (ZnMnFe)Mn₄O₅·2H₂O*

Numerous specimens of crystallized chalcophane were found lining small cavities in and forming a velvet-like overgrowth upon stalagtitic pyrolusite. The minute crystals range in size from 0.02 mm to 0.05 mm diameter and consist of very thin hexagonal plates of a lustrous deep purple-red colour.

In polished section (Plates 1 and 2) those crystals the “c” crystallographic direction of which is approximately parallel to the plane of the section, show maximum reflectivity of a strong white colour and have very strong reflection pleochroism from white to dark grey with sharp parallel extinction. These sections possess extreme anisotropism of a uniform white colour. Basal sections are not so strongly reflecting and their isotropism is always masked by a most intense carmine red internal reflection when viewed between crossed polars. Internal reflections are also observed in ordinary light but the intensity is considerably subdued. Twinning is evident in basal section (Plate 2) where the optical continuity, as evidenced by uniform reflection and the co-planar arrangement of the extensive 0001 faces suggests that the twinning occurs on the 1120 (prism) plane.

The host material consists of a rhythmically banded psilomelane of a distinctly blue-grey colour in reflected light, together with pyrolusite of a creamy white colour in perfect colloform arrangement (Plate 1). The outer layers give way to a confused aggregate of minute pyrolusite crystals with the chalcophane crystals lining the outermost surface. In a few instances the chalcophane supports isolated nests of hair-like coronadite crystals (q.v.). Chalcophane occurs also investing and, in part, replacing embolite.

2. Hydrozincite, Zn₅(OH)₆(CO₃)₂

Among the many pieces of smithsonite obtained from a large mass of coronadite ore at the base of the Open Cut were several, both of the globular and of the dog tooth type, which appeared to have been converted to a white porcellanous mineral. The white mineral proved to be hydrozincite.

The dog tooth crystals were, in most instances, complete pseudomorphs of hydrozincite after smithsonite but the globular masses were, in general, only partially replaced (Plate 3), leaving remnants of unplaced smithsonite.

The hydrozincite is of the harder compact type and is barely transluscent in thin section. The mineral is cryptocrystalline (colloidal) except for the profuse development of hysteresis fractures resulting from the hardening of the hydrozincite colloid.
3. Aurichalcite, \(2(ZnCu)CO_3 \cdot 3(ZnCu)(OH)_2\)

The 350' level of the South Mine yielded several pieces of cuprite liberally coated with malachite and externally covered with fine acicular crystals of a pale sky blue colour.

The following optical properties were determined on some detached crystals: \(X=a\) with \(n=1.65\); \(Z=c\) with \(n=1.75\); straight extinction; pleochroic in thicker pieces from colourless to faint blue-green. These determinations together with "d" and "I" values confirm the identity of the mineral as aurichalcite. This mineral, the occurrence of which at Broken Hill was alluded to by Smith (loc. cit.) but never confirmed, is much paler in colour than the classic material from Kelly, New Mexico, but the X-ray diffraction patterns of the two are identical.

4. Olivenite, \(Cu_4(AsO_4)(OH)\)

Two pieces of lode material encrusted with a fine granular apple green mineral were obtained from the southern end of the Open Cut. The green mineral has been identified as olivenite which, under high magnification, is seen to be minutely crystallized.

Olivenite has been recorded only twice previously in Australia: at Kundip in Western Australia and at Mount Diamond near Pine Creek in the Northern Territory. The very limited occurrence at Broken Hill of this rare copper arsenate is due, no doubt, to the scarcity of primary arsenic minerals.

5. Acanthite, \(Ag_2S\)

The orthorhombic form of silver sulphide was found in the 350' level of the South Mine. One large mass weighing some 70 lb. and several smaller pieces were obtained. The mineral is soft and sectile, of a dull grey colour with a shining metallic streak and contained numerous small grains of extraneous material such as garnet, quartz, plentiful iron oxides and cerussite. It is clearly of a supergene nature and was closely associated in the stope with iodrite and embolite.

A differential thermal analysis of the silver sulphide after acid leaching to remove iron oxides (Fig. 1) shows a sharp endothermic peak at 180°C representing the inversion from the orthorhombic form (acanthite) to the unstable isometric form (argentite). The progressive breakdown of the silver sulphide with loss of sulphur is spread over a range of temperatures reaching a maximum at 700°C. The D.T.A. run was repeated several times without removing the specimen from the oven. In each case the heating curve and the cooling curve were identical and the inversion point constant.

This spontaneous reversibility:

\[ \Delta_{180°C} \]

\[ \text{acanthite} \rightleftharpoons \text{argentite} \]

agrees with the earlier findings of Ramdohr (1942) and the much later work of Roy et al. (1959).

![Fig. 1](image)

Differential thermal analysis curve of Broken Hill acanthite (corrected for base line drift) showing acanthite-argentite inversion point at 180°C, the progressive exothermic rise to a 700°C peak due to loss of sulphur and the ultimate melting of the resulting metallic silver indicated by a sharp endothermic peak at ca. 960°C

Chemical analysis of the Broken Hill acanthite gave the following results:

\[
\begin{align*}
\text{Ag} & \quad \ldots \quad 62.2 \\
\text{Cu} & \quad \ldots \quad 2.1 \\
\text{S} & \quad \ldots \quad 9.0 \\
\text{Remainder, mainly iron oxides} & \quad 26.7
\end{align*}
\]

These figures indicate an Ag:Cu percent ratio of 84.8:2.8. The mineral contains insufficient copper to rank as the cuprian variety jalpaite \((AgCu)_2S\) which has been recorded from Broken Hill by Stillwell (loc. cit.) as supergene replacements of primary galena.

6. Goslarite, \((ZnSO_4 \cdot 7H_2O)\)

The only recorded sulphates from the oxidized zone at Broken Hill are the insoluble salts anglesite, linarite and brochantite. The common soluble sulphates chalcocanthite and melanterite have not been noted, and, with the abundance
of zinc minerals, it is perhaps not surprising that the rarer zinc sulphate, goslarite, occurs preferentially, though not hitherto recorded.

Several fine specimens of goslarite of a delicate coral pink colour (due to the admixture of manganese) were found in the shallow levels of the South Mine immediately beneath the Open Cut. The goslarite consists notably of stout stalactites up to four inches long adhering to quartzose lode material and as microcrystalline masses lining cavities and joints in low grade ore. The interior of some of the stalactites is more or less hollow and the inner surfaces are sometimes lined with well-formed crystals of the same mineral, up to \( \frac{3}{8} \) in length.

A partial chemical analysis showed a ZnO to MnO ratio of 33·2:4·1 and this may be sufficient to identify the Broken Hill material as a "mangangoslarite".

**Coronadite Crystals**

The occurrence at Broken Hill of coronadite (MnPbMn\(_6\)O\(_{14}\); pseudo-tetragonal) as colloform masses, rarely with a radiating fibrous texture, is well known; it is now possible to record, for the first time from this locality, single crystals of this rare mineral. The crystals are very minute—rarely exceeding 0·1 mm in length—but are well formed and of an extremely acicular habit. The X-ray data obtained by means of a Phillips 1010 diffractometer (CuK\(_\alpha\), 1·54R) agreed precisely with that of Frondel and Heinrich (1942) on material from CliftonMorenci, Arizona with the exception of a strong peak at "d" 3·02. This line is not listed by Frondel and Heinrich and may be due to impurity.

The coronadite crystals occur either in small cavities in psilomelane where they are supported by crystals of chalcanphane, or as an outer coating of clustered crystals of random orientation upon stalagmitic limonite and psilomelane. When thus aggregated the coronadite is of a distinct indigo-grey colour.

The crystals are sufficiently lustrous to examine in reflected light by immersion in cedar oil. They show strong reflectivity of a white colour and have sharp straight extinction. Between crossed polars the crystals exhibit strong anisotropism of white, dark grey and dark brown. An unusual prismatic cleavage is evident in many crystals (Plate 4) and this gives rise to a pronounced fraying at the terminal ends of the crystals and often spreads almost the full length of the crystal.

The crystals appear to consist predominantly of prism (110) and basal pinacoid (001) but there is evidence of the development of two or three pyramidal faces. One of these faces, measured in profile under the microscope, indicated an interfacial angle of approximately 55° with respect to the prism and another approximately 45°. Twinning is a feature of some crystals with a steep pyramidal face as the twin plane. This results in the development of well-formed arrow-head twins (inset of Plate 4) having an included angle of 56°; this would indicate an internal angle of 28° between this particular pyramid and the prism.

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**References**


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Explanation of Plates

PLATE 1
Tabular crystals of chalcophanite resting within a nest of crystals of the same mineral cut approximately parallel to their "c" crystallographic axes. The dark grey mottled mineral at the top is embolite. The base of the specimen consists of limonite (dark grey), psilomelane (whitish) and pyrolusite (light grey mottled) all in perfect colloform arrangement. (Oil immersion, reflected light \( \times 1000 \).)

PLATE 2
Chalcophanite crystals lining a small cavity in pyrolusite-limonite and embedded in clear plastic. The two highly reflecting crystals are orientated approximately normal to the "c" crystallographic axes and the one on the left-hand side shows twinning apparently on the (1120) plane. (Oil immersion, reflected light \( \times 1000 \).)

PLATE 3
Hydrozincite (dark—almost opaque area) showing profuse development of anastomosing hysteresis fractures, replacing smithsonite with a remnant of unplaced zinc carbonate top right. (Transmitted light. \( \times 20 \).)

PLATE 4
Single crystals of coronadite. Some of the smaller crystals, e.g. at X, show a fraying due to pronounced prismatic cleavage. Inset shows a characteristic arrow-head twin. (Oil immersion reflected light. \( \times 750 \).)

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