Cl-K amphiboles seem to be due to the difficulties in chlorine chemical analysis rather than to their limited distribution.

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Lead chromate minerals from the Argent lead-silver mine, Transvaal, South Africa: crocoite, vauquelinite, and a possible second occurrence of embreyite

THE disused Argent lead-silver mine is situated on the farms Brakfontein 559 IR., Dwarsfontein 209 IR. and Boschpoort 211 IR., about 80 km east of Johannesburg in the Transvaal Province of the Republic of South Africa. A series of sub-parallel siderite-galena-sphalerite veins cuts an outlier of Bushveld Complex rocks comprising diabase, gabbro, and minor pyroxenite (Willemse, 1944). The geology of the deposit was described by Wagner (1924), who noted the presence of several supergene minerals including crocoite, in the nearsurface zone. Willemse (1942) gave a detailed account of the ore assemblage, and noted the presence of galena, sphalerite, pyrite, chalcopyrite, pyrrhotite, arsenopyrite, gudmundite, argentite, bournonite, boulangerite, and tetrahedrite. The principal gangue minerals are quartz, siderite, and calcite. Much of the older literature does not refer to the deposit by name. Wagner (1924) described 'A Transvaal silver-lead deposit', Willemse (1942) wrote of 'Lead deposits near Argent Station', and De Jager (1966) spoke of 'A Transvaal lead silver mine . . . near Argent Station'. In keeping with modern popular usage, the occurrence is referred to here as 'The Argent lead-silver deposit'.

The locality is popular among local mineral collectors because of its abundance of well crystallized pyromorphite, vanadinite, mimetite, cerussite, crocoite, and a number of less common phases. These minerals will be the subject of a later publication. Vauquelinite was identified by X-ray diffraction in a sample of gossanous material collected by one of the authors (MJS) from an old prospecting pit some 150 m west of the workings on the 'Main Lode' (Wagner, 1924). Several examples of this mineral have since come to light from the material of local mineral collectors. The minerals crocoite and vauquelinite are described in this paper with particular reference to their chemical composition.

Paragenesis and habit. Crocoite and vauquelinite are both late minerals in the supergene paragenesis. Crocoite occurs as euhedral crystals of varying habit associated with, but post-dating, cerussite, limonite, pyromorphite, and vanadinite. Crocoite crystals commonly occur perched on almost formless masses of intensely corroded vanadinite, or associated with less-corroded pyromorphite, both



FIG. 1. Sketches to illustrate the various habits of crocoite in the Argent deposit.

of which are later minerals than cerussite, which is the most abundant of the secondary lead minerals.

The crocoite crystals occur in a variety of forms (fig. 1). Long prismatic crystals are dominated by $\{110\}$ and show a number of terminating forms, most commonly of the type $\{hkl\}$ and $\{h0l\}$. Flattened, bladed crystals are dominated by $\{101\}$ with $\{110\}$ of subordinate importance. Such crystals have complex $\{hkl\}$ terminations and commonly exhibit growth zonation. Short prismatic crystals occur less commonly with complex $\{hkl\}$ and $\{0kl\}$ terminating forms; growth zoning is rarely encountered in this habit. Striations parallel to c are encountered in all types on $\{110\}$ but never on $\{100\}$. The colour ranges from red to yellow-orange, and the lustre from adamantine/ transparent to sub-vitreous/opaque.

Vauquelinite is generally later than crocoite and shows three distinct modes of occurrence. (a) Dark olive-green porous masses of vauquelinite occupy cavities in cerussite and limonite-rich gossan, where it commonly contains highly corroded prismatic crystals of crocoite. Pyromorphite is always associated. (b) Well-formed botryoidal crusts of vauquelinite are associated with radiating sprays of yellow-green pyromorphite crystals, and with a notable absence of crocoite. (c) Well-formed botryoidal crusts of vauquelinite are associated with, and perched upon, short equant prisms of crocoite. In this case, the crocoite is not corroded and has retained its adamantine lustre.

Williams (1974) indicated that vauquelinite may replace crocoite as indeed appears to be the case in (a) above. Occurrences (b) and (c) indicate that vauquelinite can form independently of crocoite. In the occurrence described in (c), where the crocoite crystals are completely non-corroded, considerable overlap in the Eh-pH stability fields of the two minerals is indicated. Therefore it is considered that the preferred formation of vauquelinite is controlled largely by the activities of copper and phosphate ions.

The chromium content of both minerals is undoubtedly derived from the weathering of the gabbroic host rocks in which chromite occurs as an accessory mineral.

Embreyite. A single sample has been recovered by one of the authors (MJS), again from a prospecting pit to the west of the 'Main Lode' workings, on which a single spherical crust of orange-brown material was perched at the junction between a pyromorphite crystal and limonitic matrix. The orange-brown material was identified as embreyite by a powder photograph, but regrettably there was insufficient material to facilitate confirmation by microprobe analysis. The habit and colour however, as well as the X-ray results are consistent with the original description of embreyite (Williams, 1972). So far, the search for further material has proved fruitless.

Chemistry of crocoite and vauquelinite. The compositions of crocoite and vauquelinite were determined on an ARL SEMQ electron microprobe using a counting time of 20 seconds on peaks and 10 seconds on background. The accelerating voltage was 15 kV and the beam current 20 nA on a Faraday Cage. The results were processed by use of the MAGIC-IV interelemental correction procedure.

The mean compositions of crocoite (10 analyses) and vauquelinite (9 analyses) are compared with the theoretical compositions in Table I. Arsenic was determined (but not detected in either mineral) because of its occurrence in fornacite (Pb₂(CuFe) CrO₄(As,P)O₄OH), which is a mineral closely related to vauquelinite.

TABLE 1	E.	Chemical	data	for	croicite	and	vauquelinite
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	1	2	3	4
PbO	69.06	69.23	63.44	65,20
Cu0	-	0.03	11,20	10.74
FeO	-	0.01	-	0.22
CaO	-	0.20	-	0.19
Cr03	30.94	30.45	14.09	13,90
P205	-	0.40	10,00	8,97
sō,	-	0.05	-	0.06
SiŌ,	-	-	-	0.26
As 205	-	-	-	-
н ₂ 0-	-	N.A.	1,27	N.A.

1. Theoretical composition of Crocoite. PbCr04

- 2. Mean composition of Argent Crocoite. (10 analyses)
- 3. Theoretical composition of Vauquelinite. $Pb_2CuCrO_4PO_4OH$
- 4. Mean composition of Argent Vauquelinite. (9 analyses)

N.A. = Not analysed

The analyses for both Argent minerals are closely consistent with the respective theoretical compositions. Trace amounts of phosphate and sulphate probably substitute for chromate in the Argent crocoite, and sulphate and silicate for chromate and phosphate in the vauquelinite. The tiny amounts of calcium copper and iron may be present as impurities and could conceivably occur as substitutions for lead (crocoite) or for lead or copper (vauquelinite). In this respect it is notable that iron has previously been reported in vauquelinite (Williams, 1974).

Conclusions. Crocoite and vauquelinite occur at the Argent lead-silver mine, where they form minor components of the supergene assemblage. A considerable variety of crocoite habits has been found. Although vauquelinite appears to have replaced crocoite in certain instances, there is also strong evidence for the independent formation of vauquelinite in the presence of stable crocoite. Hence a considerable overlap in the Eh-pH stability of these two minerals can be inferred and the main factors influencing the preferred formation of vauquelinite are likely to be the activities of copper and phosphate ions in the groundwater.

Further material must be recovered and a detailed X-ray and chemical study is needed to confirm that the Argent deposit is indeed a second occurrence of embreyite. The diversity of ionic species in the groundwater and the variety of Eh-pH environments in the near-surface zone (Southwood, in prep.) suggest strongly that the discovery of further lead chromate minerals is possible.

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