

“CUPROSCHEELITE” FROM THE COPIAPÓ MINING
DISTRICT, NORTHERN CHILE

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ABSTRACT

Chemical and electron microprobe analyses of copper-bearing alteration products of scheelite from the Copiapó mining district indicate that, although cuprotungstite, *sensu stricto*, occurs in minor amounts, the greater proportion of the replacive phase is a calcium-copper tungstate, with a highly variable composition which does not necessarily conform to the general formula, $x\text{CaWO}_4 \cdot y\text{Cu}_2\text{WO}_4(\text{OH})_2$. It is recommended that the term “cuproscheelite” be retained as a field description for such assemblages.

INTRODUCTION

In the context of an investigation of the mineralogy and controls of the supergene oxidation and sulfide enrichment of copper deposits in the Copiapó area, Atacama Province, Chile (Sillitoe, 1969), an assessment has been undertaken of the effects of supergene alteration on several hypogene ore minerals associated with the copper-iron sulfides. This note records observations on the oxidation products of scheelite, the major tungsten mineral in this mining district.

A greenish cuprian tungstate formed by the alteration of scheelite was first adequately described by Whitney (1866) in specimens from La Paz, Baja California. Analysis established the presence of both copper and calcium, and this material was named cuproscheelite. Shortly thereafter, Domeyko (1869) presented analyses of similar alteration products from Mina Llamuco, Illapel, and from a second Chilean locality, some 24 km northeast of Santiago. Of the three analyzed specimens, one (“tungstate de cuivre”) contained only 2.00 weight percent CaO, but the others gave 15.25 and 18.05 percent, leading Dana (1892) to infer the occurrence of “cuproscheelite” solid solutions having the general composition $(\text{Ca}, \text{Cu})\text{WO}_4$, with scheelite and cuprotungstite, CuWO_4 , as end-members.

On the basis of an analysis by W. T. Schaller of material from Cave Creek, Arizona, however, Hess (1917) concluded that the water recorded by previous workers is present in the tungstate structure, and redefined cuprotungstite as a hydrous mineral with the composition, $\text{CuWO}_4 \cdot 2\text{H}_2\text{O}$. Whitney's original specimen was shown to consist of a mixture of schee-

lite, apparently copper-free, and cuprotungstite. Schaller (1932) subsequently re-interpreted his analysis of the Arizona material, and that of Domeyko for the Mina Llamuco cuprotungstite, on the assumption that all the CaO reported is present as discrete scheelite, and proposed the revised formula $\text{Cu}_2\text{WO}_4 \cdot \text{H}_2\text{O}$. He recommended that the name cuproscheelite be discarded since it had apparently been applied to a gross mixture.

In recent years, Chang (1950) and Cannon and Grimaldi (1953) have provided further analytical data for the copper-bearing oxidation products of scheelite. Chang found that green "cuproscheelite" from Shih-tzeshan, China, contains only 2.62 percent CuO, and Spencer (1953) followed Hess and Schaller in concluding that the analyzed material was a mixture of scheelite and cuprotungstite. Cannon and Grimaldi presented new analyses of the Arizona cuprotungstite, and of very pure, calcium-free cuprotungstite from Adams County, Idaho, obtaining a CuO:WO₃ ratio of 2:1 as proposed by Schaller, but suggesting that the H₂O:WO₃ ratio of this mineral may appreciably exceed unity. McAllister and Ruiz (1948) have briefly reported the occurrence of "cuproscheelite", inferred to consist of scheelite partially altered to cuprotungstite, from the Minillas deposit, Domeyko, Atacama Province, Chile. Doucet, Pierrot and Pillard (1969) have recently obtained a composition of $1.8\text{CuO} \cdot \text{WO}_3 \cdot 1.05\text{H}_2\text{O}$, closely approaching $\text{Cu}_2\text{WO}_4 \cdot (\text{OH})_2$, for cuprotungstite from Peralillo, near Santiago, Chile, thus lending support to earlier analytical studies.

"CUPROSHEELITE" IN THE COPIAPÓ REGION

Scheelite and its alteration products are present in the Copiapó area at Minas Remolinos Nuevo, Japonesa, San Pedro, and San Eduardo in the Cabeza de Vaca mining district; Mina San Samuel, Cachiyuyo de Llampos; mines in the Los Azules district; and Minas Neuva Farellón and Rincon in the Cerro Blanco district. Greisen associated with scheelite-chalcopyrite mineralization at Mina Japonesa has been shown by potassium-argon dating of muscovite to be of lower Paleocene age (62 ± 7 m.y.; Sillitoe, Mortimer and Clark, 1968), and on geological evidence it is considered that most scheelite-bearing deposits in the Copiapó region are of lower Tertiary age. Among these, tourmaline breccia pipes predominate, although the Cerro Blanco mines work veins. The ores are characterized by hypogene assemblages involving chalcopyrite, pyrite, and hematite, with accessory bornite, enargite, galena, molybdenite, and scheelite.

The hypogene scheelite has survived supergene sulfide enrichment without alteration, and occurs in intimate intergrowth with djurleite

and other supergene copper sulfides. In *oxidized* hypogene or supergene ores, however, a considerable proportion of the scheelite has assumed a green coloration in hand specimen, and is copper-bearing. The unsatisfactory name "cuproscheelite" will be used in this discussion as a field description of such alteration products, without implication as to precise constitution. The effects of the latest episode of oxidation in the Copiapó area, demonstrably of post-Miocene age in the Cabeza de Vaca and Los Azules districts (Sillitoe, Mortimer and Clark, 1968; Sillitoe, 1969), are confined to the upper parts of the orebodies, and do not extend to depths of more than 90 m in the deposits under consideration.

The "cuproscheelite" has formed as a pseudomorphous replacement of scheelite grains, both anhedral and euhedral, and has not been observed as a transported phase. It is closely associated with the hypogene- and supergene-enrichment assemblages accompanying the scheelite, and with malachite, goethite, and transported chrysocolla; these oxidate minerals also occur as inclusions in the cuproscheelite. The alteration products exhibit marked variations in color and texture and, with respect to these properties, grade megascopically into fresh scheelite. With increasing alteration, pale gray-green colors give way to strong peagreens or pistachio-greens, an original vitreous luster is replaced by a more waxy appearance, and the aggregates take on a friable, granular texture.

ANALYTICAL DATA

A series of four specimens from Mina Remolinos Nuevo, ranging from apparently unaltered scheelite to pea-green "cuproscheelite", were separated and analyzed following the procedure of Easton and Moss (1966). The analytical results are presented in Table 1.

Specimen No. 4, which appears in hand specimen to be the richest in copper of the suite, is seen to contain only 2.90 weight percent CuO, and has a specific gravity of 5.96, differing little from that of the scheelite (6.09). Specimens 2 and 3 have compositions that are transitional between those of the copper-free, unaltered scheelite and No. 4. Despite these low copper contents, the megascopic aspect of the samples is a good indication of their relative compositions. It is apparent that, in the deposits under consideration, calcium-free cuprotungstite does not occur as megascopic masses. In the light of the studies of Hess and Schaller, it might therefore be inferred that the cuproscheelite in the Copiapó ores consists of scheelite replaced to only a limited extent by cuprotungstite.

In apparent confirmation of this conclusion, two distinct and intergrown phases are observed in polished sections of "cuproscheelite" from Mina Remolinos Nuevo and other deposits. In these specimens, optically normal scheelite is veined and spotted, particularly in the

TABLE 1. CHEMICAL ANALYSES OF "CUPROSHEELITE"
AGGREGATES, MINA REMOLINAS NUEVO, CHILE

	1 Scheelite —level 4	2 Gray-green vitreous "cuproscheelite" —Lower Level 1	3 Olive-green vitreous "cuproscheelite" —Lower Level 1	4 Pistachio-green, waxy and friable "cuproscheelite" —Lower Level 1
H ₂ O	0.00	0.67	0.80	1.04
FeO	0.00	0.71 ^a	0.00	0.00
CuO	0.00	0.42	1.31	2.90
CaO	19.56	17.87	18.01	16.19
WO ₃	80.63	80.96	78.65	78.87
Total	100.19	100.63	98.77	99.00

^a Probably contributed by goethite.

vicinity of grain boundaries, by a paler phase with an appreciably higher reflectivity and polishing hardness. This mineral is strongly anisotropic, and displays yellow-brown internal reflections (Fig. 1). Veinlets of this phase average some 20–50 μm in width, and exhibit microscopically sharp contacts with the enclosing scheelite. That the replacive component cannot be cuprotungstite, *sensu stricto*, is, however, shown by the extent of the microscopic veining in the analyzed specimens; all three copper-bearing aggregates contain considerably greater proportions of the paler mineral than would be needed to satisfy the determined copper

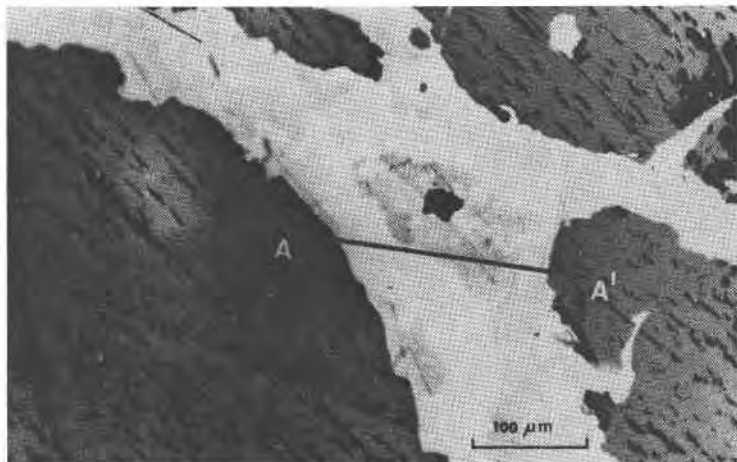


FIG. 1. Scheelite (dark gray) veined by paler, cuprian tungstate. Lower Level 1, Mina Remolinas Nuevo, Chile (Specimen 4, Table 1). Incident illumination, oil immersion.

contents. Further, each contains a significant excess of both WO_3 and H_2O over that required by calculation of the CaO and CuO as, respectively, CaWO_4 and $\text{Cu}_2\text{WO}_4(\text{OH})_2$. J. F. McAllister (written communication, 1969) has pointed out that this is also a feature of earlier bulk analyses of "cuproscheelites".

Electron microprobe scanning photographs for $\text{CaK}\alpha$, $\text{CuK}\alpha$ (Fig. 2), and $\text{WL}\alpha$ (not shown) for several areas of specimen No. 4 confirm that the pale phase is indeed copper-bearing, containing in general less calcium, as well as slightly less tungsten, than the copper-free scheelite, but it cannot consistently attain the composition $\text{Cu}_2\text{WO}_4 \cdot (\text{OH})_2$ now

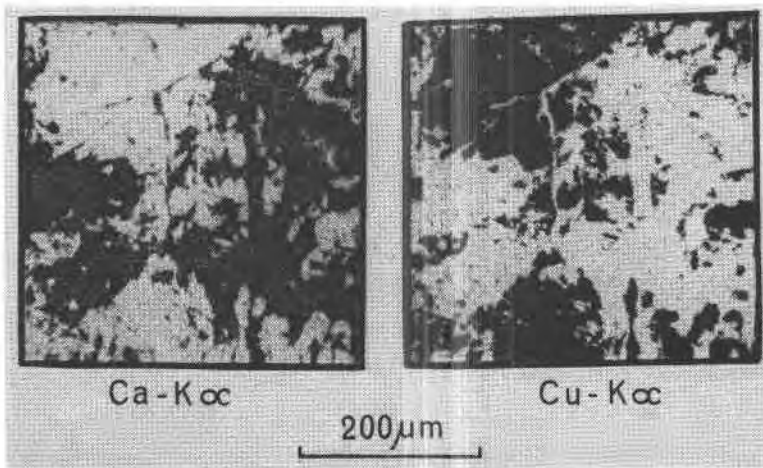


FIG. 2. X-ray scanning pictures for $\text{CaK}\alpha$ and $\text{CuK}\alpha$, "cuproscheelite" aggregate. Lower Level 1, Mina Remolinos Nuevo.

accepted for cuprotungstite. Numerous wavelength scans for $\text{CaK}\alpha$ and $\text{CuK}\alpha$ across veinlets of the replacive mineral (*e.g.* Fig. 3) show that it is strongly zoned with respect to these elements, which are quite consistently antipathetic in their concentration. The zoning is very irregular, and is not reflected in the general optical properties, although areas containing less than ~ 5 percent copper are more grayish in plane-polarized light than those richer in this element. No discrete microscopic areas rich in tungsten but lacking calcium or copper could be detected by careful scanning and point-counting of numerous vein segments. However, the observed intensity ratio, $I(\text{WL}\alpha):I(\text{CuK}\alpha)$, is highly variable.

Quantitative microprobe analysis of the veining phase has not been attempted, but semi-quantitative counting on several more homogeneous areas has yielded approximate copper contents ranging from ~ 2 to ~ 31

weight percent, this latter value approaching that given by the formula $\text{Cu}_2\text{WO}_4(\text{OH})_2$. However, the nature of these solid solutions is unclear. While they apparently have scheelite and cuprotungstite, *sensu stricto*, as end-members, the intermediate compositions may diverge significantly from the general formula, $x\text{CaWO}_4 \cdot y\text{Cu}_2\text{WO}_4(\text{OH})_2$. Neither tungstite, $\text{WO}_3 \cdot \text{H}_2\text{O}$, nor hydrotungstite, $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$, appear to be present as discrete, microscopic phases. X-ray powder study of the analyzed "cuproscheelite" specimens, however, has revealed only one reflection, at $d = 2.54 \text{ \AA}$, not referable to the standard scheelite pattern (Berry and Thomp-

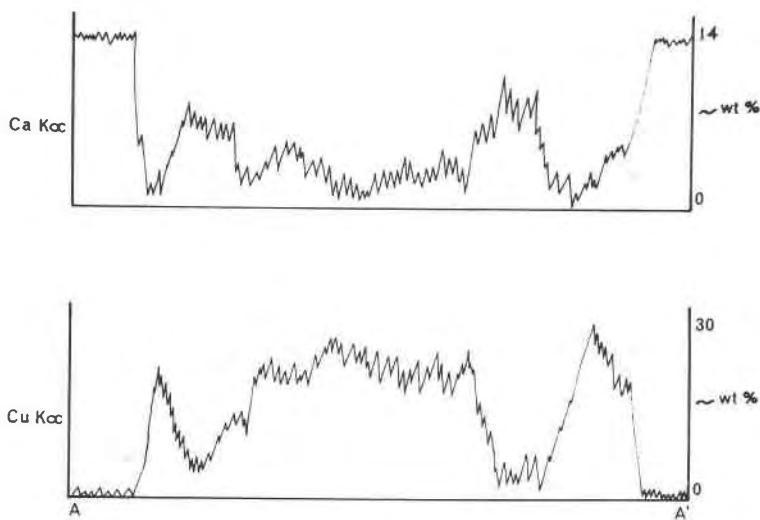


FIG. 3. Electron microprobe traverses (A-A', Figure 1) across cuprian tungstate vein in scheelite.

son, 1962). The strongest lines of tungstite ($d = 5.39 \text{ \AA}$; Berry and Thompson, 1962), and of hydrotungstite ($d = 6.95 \text{ \AA}$; Mitchell, 1963) are absent, while the rather weak relative intensity of the line at $d \approx 3.08 \text{ \AA}$ indicates that cuprotungstite, which yields a major reflection at $d = 3.07 \text{ \AA}$ (Index to the Powder Diffraction File, no. 19-392), is present in only minor amounts, as would be inferred from the analyses. We conclude, therefore, that the white phase or phases which have replaced scheelite in these ores consist largely of solid solutions, perhaps with non-stoichiometric compositions, and possibly of metastable character.

CONCLUSIONS

The above observations lead us to suggest that the "cuproscheelite" described by several earlier workers (*e.g.* Chang, 1950) consists of schee-

lite intergrown, not with calcium-free cuprotungstite, but with the copper-bearing solid solutions recognized in the Copiapó area. The name "cuproscheelite" might perhaps be usefully retained as a field term for the greenish, copper-bearing alteration products of scheelite, but without the implication that cuprotungstite is present.

The formation of "cuproscheelite" from hypogene scheelite in this region is considered to be due to the action of oxidizing solutions carrying Cu^{2+} and SO_4^{2-} ions. The minor tungsten released in the replacement would be expected (Kraynov *et al.*, 1965) to be present in solution as WO_4^{2-} ions under the weakly alkaline conditions inferred for the post-Miocene oxidation environment in these ores (Sillitoe, 1969). Pea-green cuproscheelite, megascopically resembling the most copper-rich material from Mina Remolinos Nuevo, was synthesized in less than a year by the reaction of copper sulfate solutions with scheelite from this mine. However, the activity of sulfate ions in the natural oxidizing solutions was probably considerably less than that in this experiment, since malachite was precipitated together with the natural "cuproscheelite".

ACKNOWLEDGEMENTS

Thanks are due to the United Kingdom Ministry of Overseas Development for financing the field work, and to Sr. Carlos Ruiz Puller, Director of the Instituto de Investigaciones Geológicas de Chile, and his staff for their support. We appreciate the cooperation of various mine managers, in particular that of Sr. R. Pinto of Mina Remolinos Nuevo. This work was carried out while one of us (R.H.S.) held a Natural Environment Research Council studentship at University College, London. Mr. A. M. Clark and Miss J. Zinkawich assisted in the electron microprobe analysis.

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Manuscript received, October 24, 1969; accepted for publication, February 9, 1970.