LINDGRENITE AND CUPROTUNGSTITE FROM THE SEVEN DEVILS DISTRICT, IDAHO*

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ABSTRACT

Lindgrenite was recognized by Waldemar Schaller just before World War II in specimens of contact-metamorphic copper ores from the Seven Devils Mountains in western Idaho. Hitherto this basic copper molybdate had been described only from the copper deposit at Chuquicamata in Chile. The Idaho lindgrenite, like that at the type locality, is a supergene mineral formed as a product of weathering of molybdenite, but in Idaho the molybdenite has weathered in a geochemical environment that differs in several respects from the Chilean occurrence. Chemical analyses of the lindgrenite and of associated cuprotungstite from the Seven Devils district reported here are in accord with the original analysis of lindgrenite and with analyses of cuprotungstite from Cave Creek, Arizona.

INTRODUCTION

The copper molybdate lindgrenite was described in 1935 as a new mineral species in specimens from the great porphyry copper deposit at Chuquicamata, Chile, by Palache (1935). Since then it has been recognized as one of the more abundant molybdenum minerals in the oxidized zone of the Chuquicamata ore body (Bandy, 1938; López, 1939; Jarrell, 1939, 1944). Surprisingly, it has not been reported from any other localities, even though one might expect to find it in analogous environments in other molybdenum-bearing copper deposits, as in the porphyry copper deposits of the southwestern United States.[1]

A new occurrence from a notably different geologic environment was found in 1941 when Waldemar Schaller tentatively identified as lind-

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[1] Since this manuscript was written, lindgrenite has been recognized in one of these porphyry copper deposits: at Inspiration, Ariz., by N. P. Peterson, of the U. S. Geological Survey.

grenite a green mineral on a specimen of contact-metamorphic copper ore collected by Cannon in western Idaho. Studies of the chemical, *x*-ray crystallographic, and optical properties of the Idaho mineral established its identity with lindgrenite from Chile.

OCCURRENCE

The lindgrenite described in this paper occurs on specimens of tactite collected on the dump of the upper tunnel of the Helena mine (SE $\frac{1}{4}$ sec. 25, T. 21 N., R. 3 W., Boise Meridian), about 4 miles northeast of Cuprum, in the Seven Devils mining district, Adams County, Idaho. This tunnel explores a contact between diorite and marble where an irregular zone of tactite contains shoots of copper ore with subordinate amounts of molybdenum and tungsten minerals typical of the contact-metamorphic deposits of the district. The material on the surface of the dump in the fall of 1941 was mostly low-grade oxidized copper ore that had been discarded in the course of current mining operations by H. G. and A. R. Kleinschmidt; and the material containing lindgrenite had probably been mined from a winze they sank below the tunnel floor in following a shoot of copper ore.

The matrix of the lindgrenite is hard granular tactite composed largely of quartz with subordinate amounts of silicates (fibrous hastingsite, epidote, and garnet) and suffused with a variety of oxidation products. Prior to oxidation the rock contained abundant grains of bornite, radiating clusters of plates of molybdenite, a few grains of molybdenian scheelite, and probably carbonate minerals.

Oxidation has converted the bornite almost completely to hard, resinous, dark-brown limonitic material; and its copper content has been dispersed in crusts and veinlets of chrysocolla, brochantite, lindgrenite, and other secondary copper minerals. Some of the molybdenite, especially where the rock is heavily stained with limonite, is still present as bright silvery plates that appear to show no effects of solution or alteration. Elsewhere molybdenite has been altered to pseudomorphs of powellite ($CaMoO_4$) that preserve not only the external form of the molybdenite plates but also their internal foliated structure as well, or it has been completely removed, leaving lamellar crystal cavities. The foliated powellite pseudomorphs are soft and claylike, with an earthy to waxy appearance, and range in color from gray to creamy white. A second variety of powellite, in pale-green, waxy, botryoidal masses, partly fills a cavity lined with quartz crystals and is likewise judged to be of supergene origin. The molybdenian scheelite is least affected of the ore minerals, but on most of the grains an outer shell has been partly attacked and altered to cuprotungstite, which is similar in appearance to the lindgrenite.

The lindgrenite occurs as veinlets, crusts, and possibly minor replacements of pseudomorphous powellite. A few veinlets, no thicker than 0.2 mm., fill cracks in the tactite. Some of the lindgrenite composing the veinlets is in the form of poorly developed tabular crystals lying parallel to the vein walls. Some cavities formerly occupied by molybdenite, and perhaps some formerly occupied by other minerals that have been removed by weathering, are now lined with drusy crusts of lindgrenite 0.2 to 0.5 mm. thick. These crusts are composed of better-formed tabular crystals arranged in radiating clusters approximately normal to the cavity walls. Thin films of a green copper mineral that may be lindgrenite are also interlayered with some of the foliated powellite pseudomorphs after molybdenite. The resulting mixture is so impure and so fine grained that identification of the mineral as lindgrenite is not certain. However, this green staining of pseudomorphic powellite was observed only in close proximity to veinlets and crusts of recognizable lindgrenite.

PROPERTIES

The physical and optical properties of the Idaho lindgrenite are virtually identical with those of the Chilean material. The Idaho mineral is transparent, and its color ranges from yellowish green in thin plates or aggregates to deep bottle green in thicker crystals or masses. Examined in immersion oils the powdered grains are yellowish green, nonpleochroic or possibly very faintly pleochroic, and have indices of refraction greater than 1.800 and strong birefringence. Inclined extinction measured on an unbroken crystal was $X \wedge c = 56°$ in the obtuse angle β, which compares with that reported by Palache (1935). The *x*-ray powder diffraction pattern of this mineral was found by W. E. Richmond to be identical with the pattern of the type lindgrenite from Chile.

Crystals of the Idaho lindgrenite are greatly inferior to the better crystals from Chile, but in the drusy cavities an occasional crystal is sufficiently well developed to permit comparison with the type material. These better crystals do not exceed 0.2 mm. in maximum dimension. Several of them were carefully examined with the binocular microscope, but goniometric measurements were not attempted. Referred to the orientation of Barnes (1949), the crystals are monoclinic and have a tabular habit parallel to the clinopinacoid *b* (010), some faces of which are striated parallel to the edge of the prominent prism *t* (130). The negative orthodome *A* $(\bar{1}01)$ and a clinodome, presumably ***r*** (021), are also strongly developed, and the negative orthodome is bounded by a pair of faces representing a negative pyramid form, either M $(\bar{1}21)$ or n $(\bar{1}11)$. Only one form was observed that is not listed for the type material from Chile—namely, a small sharp face observed on one crystal, evidently a negative orthodome, possibly $\bar{1}02$.

CHEMICAL COMPOSITION OF LINDGRENITE

The chemical formula of lindgrenite is $3CuO \cdot 2MoO_3 \cdot H_2O$, derived from an analysis by F. A. Gonyer (Palache, 1935) of 1.5 grams of the mineral from Chile. The Idaho material is not abundant enough for complete chemical analysis, but a minute amount was separated from the largest specimen (#520) for microanalysis. A partial analysis of an ammoniacal extract of 3.5 milligrams yielded the results shown in Table 1. The molecular ratios of the major constitutents are in close agreement with those obtained from Gonyer's analysis.

TABLE 1. PARTIAL ANALYSIS OF LINDGRENITE FROM IDAHO BY F. S. GRIMALDI

	1 Gram	2 Ratio	3 Ratio
CuO	0.0015	3.0	3.0
MoO_3	0.00188	2.078	2.080
WO_3	0.000	—	—

1. Partial analysis of lindgrenite from Helena mine, Adams County, Idaho.
2. Molecular ratios from 1, calculated on basis of CuO=3.0.
3. Molecular ratios similarly calculated from Gonyer's analysis of lindgrenite from Chile.

CUPROTUNGSTITE

Microanalyses made by this same method on three samples of cuprotungstite provide a check on the analytical procedure. In each analysis a small fraction of a gram of sample was first extracted with ammonia; then copper, molybdenum, and tungsten in the ammoniacal extract were determined. The microanalysis of cuprotungstite from Cave Creek, Ariz., was made on a portion of the same sample analyzed by Schaller (1932). The close similarity of ratios found strengthens confidence in the meth-

TABLE 2. PARTIAL ANALYSES OF CUPROTUNGSTITE BY F. S. GRIMALDI

	1. Arizona			2. Idaho			3. Idaho		
	Gram	Ratios		Gram	Ratios		Gram	Ratios	
CuO	0.00776	0.976 or 2.00		0.0255	0.321 or 2.00		0.0456	0.573 or 2.00	
WO_3	0.01120	0.483	1.01	0.0438	0.189	1.22	0.0700	0.302	1.09
MoO_3	0.00012	0.008		0.0009	0.006		0.0015	0.010	

1. Cuprotungstite from Cave Creek, Maricopa County, Ariz.; portion of sample originally analyzed by Schaller (1932).
2. and 3. Cuprotungstite from South Peacock mine, Seven Devils mining district, Adams County, Idaho (specimen #486).

ods used. In addition, the analytical results on cuprotungstite from Idaho are internally consistent and also similar to results on the cuprotungstite from Arizona (Table 2).

The microsamples of Idaho cuprotungstite were taken from a specimen collected on the dump of the South Peacock mine, another of the contact-metamorphic copper mines of the Seven Devils district. This cuprotungstite occurs as crusts and apophyses that corrode and replace the outer portions of large crystals of molybdenian scheelite embedded in garnet tactite. Cannon prepared a larger sample of this material for more complete analysis (sample 486Z), using the Frantz isodynamic separator followed by hand-picking. Impurities in the sample were thus reduced to about 5 per cent and were determined by ultraviolet fluorescence to be predominantly molybdenian scheelite. Grimaldi made the analysis (Table 3) on 0.150 gram of this purified material.

TABLE 3. ANALYSIS OF CUPROTUNGSTITE FROM IDAHO BY F. S. GRIMALDI

	Per cent	Ratios		
CuO	34.40	0.4325 or	2.00	
WO_3	54.27	0.2340	1.08	1.12
MoO_3	1.23	0.0085	0.04	
SiO_2	None			
H_2O-	1.27			
H_2O+	4.95	0.2748	1.27	
Insoluble scheelite	3.93			
	100.05			
Sp. gr. 5.40		Formula $2CuO \cdot WO_3 \cdot H_2O$		

Grimaldi's analysis was made on the purest sample of cuprotungstite that has been analyzed to date. For this reason it is worthwhile to compare the molecular ratios implied by the new analysis with those from previous analyses as reviewed by Schaller (1932) when he established the formula $2CuO \cdot WO_3 \cdot H_2O$. Four alternative interpretations of ratios of the Idaho cuprotungstite (I) are shown in Table 4 in comparison with similar interpretations for (II) the average of four analyses (recalculated to 100) of Arizona material by Schaller (1932) and for (III) an analysis of cuprotungstite from Chile by Domeyko as listed in Dana's *System of Mineralogy* (6th ed., p. 988, 1892). Much of the molybdenum found by Grimaldi in the Idaho sample probably came from ammoniacal solution of finer-grained molybdenian scheelite impurity, in which the WO_3/MoO_3 ratio would be about 1.83. Therefore, in our opinion, the alternative I.C. ($CuO/WO_3/H_2O = 2.00/1.01/1.27$) probably represents the best evaluation of the Idaho data. Similarly Schaller (1932) implied preference for alternatives II.B.(2.00/1.01/1.38) and III.C.(2.00/1.08/1.33) for the data on cuprotungstite from Arizona and Chile, respectively. This comparison clearly supports Schaller's determination of the CuO/WO_3 ratio as 2/1 and appears to raise a question whether the ratio H_2O/WO_3 may not be somewhat greater than 1/1.

TABLE 4. RATIOS OF CUPROTUNGSTITE

	I. Idaho Grimaldi, analyst		II. Arizona Schaller, analyst		III. Chile Domeyko, analyst	
	Per cent	Ratios	Per cent	Ratios	Per cent	Ratios
CaO	—	—	3.51	0.0625	2.00	0.0357
MgO	—	—	0.56	0.0139	—	—
CuO	34.40	0.4325	32.67	0.4107	30.63	0.3851
WO_3	54.27	0.2340	57.20	0.2467	56.48	0.2435
MoO_3	1.23	0.0085	—	—	—	—
$H_2O(+)$	4.95	0.2748	6.07	0.3366	4.62	0.2564
A.	2.00/1.08/1.27		2.00/1.20/1.64		2.00/1.26/1.33	
B.	2.00/1.12/1.27		2.00/1.01/1.38		2.00/1.16/1.22	
C.	2.00/1.01/1.27		2.00/0.83/1.64		2.00/1.08/1.33	
D.	2.00/1.12/1.29		—		—	

A. Molecular ratios $CuO/WO_3/H_2O$, as analyzed.

B. Molecular ratios $CuO(+CaO+MgO)/WO_3(+MoO_3)/H_2O$.

C. Molecular ratios $CuO/WO_3/H_2O$, if all CaO, MgO, and MoO_3 are assumed components of (molybdenian) scheelite and the corresponding quantity of WO_3 is deducted.

D. Molecular ratios $CuO/WO_3/H_2O$, if all MoO_3 is assumed a component of lindgrenite and the corresponding quantities of CuO and H_2O are deducted.

OXIDATION OF MOLYBDENITE

Information on the oxidation of molybdenite and on the related formation of lindgrenite and other supergene molybdenum minerals at Chuquicamata has been provided in papers by Bandy (1938), López (1939), and Jarrell (1939, 1944) published subsequent to Palache's original description of lindgrenite. Much of this information has been summarized succinctly by Jarrell (1944):

> "Molybdenite is normally quite resistant to oxidation; hence where it formed part of the hypogene mineralization at Chuquicamata, residual molybdenite probably exists above the general top of the sulphides. When it finally capitulates to the oxidizing solutions, the molybdenum and sulphur go into solution, and a brown limonite remains pseudo-

> morphic after molybdenite crystals. The molybdenum combines with copper in solution and deposits lindgrenite a few centimeters away; or it may be absorbed by coming into contact with the existing amorphous, extremely porous chenevixite, since assays of the latter mineral show it to contain up to 5 per cent Mo. Near the surface or under exceptional conditions elsewhere, yellow molybdic ochre may form. A very few specimens of wulfenite also have been found."

These limonitic pseudomorphs after molybdenite, mentioned above, deserve more study. Ferric oxide hydrate is not an expectable residue from dissolving molybdenum sulfide. According to López, the pseudomorphs are red (light gray in polished sections) and contain molybdenum as well as iron. He believes them to be a new molybdenum ochre: Bandy, however, believes them to be an iron-molybdenum sulfide.

Molybdenite in the forested Seven Devils Mountains has weathered under climatic conditions notably different from the high desert environment at Chuquicamata. Rainfall is far more abundant, and the water table is much nearer the surface and probably far more constant in the Seven Devils district. Although ratios of molybdenum to copper in the ores are similar, the mineralogy and chemistry of ores and country rock being weathered at the two localities are quite dissimilar in most respects, and it is probable that important differences exist in the chemical composition of ground waters. The marble and tactite country rocks of the contact-metamorphic deposits in the Seven Devils are characterized by abundance of calcium carbonate, and the ores themselves by scarcity of sulfur. Sulfide minerals associated with molybdenite in these Seven Devils ores generally do not exceed a few per cent and tend to be poor in sulfur. Bornite and chalcocite are the most common sulfides, chalcopyrite is scarce, and pyrite practically absent. The ore deposit at Chuquicamata, by contrast, is rich in sulfur, and the molybdenite there is associated with comparatively abundant sulfides, among which sulfur-rich pyrite predominates. Ground waters circulating through the Idaho contact-metamorphic deposits are presumed to be much richer in calcium bicarbonate and poorer in sulfate than ground waters at Chuquicamata. Their effectiveness in oxidizing metallic sulfides and transporting metals certainly has been limited for, unlike Chuquicamata, there is no zone of thorough oxidation nor any appreciable supergene enrichment.

In the Seven Devils district molybdenite does not seem notably more resistant than other sulfides to oxidation as it does at Chuquicamata, nor is it replaced by limonitic pseudomorphs like those at Chuquicamata or those described by Blanchard (1935) at other localities. Instead, much of the molybdenite has been replaced by powellite. The alteration process evidently retains most of the molybdenum within the host crystal while oxygen and calcium are substituted for sulfur. This alteration of molybdenite to powellite, together with other local evidence, suggests that very little migration of molybdenum normally accompanied oxidation of molybdenite in the Seven Devils district. Only under exceptional conditions, clearly where molybdenite was unusually abundant and perhaps where in addition ground waters were abnormally poor in calcium, was there any perceptible migration of molybdenum. Such anomalous conditions must have existed very locally at one time within the specimens that now contain lindgrenite. In parts of them molybdenite was dissolved completely away; molybdenum was taken into solution and precipitated together with copper, as lindgrenite, either in the crystal cavities or within a few centimeters of them; and some of the molybdenum combined with calcium to form a deposit of transported powellite, also only a few centimeters away. There is tenuous evidence that within this same localized area copper-bearing solutions may have attacked powellite pseudomorphs to form minor replacements by lindgrenite. No molybdic ochre nor other supergene molybdenum minerals have been identified in these specimens or elsewhere in the district.

Acknowledgments

This note on the occurrence of lindgrenite in Idaho is an outgrowth of a study of the geology and ore deposits of the Seven Devils district by the U. S. Geological Survey in cooperation with the Idaho Bureau of Mines and Geology. We take pleasure in reporting this first discovery of lindgrenite in the United States as one more of Waldemar Schaller's contributions to the mineralogy of the molybdates and tungstates. It was he who first sensed the identity of the material and guided our efforts to identify and describe it. We are indebted also to Harvard University and to A. E. Weissenborn of the Geological Survey for material from Chuquicamata that was used for comparative study.

The finding of lindgrenite in one of the contact-metamorphic deposits of the Seven Devils district has interesting historical connotations. Waldemar Lindgren, in whose honor the mineral was named, once briefly reconnoitered the Seven Devils region for the U. S. Geological Survey, and with his description of these very deposits he first clearly defined the contact-metamorphic class of ore deposits in the United States. And the other molybdate with which this lindgrenite is associated was first discovered in a specimen from one of these same deposits and described as a new mineral species by one of Lindgren's colleagues, the chemist Melville, who named it powellite in honor of Major J. W. Powell, then Director of the U. S. Geological Survey.

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