

to six when observed in thin section. The partial qualitative analyses of those remaining revealed the following, in order of decreasing abundance: calcium-iron-manganese minerals; calcium compounds containing varying quantities of titanium, cerium, lanthanum, and neodymium; barium-sulphur minerals (possibly baryte); and silicates of various compositions.

Occasionally a precipitate developed from the evaporated inclusion fluid that gave a positive response for either Ba-S or Ca-Mn-Fe (fig. 1g). Apart from calcium, none of the above elements was detected in the host carbonate. It should be noted that calcium was always detected in the analyses due to a substantial contribution from the inclusion wall.

*Conclusions.* The observations presented above lead to the conclusion that the calcite was deposited from a boiling aqueous solution of abnormally high temperature for the environment described. The apparently unusual chemistry of the fluids with respect to the host mineral, (as indicated by that of the daughter phases) may prove to be relatively common should similar studies be carried out on

other samples. The calcite was deposited after the baryte, but how long after is unknown. There is some evidence to suggest that perhaps the provenance of the calcite is not completely different from that of the baryte (e.g. the Ba-S component of the carbonate's inclusions, and the similarity in Na/K ratios for the two minerals).

Regarding the heat source involved in generating these high-temperature fluids, the local doleritic dyke swarms provide the most likely source.

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#### REFERENCE

Le Bel (L.), 1976. *Bull. Soc. Vaud. Sci. Nat.*, no. 350, 73, 1-8.

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## New data for cuprotungstite

CUPROTUNGSTITE from La Paz, Lower California, one of the type localities, and Cave Creek, Arizona, was used for proving that the powder data of cuprotungstite published by Escobar and Gifford (1961) is incorrect and does not refer to this species. The powder pattern obtained for the mineral in the new study can be indexed on the basis of a tetragonal cell with  $a$  8.93 and  $c$  14.48 Å. The three strongest lines are: 4.03 (8) 210; 3.80 (8) 113, 202; 2.53 (10) 303.

Among the secondary minerals from the Clara mine near Oberwolfach in the Black Forest, Germany, the author discovered a green mineral that according to an analysis by the electron microprobe was a copper tungstate (Walenta, 1975, p. 405). Comparison of the powder pattern of this mineral with that of cuprotungstite (Escobar and Gifford, 1961), the only copper tungstate known in nature until now, however, showed no agreement between the two patterns.

This discrepancy could be interpreted in two ways, either the mineral from the Clara mine was a new species—a copper tungstate differing from cuprotungstite in composition or in structure—or the powder data for cuprotungstite published by Escobar and Gifford and given in the ASTM powder diffraction file (No. 19-392) was wrong. As will be shown in the following, the second assumption turned out to be true.

In order to solve the problem the author sought to obtain type material of cuprotungstite. The species had been described as cuproscheelite from the vicinity of La Paz, Lower California, Mexico, by Whitney (1866), and as cuprotungstite from the copper mines of Llamuco near Santiago, Chile by Adam (1869). More information on the mineral in question was provided by Schaller (1932) who studied material from Cave Creek, Maricopa County, Arizona (see also Palache *et al.*, 1951). As to the powder data of Escobar and Gifford, they

TABLE I. *X-ray powder data*

Cuprotungstite, Cave Creek, Arizona				Cuprotungstite, Clara mine, Black Forest, Germany (Walenta, 1975, p. 405)		'Cuprotungstite', Aconcagua, Chile (Escobar and Gifford, 1961, ASTM No. 19-392)	
<i>d</i>	<i>I</i>	<i>d</i> <sub>calc</sub>	<i>hkl</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
7.76	5 d.	7.60	101	—	—	4.68	6
4.73	3	4.76	112	4.74	5	3.07	10
4.03	8	3.99	210	4.07	8 d.	2.81	3
3.80	8	{ 3.83 3.80	{ 113 202	3.84	8 d.	2.60	3
3.14	1 d.	3.14	114	—	—	2.27	5
3.06	1 d.	3.08	213	—	—	2.08	2
2.93	1 d.	2.92	301	—	—	1.97	3
2.53	10	2.53	303	2.54	10	1.91	8
2.45	4	2.44	321	2.45	3 d.	1.84	4
2.35	4	2.34	322	2.36	5	1.72	1
2.23	4 d.	2.23	400	2.24	5	1.67	6
1.729	5 d.	1.734	432	1.730	8	1.62	3
1.629	1 d.			1.639	1 d.	1.58	8
1.462	7			1.468	8	1.54	5
1.264	1			1.375	$\frac{1}{2}$ d.	1.43	2
1.236	$\frac{1}{2}$			1.271	2	1.38	2
				1.246	$\frac{1}{2}$ d.	1.35	2
				1.176	$\frac{1}{2}$ v.d.	1.32	2
				1.115	2 v.d.	1.30	2
				1.087	$\frac{1}{2}$ v.d.	1.26	1
				in addition broad diffuse band of medium intensity between <i>d</i> 3.13 and 2.95		1.24	9
						1.22	1
						1.20	4
						1.18	4
						1.16	4
						etc.	

d. = diffuse

v.d. = very diffuse

The patterns of cuprotungstite from Cave Creek and the Clara mine were obtained with Fe-K $\alpha$  radiation using a camera of 57.3 mm in diameter. *d*-spacings in Å are corrected for film shrinkage and sample thickness. Intensities were estimated from 10 to  $\frac{1}{2}$ .

refer to material from Aconcagua, Chile, and not from one of the above-mentioned localities. The author's quest for samples from one of the latter was successful. He is indebted to Dr J. S. White, National Museum of Natural History, Smithsonian Institution, Washington for providing both samples from La Paz, Lower California and from Cave Creek.

*Results of the X-ray study.* The samples of cuprotungstite from La Paz and Cave Creek—in both cases a more or less dense, in part also earthy-green material showing no crystal forms—furnished a powder pattern identical to that of the mineral from the Clara mine and differing from

that of cuprotungstite as given by Escobar and Gifford.<sup>1</sup> This is shown in Table I.

Closer inspection of the pattern of Escobar and Gifford revealed that it strongly resembles that of scheelite and there can be no doubt that these authors did not have cuprotungstite in hand but a sample of scheelite. The powder pattern of cuprotungstite can be indexed on the basis of a tetragonal

<sup>1</sup> A greenish-yellow secondary mineral forming crusts on scheelite from Natas, South-West Africa and containing Cu and W as major constituents also gave a powder pattern similar to those of the mentioned samples. Another occurrence of cuprotungstite, therefore, may be added to the already known ones.

cell with  $a$  8.93 Å and  $c$  14.48 Å,  $a:c = 1:1.6215$ . For this calculation the pattern of the mineral from Cave Creek was used, which is of better quality than that of the sample from the Clara mine and includes three additional lines between 3.14 and 2.93, which within a broad diffuse band are unresolved in the other pattern. As to the possible space groups, a body-centred cell can be excluded. Possible conditions limiting reflections may be  $h00 = 2n$  and  $00l = 4n(P4_12_12, P4_32_12)$ , but there is little reliability in such a space-group derivation based only on the scanty data of the powder pattern.  $Z$  is unknown, as no data on the gravity of cuprotungstite exist. A check in Clerici solution showed only that  $\rho$  of the mineral exceeds that of the liquid ( $\rho$  4.06 g cm<sup>-3</sup>).

By applying the rule of Gladstone and Dale and making use of the known mean index of refraction (see below) and the chemical composition, a value of 6.89 g cm<sup>-3</sup> is obtained. Therefore it may be assumed that  $Z$  is 12, because in that case a calculated density of 7.06 g cm<sup>-3</sup> results in satisfactory agreement with above value.

Mention should be made that at first a smaller cell was derived from the powder pattern ( $a$  7.60,  $c$  6.12 Å). However, in this case the agreement between measured and calculated  $d$ -values is unsatisfactory. Above all the value  $d$  3.14 Å cannot be indexed and as there is no reason to assume that the respective line is caused by an impurity, this cell was rejected.

Unfortunately, it was not possible to check the unit cell dimensions by a single-crystal study due to the smallness of the available crystals. However, the form of the minute crystals from the Clara mine was already recognized as being either tetragonal or orthorhombic (Walenta, 1975, p. 406). The bipyramidal crystals are 20 to 30 µm long, but only a few µm thick, and in addition they are somewhat rounded (fig. 1), so the exact nature of the rather steep pyramids and of the crystal symmetry could not be determined. The small size of the crystals also did not permit us to obtain axial figures, which also might have supplied a hint regarding the symmetry conditions.

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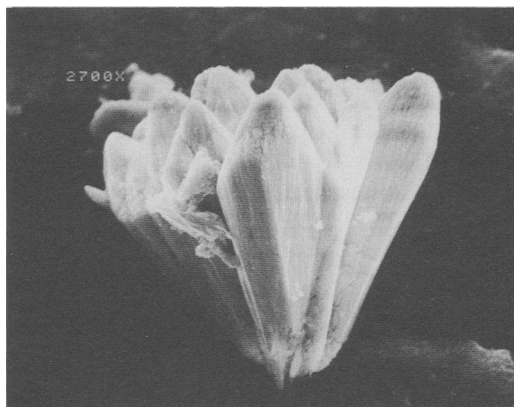


FIG. 1. Crystals of cuprotungstite in radial grouping. Clara mine, near Oberwolfach, Schwarzwald, Germany.  $\times$  c. 1610. (Photograph by electron microscope.)

As exact values of the indices of refraction are lacking—Larsen (1921) cites only 2.15 as mean index and mentions that the birefringence is strong—the crystals from the Clara mine were used for a more accurate determination giving:  $\epsilon$   $2.10 \pm 0.01$ ,  $\omega$   $2.18 \pm 0.01$ .

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#### REFERENCES

- Adam (C. J.), 1869. *Tableau minéralogique*, 31. Dunod, Paris.
- Escobar (C.) and Gifford (G.), 1961. *Bol. Acad. nac. Cienc. Córdoba [Argentina]*, 42, Entr. 2-4, 245-56.
- Larsen (E. S.), 1921. *US Geol. Surv. Bull.* 679, 64 and 282.
- Palache (C.), Berman (H.), and Frondel (C.), 1951. *Dana's Syst. Mineral.*, 7th edn. 2, 1091.
- Schaller (W. T.), 1932. *Am. Mineral.* 17, 234-7.
- Walenta (K.), 1975. *Aufschluss*, 26, 369-411.
- Whitney (J. D.), 1866. *Proc. Calif. Acad. Sci.* 3, 287-8.

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