THE FIRST REPORTED OCCURRENCE OF CREASEYITE, A HYDROUS LEAD-COPPER-IRON SILICATE MINERAL, IN SOUTH-AMERICA

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ABSTRACT An acicular deep-green mineral was discovered in an oxidation zone of the Cruz del Sur lead-copper deposit, Rio Negro province, Argentina. This mineral was studied by petrographic microscopy, X-ray powder diffraction methods, chemical analysis, infrared spectroscopy and electron microscopy and identified as the "creaseyite" reported by Williams and Bideaux (1975). The chemical analyses of the mineral here presented are somewhat different from those of the Arizona and Sonora creaseyite. This is the first reported occurrence of creaseyite in South-America.

RESUMO Um mineral acicular de coloração verde-escura foi encontrado na zona de oxidação do depósito de chumbo e cobre de Cruz del Sur, Rio Negro, Argentina. Esse mineral foi objeto de estudos por microscopia petrográfica, difração de raios X, análise química, espectroscopia de infra-vermelho e por microscopia eletrônica, tendo sido identificado como "creaseyita", de acordo com Williams e Bideaux (1975). As análises químicas apresentadas diferem um pouco daquelas obtidas para a creaseyita do Arizona e de Sonora. Essa é a primeira ocorrência descrita de creaseyita na América do Sul.

INTRODUCTION Creaseyite, first found by R. A. Bideaux in 1967, and by S.A. Williams in 1968, is a new mineral of formula $\text{Cu}_2\text{Pb}_2(\text{Fe}, \text{Al})_2\text{Si}_5\text{O}_{17} \cdot 6\text{H}_2\text{O}$, orthorhombic diffraction symbol *mmmCb* (Williams and Bideaux, 1975).

A brittle, finely acicular, deep-green mineral was found in 1973 by the present authors in an oxidation zone of a lead-copper deposit of Cruz del Sur mine, Rio Negro Province, Southwestern Argentina. Its X-ray powder pattern did not correspond to that of any known species, and the mineral could not be identified at that time. Its definitive chemical composition was determined only three years later; in the meantime, the mineral was considered to be a hydrous lead-copper-iron silicate, on account of preliminary spectroscopic and microchemical tests.

Further study by the writers, by means of X-ray diffraction, wet chemical analysis, infrared spectroscopy and petrographic and electron microscopy, showed this mineral to be creaseyite, though with a chemical composition somewhat different from that reported by Williams and Bideaux (1975). This is the first occurrence of creaseyite in South America.

OCCURRENCE The lead-copper deposit of the Cruz del Sur mine is situated at about 38 km east-south-eastward of Los Menucos village, Rio Negro province, Argentina (Fig. 1). A shallow inclined shaft, about 15 m deep, exposes only the outer oxidation zone with a complex mineralogy, presenting galena, chalcocite, digenite, covellite, malachite, azurite, cerussite, wulfenite, vanadinite, atacamite, paratacamite, motttramite (Hayase and Dristas, 1972), calcite, gypsum, limonite, and quartz. In addition, the writers have found in this oxidation zone a new mi-

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neral, "surite", a PbCO_3 -montmorillonite mixed layer mineral. The report on this new mineral has been submitted to I.M.A.

The mineral of this study has a fine acicular shape showing a deep green color, sometimes occurring as radial or bundle-like aggregates, associated to gypsum, quartz, cerussite and iron oxide minerals. Its crystals often reach up to 1 mm in length and 0.2 mm in width, but are usually much smaller.

Figure 1 — Locality of Cruz del Sur mine

OPTICAL PROPERTIES Under a petrographic microscope, the creaseyite crystals have fine prismatic or tabular shapes with a distinct cleavage parallel to the elongation; sometimes creaseyite appears as bundle-like aggregates of fine needles. Frequently, termination of the needles is by planes perpendicular to their elongation, probably representing cleavages. The crystals show straight extinction with positive optic elongation and the following pleochroism: parallel to the elongation = Z' , green; perpendicular to the elongation = X' , pale yellowish green. The indices of refraction are: $N_o = 1.696 \pm 0.002$, $N_p = 1.746 \pm 0.002$, $N_y = 1.788 \pm 0.002$, $N_y - N_o = 0.092$, with a calculated $2V_x$ of 82° .

Fresh needles of this mineral appear sometimes as inclusions in rather large quartz crystals (Fig. 2) without being associated to other secondary oxidation minerals, such as iron oxide minerals, cerussite, etc. This observation suggests the possibility that this mineral is a product of hydrothermal activity or of the earliest step of oxidation.

Figura 2 — Microphotograph of creaseyite. a) Lower Nicol only. b) Crossed Nicols. Acicular crystals are creaseyite, Q quartz, Ce, Cerussite

X-RAY POWDER DIFFRACTION DATA The X-ray powder diffraction data of this mineral are shown in Tab. I. Almost all of the diffraction peaks coincide with those of the creaseyite reported by Williams and Bideaux (1975). The

Table I — X-ray powder diffraction data of creaseyite

Mineral from Cruz del Sur mine				Creaseyite from Tiger, Arizona (1)		
<i>hkl</i>	<i>d_{meas.}</i> (Å)	<i>d_{calc.}</i> (Å)	<i>I/I₀</i>	<i>hkl</i>	<i>d</i> (Å)	<i>I/I₀</i>
110, 020	10.68	10.782	100	110	10.726	10
130	6.21	6.202	17	130	6.200	3
111	6.03	6.029	18	111	6.024	5
040, 220	5.356	5.362	29	040	5.352	4
131	4.729	4.719	6	131	4.720	3
—	—	—	—	221	4.327	2
240	4.066	4.065	24	240	4.067	5
			—	002	3.642	2
330	3.584	3.594	23	330	3.592	1/2
060	3.562	3.574	23	060	3.555	5 B
112	3.444	3.445	10	112	3.448	3
061	3.210	3.208	18	061	3.216	4 B
042, 222	3.010	3.009	41	042	3.013	5
350	2.985	2.985	40	350	2.982	5
351	2.758	2.761	11	351	2.761	2
440	2.692	2.695	46	440	2.696	5
080	2.680	2.681	53	080	2.674	4
332	2.556	2.556	5	332	2.557	2
081	2.517	2.515	8			
370	2.466	2.466	24			
402	2.367	2.367	13			
371	2.338	2.336	18			
352	2.307	2.307	7			
461	} 2.231	2.235	} 14			
191		2.228				
082	2.159	2.158	7			
600	2.081	2.079	7			
0101	2.057	2.057	11			

(1) Williams and Bideaux (1975), cell constants:

$$a = 12.483 \pm 0.006 \text{ Å},$$

$$b = 21.395 \pm 0.011 \text{ Å},$$

$$c = 7.283 \pm 0.004 \text{ Å}.$$

(B, broad)

d_{meas.}, measured value; *d_{calc.}*, calculated value with the following cell constants: $a = 12.4721 \text{ Å}$, $b = 21.4465 \text{ Å}$, $c = 7.2717 \text{ Å}$, $\alpha = \beta = \gamma = 90^\circ$.

X-ray diffraction conditions: Diffractometer-Rigaku Denki Co.; anticathode-Cu; Ni-filter; 35 kV; 12 mA; scanning-1°/min; chart speed-20 mm/min; slits 1°, 1°, 0.2 mm; time const. 4 sec; rate-meter- X8; multiplier X 0.8; halite (NaCl) was used as internal standard

cell constants of this mineral were calculated with a least square computer program using reflections 130, 111, 040, 131, 240, 112, 061, 350, 080 and 332 with the following results: $a = 12.4721 \text{ \AA}$, $b = 21.4465 \text{ \AA}$, $c = 7.2717 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, ($\sigma = 0.00343 \text{ \AA}$)*

The indices attributed to the reflections of the powder pattern indicate the presence of a C-centered lattice and a probable diffraction symbol $mmmCb$ (Stout and Jensen, 1968), as indicated by Williams and Bideaux (1975).

X-ray peaks in the diffractogram are generally fairly sharp, thus indicating that the mineral is well-crystallized and probably formed hydrothermally before the onset of the oxidation process.

CHEMICAL COMPOSITION A sufficient amount of this mineral for analytical purposes was obtained by a repeated manual separation technique. The sample was then decomposed with gently heated aqua-regia. The insoluble residue was filtered and SiO_2 in the residue was analyzed by the evaporation technique with

Table II — Chemical analysis of creaseyite

Component	%	Molecular weight	Molecular number	Cation number	Calculation (1)	Calculation (2)
SiO_2	26.86	60.09	0.44700	0.4470	5.4897	4.9130
Al_2O_3	6.92	102.00	0.06785	0.1357	1.6667	1.4915
Fe_2O_3^*	7.13	159.69	0.04465	0.0893	1.0967	0.5085
					2.7634	0.4730
						2.000
PbO	33.94	223.19	0.15207	0.1521	1.8960	1.6717
CuO	12.48	79.54	0.15690	0.1569	1.9557	1.7245
ZnO	0.97	81.37	0.01194	0.0119	0.1483	0.1308
$\text{H}_2\text{O} (+)$	5.19	18.00	0.48611	0.4861	5.9699	5.3427
$\text{H}_2\text{O} (-)$	3.56	18.00				
Insol.**	0.11					
Total	97.16					

* All Fe analyzed as Fe^{3+} ; amount of sample was not sufficient to allow for Fe^{2+} analysis

** Insoluble and inert in HF and aqua-regia

(1) Cation number of (Pb + Cu + Zn) fixed at 4.00 — composition as follows:

$(\text{Pb}_{1.896}\text{Cu}_{1.956}\text{Zn}_{0.148})_{4.00}(\text{Al}_{1.667}\text{Fe}_{1.097}^{3+})_{2.764}\text{Si}_{5.490}\text{O}_{19}5.970(\text{H}_2\text{O})$

(2) Cation numbers of ($\text{Fe}^{+2} + \text{Pb} + \text{Cu} + \text{Zn}$) and ($\text{Al} + \text{Fe}^{+3}$) fixed at 4.00 and 2.00, respectively — composition as follows:

$(\text{Pb}_{1.672}\text{Cu}_{1.724}\text{Fe}_{0.473}^{+2}\text{Zn}_{0.131})_{4.00}(\text{Al}_{1.491}\text{Fe}_{0.509}^{+3})_{2.00}\text{Si}_{4.913}\text{O}_{17}5.343(\text{H}_2\text{O})$

⊙ Calculated ferric iron

○ Calculated ferrous iron

$$* \text{ Standard deviation } \sigma = \sqrt{\frac{\sum (d_{\text{meas.}} - d_{\text{calc.}})^2}{n - 1}}$$

HF. Lead in the filtrate was determined by a lead sulphate precipitate and checked with the results of analysis by atomic absorption spectroscopy. After the filtration of PbSO_4 , the total amount of $(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$ was determined by gravimetry. The titration with a standard permanganate solution was carried out to determine Fe_2O_3 . The quantity of Al_2O_3 was calculated by subtraction of Fe_2O_3 from the total amount of $(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$. Copper was analyzed by the KI method, and Zn by atomic absorption spectroscopy. The positive water (released over 110°C) was determined by the Penfield technique. Results are shown in Tab. II.

The most important differences between the results of this analysis and the one reported by Williams and Bideaux (1975) are that the Cruz del Sur mineral has larger Al_2O_3 and lower Fe_2O_3 contents. Tab. 2 shows two possible formulas for the Cruz del Sur mineral; the first calculation was performed taking $(\text{Pb} + \text{Cu} + \text{Zn})$ atoms equal to 4, the second taking $(\text{Al} + \text{Fe}^{+3}) = 2$ and $(\text{Fe}^{+2} + \text{Pb} + \text{Cu} + \text{Zn}) = 4$. The formula found by Williams and Bideaux (1975):

can not be applied to the Cruz del Sur specimen. On the other hand, the second calculation suggests the following as the valid formula for the Argentine creaseyite:

although the analysis shows a 1.08% H_2O deficiency, probably due to analytical errors by the Penfield method.

INFRARED SPECTROSCOPY AND ELECTRON MICROSCOPY Fig. 3 shows the result of the infrared spectroscopy of this mineral. Two distinct absorption peaks are recognized near 1000 cm^{-1} , one at about 900 cm^{-1} and the other at about 960 cm^{-1} . The former may represent the stretching of Si-O-M and the latter that of H-O-M . ($\text{M} = \text{Pb}, \text{Cu}, \text{Zn}$ and Fe) Fig. 4 shows the electron microphotography of this mineral revealing that its crystal habit is tabular.

Figure 3 — Infrared spectroscopic pattern

Figure 4 — Electron microphotograph of creaseyite

CONCLUSION X-ray powder diffraction data and chemical analysis identify the fine acicular green mineral found in the oxidation zone of the lead-copper deposit of the Cruz del Sur mine, Rio Negro Province, Argentina, as “creaseyite”, first reported by Williams and Bideaux (1975). But there are some differences between the amounts of elements in the mineral from Arizona and Sonora, as reported by those authors and the Cruz del Sur specimen. The ideal composition of creaseyite indicated by Williams and Bideaux (1975) can not be applied to the mineral of this study, and the writers propose the following ideal composition for it:

Acknowledgements The writers wish to thank Dr. Sadao Tsutsumi of the Waseda University for his kindness in obtaining the infrared spectroscopic data, and staff members of the Consejo Nacional de Investigaciones Cientificas y Tecnicas for taking the scanning electron microphotograph of this mineral.

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