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Rouseite, a new lead manganese arsenite from Långban, Sweden

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Abstract

Rouseite, ideally $Pb_2Mn(AsO_3)_2 \cdot 2H_2O$, is a new mineral species found associated with trigonite and finnemanite from Långban, Värmland, Sweden. Rouseite is triclinic, space group $P1$ or $P\bar{1}$, with $a = 6.36(2)$, $b = 7.29(2)$, $c = 5.54(2)$ Å, $\alpha = 97.3(3)$, $\beta = 114.2(2)$, $\gamma = 106.0(2)°$, V = 216.5 Å^3, and Z = 1. The eight strongest reflections in the X-ray powder-diffraction pattern are (d,I/I_0,hkl) 6.81,100,010; 3.38,60,020; 3.25,60,02$\bar{1}$,1$\bar{1}$1; 3.06,70,2$\bar{1}\bar{1}$; 2.983,80,101; 2.849,90,1$\bar{2}\bar{1}$; 2.751,50,10$\bar{2}$; and 2.016,60,3$\bar{2}\bar{1}$.

Microprobe and thermogravimetric analyses gave PbO 59.6, MnO 10.0, As_2O_3 27.0, H_2O 4.8, sum = 101.4 wt%, leading to the above formula. Rouseite is light yellow, with perfect {010} and {110} cleavages, density (calc.) = 5.70 g/cm^3, hardness approximately 3 (Mohs). Optically, rouseite is biaxial (−), $2V_x = 46°$, with strong dispersion of the optic axes, $r > v$, indices of refraction > 1.80, and maximum birefringence = 0.07. The name honors Dr. Roland Rouse of the University of Michigan.

Introduction

The new mineral described herein was noted during a systematic study of the minerals from reduced assemblages from Långban, Värmland, Sweden. It was initially discovered on a sample of greenish-yellow trigonite, $Pb_3Mn(AsO_3)_2(AsO_2OH)$, in part because of its contrasting yellow orange color. Preliminary examination by powder diffraction suggested its uniqueness. This was borne out by subsequent detailed investigation. Additional samples were sought in the mineral collections at Harvard University and the American Museum of Natural History, but without success; rouseite is presently known on only one specimen, the holotype, preserved at the Smithsonian Institution under catalogue number NMNH 94942. Both the species and the name were approved by the Commission on New Minerals and Mineral Names, IMA.

Occurrence

Rouseite occurs on one specimen (2 × 3 × 4 cm) from the Långban Mine, Värmland, Sweden. The specimen was obtained by the Smithsonian Institution 60 years ago and nothing is known of its specific occurrence within the mine. The matrix is a banded calcite-hausmannite ore. Secondary minerals are deposited on a fracture surface that cuts across the ore banding. The assemblage is an intimate mixture of calcite, trigonite, and an unnamed Mn arsenite currently under investigation. Part of the secondary assemblage appears to be superficially etched, as might occur through interaction with groundwater, but the sample is much too small to ascertain this with certainty. On the altered portion, calcite has been dissolved away. Two generations of finnemanite, $Pb_5(AsO_3)_3Cl$, are present: a druse of colorless blebs and a secondary growth of the more typical grayish prisms. The unnamed Mn arsenite mentioned above survived this etching, but trigonite is less abundant and appears to have been replaced by rouseite, a relation supported by the formula, especially in view of the hydrated state of rouseite. Additionally, both phases are chemically and crystallographically related. On the basis of a diligent, but fruitless, search in three major public collections for additional samples, rouseite must be considered to be a rare and uncommon species.

Physical and optical properties

Rouseite is yellow orange in color, similar in hue to some wulfenite. The streak is light yellow. The luster is vitreous on cleavage surfaces and otherwise dull. The estimated hardness (Mohs) is approximately 3. Cleavage is perfect on {010} and {110}, the latter subordinate in development, and both easily produced. Indices for cleavages were determined by reference to orientations as defined by single-crystal methods. The density was inferred to be >4.2, measured using Clerici solution. A more precise determination could not be made with other techniques owing to small grain size and the intimate mixture with other phases. The calculated density is 5.73 g/cm^3 corresponding to Z = 1. We consider the calculated density of 11.46 g/cm^3 for Z = 2 to be impossible given that the corresponding cell contents require an anion-packing

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efficiency greater than that of oxygen closest packing. Rouseite is slightly turbid, moderately brittle, and does not fluoresce in ultraviolet radiation.

Optically, rouseite is biaxial, negative, with $2V_X = 46(2)°$ (meas.). It occurs in very small (0.2 mm in length) crystals, elongate parallel to [001], with large {010} and smaller {110} faces; on smaller crystals, the form {102} was observed. Indices were determined utilizing a crystal for which the orientation was also determined using single-crystal X-ray methods. Rouseite is colorless in transmitted light. The refractive indices could not be determined because rouseite reacted with the immersion liquids with indices higher than 1.78; α is estimated as being 1.8–1.9. The partial birefringence, $\gamma - \beta = 0.011(1)$, was measured on the spindle stage with a tilting compensator. This partial birefringence, combined with the measured optic-axes angle, gives a maximum birefringence of $\gamma - \alpha = 0.070(10)$. Rouseite has a very strong dispersion of the optic axes, $r > v$. The dispersion of the principal vibration directions Z and Y is very strong (over 45°) in the plane (010). The position of the indicatrix for sodium light is X = phi −82°, rho 40°; Y = phi 110°, rho 51.5°; Z = phi 14.5°, rho 83.5°.

Table 1. X-ray powder-diffraction data for rouseite

I/I_o	d(Obs)	d(Calc)	hkl	I/I_o	d(Obs)
100	6.81	6.74	010	10	1.864
40	5.45	5.41	100	20	1.806
10	5.25	5.24	$1\bar{1}0$	2	1.776
30	4.98	4.93	$10\bar{1}$	2	1.741
20	4.06	4.09	$1\bar{1}1$	5	1.713
20	3.85	3.88	$11\bar{1}$	10	1.620
60	3.38	3.37	020	10	1.549
60	3.25	3.21	$02\bar{1}$	5	1.526
		3.20	$1\bar{1}1$	2	1.510
70	3.06	3.05	$2\bar{1}1$	5	1.503
80	2.983	2.989	101	2	1.428
90	2.849	2.854	$12\bar{1}$	1	1.409
50	2.751	2.746	$10\bar{2}$	2	1.341
1	2.702	2.705	200	20	1.277
2	2.663	2.661	$11\bar{2}$		
10	2.620	2.622	$2\bar{2}0$		
30	2.550	2.555	$21\bar{1}$		
20	2.515	2.515	$01\bar{2}$		
10	2.488	2.485	120		
20	2.423	2.430	002		
		2.422	111		
20	2.262	2.272	$12\bar{2}$		
10	2.141	2.152	$23\bar{0}$		
5	2.085	2.087	$13\bar{1}$		
60	2.016	2.016	$3\bar{2}1$		

Intensities estimated visually. d-values calculated using the parameters a = 6.359, b = 7.286, c = 5.537 Å, α = 97.26, β = 114.17, γ = 105.99°. Ni-filtered CuK_α radiation. 114.6 mm diameter Gandolfi camera. Polycrystalline sample.

Chemical composition

Rouseite occurs in very small crystals that are intimately admixed with other phases, thus precluding a wet-chemical analysis. Accordingly, it was analyzed using an ARL-SEMQ electron microprobe with an operating voltage of 15 kV, and a beam current of 0.025 μA, measured on brass. For standards, we used PbO (Pb), synthetic olivenite (As), and manganite (Mn). There were no additional elements with atomic number greater than eight in detectable quantities as evidenced by a wavelength-dispersive microprobe scan. The data were corrected using a modified version of the MAGIC-4 program. The water content was determined using a Mettler TA-1 thermoanalyzer equipped with an IQ 200 quadrupole mass spectrometer for the detection of gases evolved during heating. The sample was crushed and lightly ground in acetone, and then dried and weighed at 20°C and approximately 45% relative humidity. The sample lost 0.2 ± 0.1 wt% in the thermoanalyzer during pumping to establish a vacuum of 1×10^{-8} torr. The sample was heated at 10°C/min from 20 to 520°C and lost 4.8 ± 0.1 wt% in a well-defined, single-step weight loss between 85 and 360°C forming a sharp peak at 285°C. The evolved gases produced during this weight loss were mainly H_2O with less than 0.1 wt% associated F_2. The small weight loss of 0.2 wt% during pump-down can be attributed to minor water absorbed on the surface of the particles. The 4.8 wt% water loss between 85 and 360°C can be attributed to water molecules bound in the structure of rouseite.

The resultant analysis yielded PbO 59.6, MnO 10.0, As_2O_3 27.0, H_2O 4.8, sum = 101.4 wt%. The chemical formula, calculated on the basis of eight oxygens, is $Pb_{1.97}Mn_{1.04}(AsO_3)_{2.01} \cdot 1.96H_2O$ or, ideally, $Pb_2Mn(AsO_3)_2 \cdot 2H_2O$, for which Z = 1. Because Pb interferes with microchemical tests for trivalent As, we have assigned the As to the trivalent state on the basis of a number of assumptions. First, the mineral occurs wholly within a reduced assemblage of trigonite and finnemanite, both phases containing As^{3+}. Second, if the As were pentavalent, the sum of our analysis would be much higher, well over 100%, and unreasonable. We consider the sum (101.4 wt%), as calculated for As^{3+}, to be slightly high, presumably from enhancement of weights percent determined oxides by loss of H_2O as a volatile during analysis, or from the inherent limitations of microprobe analyses. Thus, the even higher sum (105.8) required by As^{5+} would be unreasonable.

X-ray crystallography

Precession and Weissenberg photographs showed that rouseite is triclinic with space group $P1$ or $P\bar{1}$. The lattice parameters, $a = 6.36(2)$, $b = 7.29(2)$, $c = 5.54(2)$ Å, $\alpha = 97.3(3)$, $\beta = 114.2(2)$, $\gamma = 106.0(2)°$, were determined utilizing least-squares refinement (program LCLSQ, written by Charles W. Burnham) of powder-diffraction data (Table 1). These data were obtained using a Gandolfi camera (diameter = 114.6 mm), a polycrystalline sample, and Cu$K\alpha$ X-radiation. The lattice parameters are closely related to those of trigonite, $Pb_3Mn(AsO_3)_2(AsO_2OH)$, as determined by Pertlik (1978): monoclinic, $a = 7.26$, $b = 6.78$, $c = 11.09$ Å, $\beta = 91.5°$. The values of a and $c/2$ (7.26 and 5.55 Å) are very similar to b and c of rouseite, respectively. In addition, b of trigonite (6.81 Å) is only slightly greater than a of rouseite. These relations, coupled with the close similarity in chemical composition of these

two phases, imply that rouseite and trigonite have closely related structures.

Acknowledgments

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Reference

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