

## MANDARINOITE, A NEW FERRIC-IRON SELENITE FROM BOLIVIA

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### ABSTRACT

Mandarinoite, a new ferric-iron selenite mineral, occurs at the Pacajake mine, near Hiaco, Colquechaca, Bolivia. It is associated with selenium, siderite, penroseite and alteration products of penroseite such as ahlfeldite, cobaltomenite, chalcomenite and molybdomenite. The mineral is monoclinic, space group  $P2_1/c$  with  $a$  16.78(3),  $b$  7.86(1),  $c$  9.96(6) Å,  $\beta$  98.3(6)° and  $Z = 4$ . The mineral occurs as prismatic crystals, always twinned on (100), elongate on  $c$ , with the forms  $a$  {100},  $m$  {110},  $d$  {011} and  $e$  {101}. The chemical composition of mandarinoite is  $\text{Fe}^{3+}_2\text{Se}_2\text{O}_9 \cdot 4\text{H}_2\text{O}$ . Partial microprobe analysis yielded  $\text{Fe}_2\text{O}_3$  28.68%,  $\text{SeO}_2$  59.53%, with 11.79%  $\text{H}_2\text{O}$  by difference. The strongest lines in the X-ray diffraction pattern are 7.10 (100) (110), 2.977 (70) (213, 321, 122), 3.55 (50) (212, 220, 312), 3.43 (40) (302, 402) and 8.25 (40) (200); ( $d$  in Å,  $l$ / $h$ ,  $hkl$ ). Mandarinoite is light yellowish green in daylight,  $D$  (obs.) = 2.93,  $D$  (calc.) = 2.89 g/cm<sup>3</sup>. No cleavage was observed. The Mohs hardness is approximately 2½. Optically, mandarinoite is biaxial negative with  $a$  1.715(3),  $\beta$  1.80(1),  $\gamma$  1.87(1);  $X$  is parallel to  $b$  and  $c$   $\wedge$   $Z = 2^\circ$ ; dispersion is indiscernible,  $2V = 85^\circ$ .

### SOMMAIRE

On trouve la mandarinoïte, nouveau minéral, sélénite de fer ferrique, dans la mine Pacajake, près de Hiaco, Colquechaca (Bolivie). Elle est accompagnée de sélénium, sidérite et penroseïte avec produits d'altération de cette dernière: ahlfeldite, cobaltoménite, chalcoménite et molybdoménite. Monoclinique, de groupe spatial  $P2_1/c$ ,  $a$  16.78(3),  $b$  7.86(1),  $c$  9.96(6) Å,  $\beta$  98.3(6)° et  $Z = 4$ , elle se présente en cristaux prismatiques, toujours maclés sur (100), allongés suivant  $c$  et montrant les formes  $a$  {100},  $m$  {110},  $d$  {011} et  $e$  {101}. Sa composition chimique est  $\text{Fe}^{3+}_2\text{Se}_2\text{O}_9 \cdot 4\text{H}_2\text{O}$ . Une analyse partielle à la microsonde donne

28.68%  $\text{Fe}_2\text{O}_3$ , 59.53%  $\text{SeO}_2$  et 11.79% d'eau (par différence). Les espacements des cinq raies les plus intenses du cliché de poudre se classent comme suit par ordre d'intensité décroissante: 7.10(100)(110), 2.977(70)(213,321,122), 3.55(50)(212,220,312), 3.43(40)(302,402) et 8.25(40)(200). La mandarinoïte est d'un vert jaunâtre pâle à la lumière du jour,  $D$ (obs.) 2.93, (calc.) 2.89. Nul clivage n'a été observé. Sa dureté Mohs est de 2½. Optiquement biaxe négative,  $a$  1.715(3),  $\beta$  1.80(1),  $\gamma$  1.87(1),  $X$  //  $b, c$   $\wedge$   $Z = 2^\circ$ ; dispersion indiscernible;  $2V = 85^\circ$ .

(Traduit par la Rédaction)

### INTRODUCTION

The new mineral mandarinoite,  $\text{Fe}^{3+}_2\text{Se}_2\text{O}_9 \cdot 4\text{H}_2\text{O}$ , occurs on specimens from the oxidized zone of the Pacajake mine in Bolivia. The parent mineral, penroseite (blockite),  $(\text{Ni}, \text{Co}, \text{Cu})\text{Se}_2$ , is associated with siderite and quartz. This new ferric-iron selenite had been noted previously by several investigators. It was brought to the attention of the senior author by William Pinch of Rochester, New York, who had X-rayed this material using the powder method and correctly inferred that it was a new species. His devotion to mineralogy is worthy of the highest praise. The label of the type penroseite at Harvard University contained a notation of associated "unknown green crystals" but gave no indication as to the identity of the investigator who originally noted their uniqueness. Another sample was found in the Smithsonian collections, after the characterization of the species. In addition, Ahlfeld & Muñoz Reyes (1943) note, on p. 169 of their book *Los Minerales de Bolivia*, the existence of "selenito de hierro hidratado", but they did not characterize the species. Hence, this new

mineral had been known to certain mineralogists for some time but had not been characterized, probably owing to the shortage of the mineral.

We take pleasure in naming this new species in honor of Dr. Joseph A. Mandarino of the Royal Ontario Museum. His contributions to mineralogy are outstanding; in particular, the insights he has provided into the relationships of the Gladstone-Dale rule are of special merit. In view of Dr. Mandarino's work on selenite minerals, we think it fitting that this selenite be named for him. The new mineral and name have been approved by the Commission on New Minerals and Mineral Names, I.M.A., prior to publication. Holotype material will be deposited in The Smithsonian Institution, Washington, D.C. 20560, under catalog # 142878. Additional holotype material will be deposited in the Pinch Mineralogical Museum, 82 Kensington Court, Rochester, New York 14612, U.S.A. Several metatype samples have been so designated and repose in the mineral collections of the Royal Ontario Museum, Toronto, Ontario (catalog # M35273) and the Mineralogical Museum, Harvard University, 24 Oxford Street, Cambridge, Massachusetts 02138, U.S.A. under catalog, # H111364.

#### X-RAY CRYSTALLOGRAPHY

Single crystals of mandarinoite were studied using standard Weissenberg and precession techniques. Initial examination indicated that the diffraction symmetry was  $2/m\ 2/m\ 2/m$ ; however, one extinction rule is inconsistent with all possible space groups, indicating the crystals are twinned. Subsequent analysis showed that mandarinoite is monoclinic, space group  $P2_1/c$ , and twinned on (100). SEM photomicrographs then clearly showed that the crystals are twinned on composition plane (100).

A powder photograph was obtained using a 114.6 mm diameter Gandolfi camera, a powder-ball mount and NBS silicon as an internal standard. The lattice parameters resulting from the single-crystal patterns were refined by least-squares. The refined unit-cell parameters are  $a\ 16.78(3)$ ,  $b\ 7.86(1)$ ,  $c\ 9.96(6)\text{\AA}$ ,  $\beta\ 98.3(6)^\circ$ . The relatively high standard errors reflect the fact that the lattice pseudosymmetry, which leads to the twinning, results in only a small proportion of the  $d$  values being unambiguously indexable. The indexed powder diffraction data are listed in Table 1.

#### MORPHOLOGY

The crystals of mandarinoite examined, 0.5

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR MANDARINOITE

$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$I/I_0$	$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$I/I_0$
8.25	8.30	200	40		3.05	11 $\bar{3}$	
7.10	7.10	110	100	3.04	3.04	51 $\bar{1}$	5
6.14	6.15	011	5		3.03	01 $\bar{3}$	
4.94	4.93	002	5	2.977	2.978	21 $\bar{3}$	
4.74	4.92	102	5		2.975	321	70
4.74	4.74	211	5		2.974	122	
4.53	4.53	202	10	2.804	2.801	222	20
	4.53	310			2.768	51 $\bar{2}$	
	4.18	012		2.741	2.767	600	5
4.16	4.17	11 $\bar{2}$	10		2.733	213	
	4.15	400			2.590	322	
	3.98	30 $\bar{2}$		2.591	2.588	130	10
	3.94	311			2.587	502	
3.95	3.94	112	5		2.452	123	
	3.93	020		2.451	2.448	61 $\bar{2}$	10
	3.93	21 $\bar{2}$			2.447	231	
	3.67	410		2.275			10
3.65	3.65	021	5	2.195			5
	3.56	212		2.140			5
3.55	3.55	220	50	2.042			10
	3.55	31 $\bar{2}$		1.964			10
3.43	3.44	302	40	1.521			15
	3.43	402		1.482			15
3.31	3.32	500	5				
	3.30	411					

$\text{CuK}\alpha$  nickel-filtered X radiation. Gandolfi camera 114.6 mm diameter, polycrystalline sample. Intensities visually estimated. Values of  $d_{\text{obs}}$  corrected using a Si internal standard.

mm in length, are elongate parallel to [001] and flattened parallel to {100}. All of the crystals examined are twinned, with (100) the twin plane and the composition plane. The forms

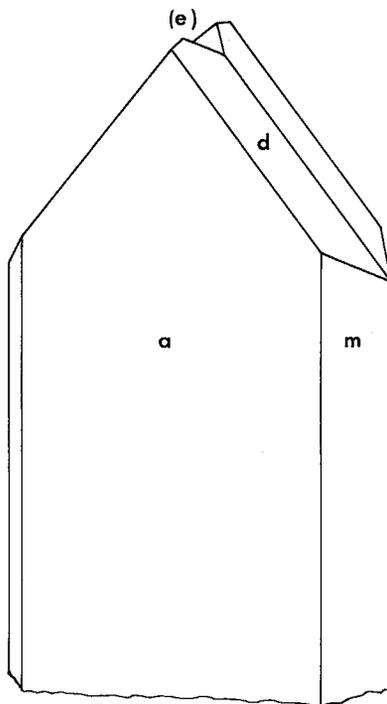


FIG. 1. Crystal drawing of mandarinoite. The forms present are  $a$  {100},  $m$  {110},  $d$  {011} and  $e$  {101}.

present are  $a \{100\}$ ,  $m \{110\}$ ,  $d \{011\}$  and  $e \{\bar{1}01\}$ . The first three forms listed were observed on three crystals measured by optical goniometry; the form  $\{\bar{1}01\}$  can be seen only on the SEM photomicrographs. This form may be developed only on very small crystals.

Because only twinned crystals were available for study and because the  $a$  axis of each of the two components of the twin has a different direction that could not be determined, the  $h$  index of all forms has a two-fold ambiguity. The Miller indices were arbitrarily chosen relative to one of the two possibilities. The  $hkl$  indices of the form  $\{\bar{1}01\}$  were determined on the SEM photomicrographs using a special construction, to be the subject of a separate paper.

#### PHYSICAL AND OPTICAL PROPERTIES

Mandarinoite is light green without obvious color-zoning. The hue is similar to that of good-quality gem peridot. The mineral may appear a darker green if resting on a black surface of native selenium or penroseite, and in these cases the mineral is notable for its ugliness. The streak is very light green. The mineral is transparent and almost colorless in oil immersion or thin section. Its lustre is vitreous to slightly greasy both on faces and fracture surfaces. The

crystals are very small, less than 0.5 mm in length, and cleavage observations are difficult; several crystal groups were deliberately broken and examined with the scanning electron microscope. No cleavage was observed, but a possible weak parting was noted parallel to the composition or twin plane (100). The Mohs hardness is approximately  $2\frac{1}{2}$ . The density, measured by flotation in Clerici's solution, is  $2.93(3) \text{ g/cm}^3$ , in good agreement with the calculated value of  $2.89 \text{ g/cm}^3$ . Mandarinoite does not luminesce in either ultraviolet radiation or the beam of the electron microprobe.

Only a few very small crystals were available for the determination of optical properties. The accuracy of the determinations was further lowered by twinning. The refractive indices and orientation of the indicatrix were determined on the spindle stage on twinned crystals previously oriented by X-ray methods. The optic axial angle and the orientation of the indicatrix were determined on the universal stage, but with an accuracy much lower than that usually obtained because of the small crystal size and twinning.

Mandarinoite is biaxial negative,  $2V = 85(10)^\circ$ , with refractive indices  $\alpha 1.715(3)$ ,  $\beta 1.80(1)$ ,  $\gamma 1.87(1)$ . Principal vibration direction  $X$  is parallel to the  $b$  axis, and  $c \wedge Z$  is  $2(1)^\circ$  in the acute angle between  $a$  and  $c$ .

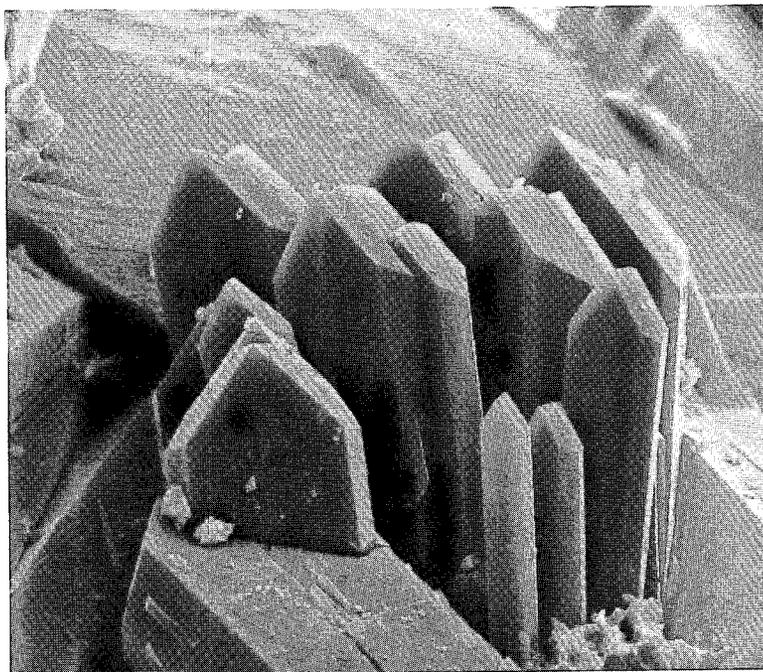


FIG. 2. Scanning electron microscope photomicrograph of a group of sub-parallel mandarinoite crystals. Magnification  $\times 1850$ .

Dispersion of the optic axes is indiscernible. The specific refractive energy  $k$  of mandarinoite, calculated from the chemical composition and the constants given by Mandarino (1976), is 0.252. The value obtained from the measured density and refractive indices is 0.271.

#### CHEMICAL COMPOSITION

The idealized chemical formula of mandarinoite is  $\text{Fe}^{3+}_2\text{Se}_3\text{O}_9 \cdot 4\text{H}_2\text{O}$  ( $Z=4$ ). The mineral was chemically analyzed with an ARL-SEMQ electron microprobe using an operating voltage of 15 kV and a beam current of 0.15  $\mu\text{A}$ . The intensities were corrected using the MAGIC-4 computer program. A wavelength-dispersive scan indicated the absence of elements with atomic number greater than nine except iron and selenium. We had insufficient material for a spectrographic analysis, but light elements are not common in the nickel and selenium-rich geochemical environment of mandarinoite. Water was calculated by difference.

The standards used for analysis were pyrite for iron and selenium metal for selenium. Duplicate analyses using other standards confirmed the composition given. The resultant analyses yield  $\text{Fe}_2\text{O}_3$  28.68%,  $\text{SeO}_2$  59.53%, with 11.79%  $\text{H}_2\text{O}$  by difference. This is in good agreement with the theoretical composition of  $\text{Fe}_2\text{O}_3$  28.28%,  $\text{SeO}_2$  58.96% and  $\text{H}_2\text{O}$  12.76%. Iron was determined to be in the 3+ oxidation state by microchemical tests (Kraus *et al.* 1959); on different samples, these repeatedly gave a very strong reaction for  $\text{Fe}^{3+}$  and a very weak reaction for  $\text{Fe}^{2+}$ . The empirical formula, calculated on the basis of 9 oxygen atoms, is  $\text{Fe}^{3+}_{2.01}\text{Se}_{2.99}\text{O}_9 \cdot 3.65\text{H}_2\text{O}$ , in good agreement with the theoretical idealized formula  $\text{Fe}^{3+}_2\text{Se}_3\text{O}_9 \cdot 4\text{H}_2\text{O}$ . The estimated accuracy of the microprobe analysis is  $\pm 3\%$  relative for selenium and iron.

#### OCCURRENCE AND LOCAL GEOLOGY

The type locality for mandarinoite is the Pacajake mine, near Hiaco, about 24 km ENE of Colquechaca on the eastern side of the central cordillera in Bolivia. According to Block & Ahlfeld (1937), the deposit occurs in Devonian sandstone as a vein striking N30°W and dipping 65°SW. The predominant primary minerals in the deposit are penroseite (blockite), clausenthalite and siderite. Other less common primary minerals are naumannite, tiemannite, calcite, hematite, barite and pyrite. These, together with the secondary minerals wulfenite, limonite, anglesite, cerussite, chalcocite, cobaltomenite, selenium and ahlfeldite have been noted by a number of investigators:

Herzenberg & Ahlfeld (1935), Palache (1937), Herzenberg (1944, 1945), Block & Ahlfeld (1937). In addition, Ramdohr (1969) noted the occurrence of two as yet unidentified primary minerals ( $e$  and  $f$ ). Several recent studies on minerals from this deposit include the description of olsacherite by Hurlbut & Aristarain (1969), a redefinition of ahlfeldite by Aristarain & Hurlbut (1969) and some observations on the doubtful validity of "selenolite" by Finkelman & Mrose (1977). Of the secondary minerals, the most common, resulting from the oxidation of penroseite, are chalcocite,  $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ , ahlfeldite,  $\text{NiSeO}_3 \cdot 2\text{H}_2\text{O}$ , and cobaltomenite,  $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$ . In addition, goethite is present on many specimens, both as cellular aggregates and as pseudomorphs after the previously existing gangue siderite. For further information on the cobaltomenite-ahlfeldite series, the reader is referred to the work of Sturman & Mandarino (1974).

As penroseite contains very little iron (Banister & Hey 1937), mandarinoite has likely formed from the simultaneous oxidation of penroseite and siderite or pyrite. This assumption is supported by the presence of goethite on all mandarinoite specimens seen to date. One specimen in the Harvard collection consists almost entirely of impure goethite and sparse mandarinoite.

Dr. Sidney Williams (pers. comm. 1977) found what is surely mandarinoite in 1973 at the Skouriotissa mine in Cyprus. Microchemical tests showed only iron and selenium. The strongest lines in the X-ray pattern are in good agreement with those of mandarinoite described here. The mineral occurs as apple-green bladed crystals up to 0.7 mm long, elongate along  $c$ . The crystals impregnate leached porous quartz, and no other species were found on the specimen. The cell dimensions of the Skouriotissa-mine mandarinoite are  $a$  16.808,  $b$  7.862,  $c$  10.10 Å,  $\beta$  98.26°.

In addition, there is some possibility that mandarinoite may form in other environments. For further information on the activity of selenium under different geochemical conditions, the reader is referred to the work of Lakin & Trites (1958), and in particular, to the studies of Howard (1972, 1977).

#### ACKNOWLEDGEMENTS

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## Note added in proof

Subsequent to the characterization of mandarinoite, we examined some very small yellowish green spherules, about 0.2 mm in diameter, that occur with poughite at the El Plomo mine, Ojojoma district, Tegucigalpa, Honduras. The spherules occur in vugs and are the last phase to form in the assemblage. The X-ray diffraction pattern is identical to that of mandarinoite; the mineral yields a strong reaction for ferric iron by microchemical test. Semi-quantitative analysis using an electron microprobe indicates that tellurium is present, but that the Se:Te ratio is approximately 7:3. Thus, the mineral is a tellurian mandarinoite, a third example of this new mineral.