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Schoonerite, a new zinc–manganese–iron phosphate mineral

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Abstract

Schoonerite, $ZnMn^{2+}Fe_2^{2+}Fe^{3+}(OH)_2(H_2O)_7(PO_4)_3 \cdot 2H_2O$, $Z = 4$, orthorhombic, space group *Pmab*, $a = 11.119(4)$, $b = 25.546(11)$, $c = 6.437(3)$A, is a new late-stage species from the Palermo No. 1 pegmatite, North Groton, New Hampshire. Biaxial (−), $\alpha = 1.618(5)$, $\beta = 1.652(3)$, $\gamma = 1.682(3)$, $2V_{obs} = 70$-$80°$, Z(brown) > Y(pale brown) > X(pale yellow), $X \| b$, $Y \| c$, $Z \| a$. Hardness about 4, cleavage {010} micaceous and {001} good. Specific gravity 2.87–2.92. The formula was established on the basis of microprobe and formal crystal structure analysis.

The mineral occurs as rosettes, mats, scales, and laths up to 2 mm in length, thin-tabular parallel to {010} and elongated parallel to [100], brown to reddish-brown in color, passing into coppery tones in oxidized material. It is a late-stage low-temperature mineral and occurs associated with siderite, mitridatite, jahnsite, whitmoreite, laueite, *etc.*, in oxidized masses of ludlamite, messelite, and vivianite derived from parent triphylite.

Introduction

We have been much interested in the structure systematics and paragenetic relationships among the basic phosphates of the first transition series metals. Continued study has indicated that many phases were previously inadequately characterized and required careful reinvestigation; others proved new and demanded comprehensive examination. Crystal-chemical interpretation of these compounds is difficult and usually requires detailed crystal structure analysis before their relationships are apparent.

The Palermo No. 1 pegmatite near North Groton, New Hampshire, continues to be a prolific source of these secondary phosphates (Moore *et al.*, 1975). Schoonerite is another new species to add to the mineralogical complexity of this pegmatite. The details of its crystal structure are given in the following paper.

Occurrence and paragenesis

Numerous phosphate pods from the Palermo pegmatite show a range of alterations as a result of retrograde hydrothermal attack by aqueous rest liquid formed during the evolution of the pegmatite. Further attack, doubtless postdating the consolidation of the pegmatite, involves surficial weathering and oxidation along fracture surfaces in the pods. The pods range from rather clean triphylite with varying amounts of sulfides (pyrite, pyrrhotite, sphalerite, and occasional galena), to extensively leached and oxidized material, porous like coke. In between, triphylites show zones of successive replacement, such as triphylite–ludlamite–vivianite, triphylite–siderite, triphylite–hydroxylapatite and whitlockite, *etc.* The replacing phases in turn frequently suffer further reworking by aqueous fluid and often are themselves replaced by more oxidized assemblages.

Schoonerite is a very sparse but widely distributed phase at Palermo, occurring locally in minute quantities. It is clearly the latest product in the assemblage; associated phases include mitridatite, laueite, strunzite, whitmoreite, and Fe–Mn oxyhydroxides. It has been noted as local patches and mats coating thin fracture surfaces cutting whitlockite–apatite rock, usually upon a thin black base of the oxides. It also occurs as scattered to bunched thin, friable laths in small open cavities in siderite, ludlamite, and messelite; and in solution cavities in vivianite, which schoonerite replaces. The new mineral is interpreted as a product of low-temperature hydrothermal at-

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tack, weathering, and oxidation of more reduced phases such as triphylite, ludlamite, vivianite, and sphalerite, all of which occur as common constituents of the pods.

Two samples afford a contrasting paragenetic setting for the mineral. One is a 6 × 8 × 4 cm mass of dense fine-grained whitlockite and hydroxylapatite. Granular siderite occurs along one side of the mass. Implanted upon solution cavities in the whitlockite and apatite are radial aggregates of childrenite, warty brown jahnsite, and a film of dull green mitridatite. Joints through the mass are easily split and display a sooty black coating of ferric and manganic oxides. The schoonerite occurs as copper-red glistening scales and mats across the surface, the latest mineral in the sequence. Individual scales rarely exceed 50 μ in greatest dimension.

The type sample measures 3 × 4 × 2 cm and came from an enormous triphylite pod, now trenched away, in the northeast corner of the pegmatite. Portions of the triphylite, especially along the periphery, are completely replaced by granular siderite, coarse patches of ludlamite, and remnant arrojadite. Cavities in the sample are studded with lustrous siderite rhombohedra, bipyramids of quartz, colorless cockscomb aggregates of messelite, and pale blue laths of vivianite. Upon these are perched radial sprays of whitmoreite, orange laths of jahnsite, a dull green layer of mitridatite, and thin laths of the schoonerite. The last four minerals constitute an oxidized assemblage derived from the earlier-formed aquated ferrous phosphates. The sequence is triphylite–arrojadite–ludlamite, siderite–messelite–vivianite–mitridatite–rockbridgeite–jahnsite, whitmoreite–schoonerite. The schoonerite is brown to copper-red and occurs as isolated laths to bunches of flattened straw-like aggregates up to 2 mm in length. Of the species noted, schoonerite is distinct in containing essential zinc.

Although the new species was familiar to us for the past four years, the quantity of material available was insufficient for complete wet-chemical analysis. Consequently, appeal was made to full three-dimensional crystal-structure analysis where bond distances, atomic positions, thermal parameters, and electrostatic valence bond-strength sums allowed us to formulate a complete and unambiguous composition. The species is a basic zinc, manganous, ferrous, ferric phosphate, and its limited occurrence may result from the fact that few pegmatites carry significant quantities of zinc minerals necessary for its production. The only other well-known pegmatite which contains basic zinc manganese iron phosphates is Hagendorf-Süd in the Oberpfalz, Germany. In fact, in a recent note by Strunz *et al.* (1975, Fig 65) there is an illustration of a small, very thin, friable red-brown tabular crystal with orthogonal contour. They state that the symmetry is probably orthorhombic. Parallel to one edge, the axial dimension is ~6.45A. As no further information is at hand, we can only speculate that this may in fact prove to be a new occurrence for schoonerite or some closely related phase.

Physical properties

Schoonerite occurs as thin laths whose average ratio in dimensions (along *a*, *b*, *c*) is about 20:1:5. Free-standing laths are elongated parallel to [100] and thin tabular parallel to {010}. Crystal aggregates occur as rosettes, laminae (parallel to {010}), sprays and mats, and individuals rarely exceed 1 mm in greatest dimension. The color is pale tan to brown, reddish-brown to bronzy on exposed, oxidized surfaces, much resembling switzerite with which it is easily confounded. Inclined extinction parallel to the lath for switzerite is a simple means of distinguishing the two. Confusion with beraunite (the oxidized variety), rockbridgeite (oxidized), strunzite, and cacoxenite is also possible. The streak is pale brown. Forms observed are {001}, {010}, and {100}. The mineral is transparent along [010] although most crystals are translucent and turbid. Good single crystals are exceedingly rare, most individuals being curved and crinkled.

The hardness is about 4 (estimated by needle pressure), and cleavage is perfect to micaceous parallel to {010} and good parallel to {001}. Specific gravity (sink-float in methylene iodide–toluene mixtures) is variable. Dark reddish-brown (oxidized ?) crystals remain suspended at 2.92(4). The type crystals had specific gravity 2.87(4). The calculated density (formula in the title) is 2.79 gm cm^{-3}. The mineral is rapidly soluble in cold 1:1 HCl solution, coloring the solution greenish-yellow.

The structure analysis afforded no evidence for atoms beyond those in the title formula. An observed specific gravity higher than that calculated may result from adsorption of methylene iodide onto and into rather large open spaces in the structure. Providing the volume change is small, the net effect would be to increase the density of the crystals.

Crystallography

With considerable difficulty, a crystal suitable for three-dimensional crystal-structure analysis was

TABLE 1. Schoonerite. Observed and calculated powder data*

I(obs)	d(obs)	I(calc)	d(calc)	hkℓ	I(obs)	d(obs)	I(calc)	d(calc)	hkℓ
10	12.77	100	12.77	020	3	2.127	2	2.128	0.12.0
7	8.35	28	8.39	120			2	2.127	391
4	6.43	8	6.44	001	3	2.092	2	2.097	412
2	6.26	6	6.25	011			1	2.091	192
3	5.52	14	5.54	140	3	1.994	1	1.998	442
3	5.44	11	5.44	111			1	1.994	481
3	5.09	6	5.10	220	2	1.940	2	1.944	551
2	4.53	4	4.53	041	2	1.916	2	1.917	063
3	4.25	8	4.26	060	b 2	1.881	1	1.883	0.11.2
2	4.19	5	4.19	240			1	1.881	4.10.0
1	4.01	2	4.00	051	2	1.845	2	1.846	392
4	3.761	13	3.766	151	3	1.822	2	1.825	580
2	3.539	2	3.551	061			1	1.823	472
1	3.371	1	3.380	260	2	1.780	1	1.780	640
4	3.182	8	3.187	311	2	1.757	1	1.757	482
3	3.054	5	3.053	171	3	1.690	3	1.690	492
b 1	2.850	1	2.860	081	3	1.622	2	1.624	4.10.2
		2	2.795	360	4	1.600	3	1.603	612
9	2.768	15	2.780	400	3	1.578	2	1.581	124
		26	2.770	212	1	1.560			
3	2.711	6	2.722	222	1	1.535			
		2	2.719	351	1	1.528			
		1	2.716	420	3	1.500			
1	2.651	1	2.648	232	2	1.453			
1	2.536	1	2.529	191	1	1.437			
2	2.372	2	2.374	0.10.1	2	1.388			
3	2.318	4	2.321	2.10.0	2	1.322			
3	2.212	4	2.214	272	2	1.271			
1	2.179	1	2.183	2.10.1	1	1.249			

*114.6 mm Gandolfi camera. The calculated data are from the crystal structure parameters.

obtained, the details and results of which appear in the following paper. All atoms (excluding H) were unambiguously located. The ideal formula is $ZnMn^{2+}Fe_2^{2+}Fe^{3+}(OH)_2(H_2O)_7(PO_4)_3 \cdot 2H_2O$, $Z = 4$, but owing to a structural kinship with montgomeryite, we prefer to express it as $Mn_2^{2+}Fe_2^{2+}Zn_2(H_2O)_{14}[Fe_2^{2+}Fe_2^{3+}(OH)_4(PO_4)_6] \cdot 4H_2O$, the bracketed region corresponding to a structurally similar region in montgomeryite.

The structure-cell criteria were obtained by monitoring high-angle reflections on a Picker FACS-1 automated diffractometer (Mo$K\alpha$ radiation, graphite monochromator) and refining the results by least squares. Schoonerite is orthorhombic, space group *Pmab*, $a = 11.119(4)$, $b = 25.546(11)$, $c = 6.437(3)$A. The indexed powder pattern appears in Table 1 and was obtained with a 114.6 mm diameter Gandolfi-type camera, utilizing single crystal fragments of the type sample and Mn-filtered Fe$K\alpha$ radiation. The film intensities were read visually, and the low-angle reflection at 12.77A was obviously overexposed. Multiplying the remaining observed intensities by a factor of about 3 affords fair agreement with the calculated values.

Optical properties

Schoonerite is orthorhombic, biaxial (−), $\alpha = 1.618(5)$, $\beta = 1.652(3)$, $\gamma = 1.682(3)$, $2V_{obs} = 70$–$80°$. The pleochroism is weak, Z(brown) > Y(pale brown) > X(pale yellow) and the orientation is $X \| b$, $Y \| c$, $Z \| a$. Measurements were taken from the type crystals. Owing to rather diffuse isogyres, we could not unambiguously determine the dispersion.

Chemical analysis

It was impossible to secure enough material for wet-chemical analysis. Since the structure analysis afforded not only atomic positions but also bond distances and bond strengths, it was possible to unambiguously discriminate between O^{2-}, OH^-, and H_2O. Two kinds of water molecules occur in the structure, one kind ligated to the transition metals, and the other cavity water, the latter loosely held by rather weak hydrogen bonds. The cavity water occurs along the spaces between the dense sheets in the structure, which are oriented parallel to {010}. This observation is important since the electron-probe results give high totals. This can be explained by loss of

the loosely held water and slight collapse of the structure.

Mr. Todd Solberg of this laboratory examined two crystals from the type sample. The elements were analyzed on a solid-state detector, the corrections directly applied via an on-line computer employing the local program SSOLID. Standards used in the probe analysis included apatite (Ca,P); chromite (Mg,Al,Fe); sphalerite (Zn); microcline (K); manganoan hortonolite (Mn). Low beam current and voltage were necessary owing to the thermal instability of the compound. The program SSOLID includes corrections for dead time, absorption and fluorescence, efficiency of generation, and peak overlap. The results appear in Table 2.

An independent probe analysis was performed at the Massachusetts Institute of Technology by Dr. A. J. Irving on crystals from a sample other than the type. The standards included a homogeneous arrojadite (BZ-3) for Na, K, Ca, Mg, Mn, Fe, Al and P; and willemite for Zn. The results in Table 2 are compared with the ideal formula. It is obvious that both analyses afford high totals, doubtless due to loss of some water and shrinkage of the crystals. Ranges for the first set of analyses are stated; Dr. Irving informed us that Fe, Mn, Ca, and Zn gave ranges up to ±10 percent. This reflects inhomogeneities and compositional variations in schoonerite crystals. Since P varied only slightly, we suspect that extensive substitutions at the octahedral (Mn^{2+}, Fe^{2+}, Fe^{3+}) and irregular five-coordinated (Zn^{2+}) sites are possible. A reciprocal relationship between K + Ca and Zn + Mg was noted. The results of analysis 1 were computed to cation contents (other than hydrogen) based on 6 phosphorus per formula unit and gave: $K_{0.1}Ca_{0.4}Mg_{0.6}Mn_{1.5}Fe_{6.0}Zn_{1.4}Al_{0.2}P_{6.0}$, with a sum of 16.2 cations, somewhat higher than the ideal requirement of 16.0 cations. Analysis 2 gives the following cation contents: $Na_{0.1}Ca_{0.3}Mg_{0.4}Mn_{1.6}Fe_{5.6}Zn_{1.6}P_{6.0}$, with a sum of 15.6 cations.

Both analyses support the proposed end-member compositions based on the structure study. Assignment of valences to Fe was possible through the structure study discussed in the following paper.

Name

Both species and name have been approved by the International Commission on New Minerals and New Mineral Names. The type specimen (NMNH 135934) is preserved in the collection of types at the U.S. National Museum, Smithsonian Institution. About 100 specimens are presently known, but it is anticipated that more will be found during continued collecting activity at the Palermo pegmatite.

It is with great pleasure we honor Mr. Richard Schooner of Woodstock, Connecticut, lifelong collector and student of New England minerals and mineralogy.

TABLE 2. Schoonerite. Chemical analyses

	1	2	3
Na_2O	nil	0.14	-
K_2O	0.47 (0.22-0.68)	nil	-
CaO	1.38 (0.38-2.11)	1.3	-
MgO	1.74 (1.52-1.99)	1.2	-
MnO	7.32 (5.58-8.42)	9.3	9.23
FeO	29.84 (25.73-32.46)	32.1	18.69
ZnO	7.95 (5.16-11.48)	10.6	10.59
Al_2O_3	0.73 (0.62-0.91)	nil	-
Fe_2O_3	-	-	10.39
P_2O_5	29.45 (28.08-30.72)	34.0	27.69
H_2O	[23.41]	[23.4]	23.41
	102.29	112.0	100.00

[1]Electron probe analysis (five points over two crystals) showing range of values. Todd Solberg, analyst. Water (ideal formula) added in brackets.

[2]Electron probe analysis (ten data points). A. J. Irving, analyst. Water (ideal formula) added in brackets.

[3]$Mn^{2+}ZnFe_2^{2+}Fe^{3+}(OH)_2(H_2O)_7(PO_4)_3 \cdot 2H_2O$.

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Forrest F. Fogg and Robert W. Whitmore, owners of the Palermo pegmatite and devoted amateur mineralogists, sacrificed fine specimens of schoonerite so that this study could be completed. We thank Mr. Todd Solberg and Dr. Anthony J. Irving for the probe analyses.

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