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Jarosewichite and a related phase: basic manganese arsenates of the chlorophoenicite group from Franklin, New Jersey

PETE J. DUNN

Department of Mineral Sciences
Smithsonian Institution
Washington, D.C. 20560

DONALD R. PEACOR

Department of Geological Sciences
University of Michigan
Ann Arbor, Michigan 48109

PETER B. LEAVENS

Department of Geology
University of Delaware
Newark, Delaware 19711

AND WILLIAM B. SIMMONS

Department of Earth Sciences
University of New Orleans
New Orleans, Louisiana 70148

Abstract

Jarosewichite, $Mn^{3+}Mn_3^{2+}(AsO_4)(OH)_6$, is a new mineral, closely related to chlorophoenicite, from the Franklin mine, Franklin, Sussex County, New Jersey, where it occurs associated with andradite, franklinite, flinkite, cahnite and hausmannite. Jarosewichite is orthorhombic, space group *C*2/*m*2/*m*2/*m*, *C*222 or *Cmm*2, with $a = 6.56(3)$, $b = 25.20(10)$, $c = 10.00(5)$Å, and Z = 8. The strongest lines in the X-ray powder diffraction pattern are (*d*, *I*, *hkl*) 2.669 *100* 222,082; 3.91 *60* 042, 061; 1.788 *50* (not indexed); 2.503 *30* 242, 261, 004, 0 10 0. Jarosewichite is dark red, occurs in prismatic barrel-shaped aggregates, has a density of 3.66 (obs), 3.70 g/cm^3 (calc). It is biaxial (−) with refractive indices $\alpha = 1.780(5)$, $\beta = 1.795(5)$ and $\gamma = 1.805(5)$; the orientation is $X = a$, $Y = b$, $Z = c$; pleochroism is weak, $Z > X$. Microprobe analysis with Mn^{3+} calculated, yields: FeO 0.4, MgO 2.1, CaO 0.2, ZnO 1.2, MnO 42.3, Mn_2O_3 17.7 (ΣMn = 45.1 wt.%), As_2O_5 24.0, with H_2O 12.1 percent by difference, sum = 100.0 percent.

A second manganese arsenate from Franklin, New Jersey, is also related to chlorophoenicite, but may be heterogeneous. Although optical, chemical and crystallographic properties are characterized, there is sufficient ambiguity to deny it species status at this time. The data for this mineral, jarosewichite and chlorophoenicite imply the existence of a large family of related arsenates based on the structure principles outlined by Moore for chlorophoenicite.

Introduction

In early 1981, Mrs. Alice Kraissl of River Edge, New Jersey, called to our attention some dark red crystals. They were then assumed to be carminite, associated with flinkite. The crystals had originally been noted by Cook (1973) and he described them as carminite without providing the data which led to this identification. However, the material did not appear to have the usual appearance of carminite and an investigation of the assemblage was undertaken. Our study revealed that it is not carminite but that it is a new mineral, herein described as jaroswichite.

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Jarosewichite is named in honor of Eugene Jarosewich, chief chemist in the Department of Mineral Sciences at the Smithsonian Institution, in recognition and appreciation of his many contributions to mineralogy through analysis of minerals, meteorites and rocks, and especially in the area of electron microprobe analysis. The mineral and the name were approved by the Commission on New Minerals and Mineral Names, IMA. Type material is preserved in the Smithsonian Institution under catalog # NMNH 148972. Identical material, obtained from the same sample, is in the personal mineral collection of Mrs. Alice Kraissl, who generously donated the type material. Another sample is in the Mineralogical Museum at Harvard University (# 109463) and is identical in every feature. Given the fact that Mrs. Kraissl's material was obtained from David Cook, who also provided the Harvard sample, it is likely that all these samples are parts of the original piece. The Harvard sample is designated cotype.

Occurrence

Jarosewichite occurs at the Franklin mine, Franklin, Sussex County, New Jersey. The type specimen was collected on the dumps and nothing is known of its location in the mine. The specimen consists of massive green andradite intergrown with franklinite of composition $(Zn_{0.48}Mn_{0.43}Mg_{0.03}Fe_{0.02}Al_{0.01})_{\Sigma 0.97}Fe^{3+}_{2.00}O_{3.97}$. The ore is vuggy and the vugs are lined with a dark brown druse of an unknown mineral, the X-ray powder diffraction pattern of which suggests it is in the friedelite group. Upon the brown druse are 0.5 mm crystals of hausmannite and sharp euhedral crystals of cahnite and allactite. Cahnite is coated with a light brown film and, in turn, with fascicles of flinkite and jarosewichite, which appear to have formed at the same time. Some jarosewichite encrusts flinkite, indicating it was the last phase formed. The associated minerals were identified by X-ray powder diffraction.

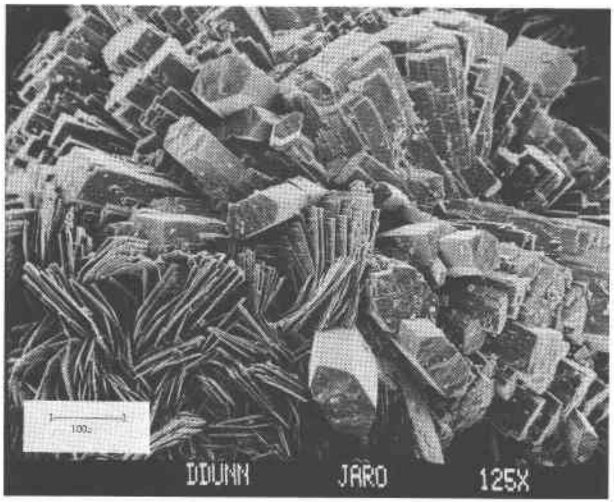

Fig. 1. Radial divergent spray of prismatic jarosewichite crystals with bladed flinkite crystals, from Franklin, New Jersey.

Physical and optical properties

Jarosewichite is dark red in color and appears to be black except in thin splinters or crystals. The luster of fracture surfaces is sub-vitreous and the streak is reddish orange. Cleavage was not observed. The Mohs' hardness is approximately 4. The density, determined using heavy liquid techniques, is 3.66(4) g/cm^3, in excellent agreement with the calculated value of 3.70 g/cm^3.

Optically, jarosewichite is biaxial (−) with refractive indices $\alpha = 1.780(5)$, $\beta = 1.795(5)$ and $\gamma = 1.805(5)$. 2V could not be accurately measured due to minute crystal size and the fact that jarosewichite reacts with the refractive index liquids, a factor which also caused the high standard errors in the refractive index determinations. 2V calculated from the refractive indices is 78°. The orientation is $X = a$, $Y = b$ and $Z = c$. Pleochroism is weak, $Z > X$, with Z = dark brownish red and X = medium brownish red. Calculation of the Gladstone–Dale relationship, using the constants of Mandarino (1976) yields: $K_C = 0.224$ and $K_P = 0.217$, indicating excellent agreement of the analytical and physical data (Mandarino, 1979). Jarosewichite does not respond to ultraviolet radiation.

Most of the jarosewichite occurs as aggregates which are barrel-shaped, have a rough, irregular surface, and physically resemble some synadelphite, particularly that from Sterling Hill. A few very small crystals, up to 0.5 mm in length, were observed. They are euhedral with flattened habit, elongate on a, and tabular on b. The best crystals, for which only a limited number of faces could be observed for the [100] zone, have {010} as the dominant form and {021} as a less prominent form, as determined using a two-circle optical goniometer. A scanning electron photomicrograph of a divergent spray of jarosewichite crystals is shown as Figure 1.

Chemical composition

Jarosewichite was chemically analyzed using an ARL–SEMQ electron microprobe utilizing an operating voltage of 15 kV and a sample current of 0.025 μA, standardized on brass. The standards used for analysis were manganite (Mn), synthetic olivenite (As), synthetic ZnO (Zn), and hornblende (Ca, Mg, Fe). No other elements with atomic number greater than 9 were found with a wavelength-dispersive scan. A spectrographic analysis proved the absence of boron. Type chlorophoenicite (Dunn, 1981) was used as a control standard. Water could not be directly determined due to extreme paucity of material; it is calculated by difference. The oxidation state of As is inferred from the As^{5+} present in the associated cahnite and flinkite, both of which are intimately associated with jarosewichite. The oxidation state of Mn could likewise not be determined. We have assigned the 4 Mn per formula unit to $Mn^{3+}_1Mn^{2+}_3$ using the Gladstone–Dale relationship as a guide. We infer the probable presence of some Mn^{3+} based on: (a) the associated flinkite and hausmannite contain Mn^{3+} and Mn^{2+}, indicating that the oxidation potential of the mineral-forming solutions was compatible with such oxidation states; (b) all associated minerals have (OH) rather than H_2O, the latter which would be necessary for jarosewichite if all the Mn was Mn^{2+}; and (c) the color and high absorption of jarosewichite are consistent with the presence of Mn^{3+}, which is an intense absorber in the visible range, either by itself or through charge transfer with Mn^{2+}.

The resultant analysis, with Mn^{3+} calculated, yields: FeO 0.4, MgO 2.1, CaO, 0.2, ZnO, 1.2, MnO 42.3, Mn_2O_3 17.7 (Mn = 45.1 wt. %), As_2O_5 24.0 percent, with H_2O 12.1 percent by difference, sum = 100.0 percent. Calculation of unit cell contents, using the observed density and the unit cell parameters, yields: $[Mn^{3+}_{1.00}(Mn^{2+}_{2.74}Mg_{0.24}Fe_{0.03}Ca_{0.02}Zn_{0.07})_{\Sigma 3.10}(AsO_4)_{0.95}(OH)_{6.35}]$, with $Z = 8$, in excellent agreement with the theoretical end member formula of jarosewichite, $Mn^{3+}Mn^{2+}_3(AsO_4)(OH)_6$, for which the weight percents are Mn_2O_3 17.14, MnO 46.20, As_2O_5 24.95, H_2O 11.71, sum = 100.00 percent.

X-ray crystallography

Single crystals were studied using standard precession and Weissenberg techniques. The resulting photographs showed that jarosewichite is orthorhombic with space group $C2/m\ 2/m\ 2/m$, $Cmm2$ or $C222$, with $a = 6.56(3)$, $b = 25.20(10)$ and $c = 10.00(5)$Å. These lattice parameters were determined in part by utilizing d-values from a powder diffraction pattern prepared using Si as an internal standard. The powder data, which were obtained with a polycrystalline mount in a Gandolfi camera using Cu$K\alpha$ X-radiation, are listed in Table 1. The number of unambiguously indexable reflections was not sufficient to permit least squares refinement of the lattice parameters.

All reflections having h or k odd are extremely weak, and therefore were excluded from the process of indexing the powder pattern. These reflections are so weak that they are not discernible on photographs obtained with very small crystals and very long exposures. There is thus a pronounced substructure having cell parameters $A = 3.28$ $(a/2)$, $B = 12.60$ $(b/2)$ and $C = 10.00$ (c)Å. The short translation of 3.3 Å was shown by Moore (1968) to occur in the structure of chlorophoenicite, $(Mn,Mg)_3Zn_2(AsO_4)(OH)_7$, although in that case there are streaks requiring translation of 2 × 3.3Å. This phase is not only structurally and chemically similar to jarosewichite, but also occurs at Franklin, New Jersey. Moore showed that the 3.3Å translation in chlorophoenicite corresponds to the length of the edge of a Mn–oxygen octahedron, resulting in a chain of edge-sharing octahedra of infinite length in

Table 1. X-ray powder diffraction data for jarosewichite

d(Obs.)	d(Calc.)	hkl	I/I_o
6.29	6.30	040	20
5.30	5.33	041	5
3.91	3.92	042	60
	3.87	061	
3.21	3.22	023	5
	3.22	062	
3.17	3.15	080	5
2.669	2.680	222	100
	2.665	082	
2.612	2.611	063	2
2.573	2.585	260	2
2.503	2.520	0,10,0	30
	2.515	242	
	2.503	261	
	2.501	004	
2.451	2.453	024	10
	2.444	0,10,1	
2.289	2.299	223	5
	2.297	262	
	2.290	083	
2.256	2.251	0,10,2	5
1.873	1.878	283	1
1.788			50
1.738			1
1.576			20
1.558			30
1.501			20
1.468			2
1.385			1
1.361			1
1.126			2

the direction of the 3.3Å translation. Such chains are bonded to other chains to form bands, which in turn can be viewed as strips from pyrochroite-like sheets. The structure of jarosewichite may be based on similar principles, with a unique pattern of chain-sharing and band formation. Indeed, one can imagine that an entire family of such related phases might occur. Another phase whose structure is based on these principles, but whose properties are not well enough defined to permit characterization as a separate species, is described below.

A second phase related to chlorophoenicite

In early 1981, Mr. James Kaufmann and Mr. Andrew Delatesh called to our attention a specimen from Franklin, New Jersey, consisting of dark brown to black acicular crystals intergrown with acicular secondary willemite. Our examination of this phase (NMNH 149091) indicates that it is very similar to chlorophoenicite in several respects. However, we were unable to obtain data of sufficient rigor to be confident that it is a unique species. The lack of unambiguous results has prompted us to leave this phase unnamed, while presenting our data for the record, in anticipation that they might eventually contribute to a resolution of the many complex structural features of compounds related to chlorophoenicite.

The crystals are bladed in part, but predominantly consist of rectangular, elongated prisms which are terminated by either a very rough pinacoid or a tree bud-like branching termination. The crystals are lustrous, very brittle and have a light brown streak. No cleavage was observed and the hardness was not determined. The density, determined using heavy liquid techniques, is 3.62(10) g/cm^3.

This unknown mineral was chemically analyzed using the same operating conditions as were used for jarosewichite. The resultant analysis yielded: FeO 0.3, MgO 2.4, CaO 0.5, ZnO 28.4, MnO 31.0, As_2O_5 18.7, SiO_2 1.1 percent, with H_2O 16.7 percent by difference, sum = 100.0 percent. We have not calculated unit cell contents because the probable altered nature of the crystals suggests that our density might be low. The ratio of M^{2+} cations: (As+Si) is approximately 9.3:1.9, which is close to the 10:2 ratio expected for chlorophoenicite (Dunn, 1981; Moore, 1968). These data are consistent with the theoretical composition of a hydrated and oxidized chlorophoenicite. Assignment of Mn to various oxidation states is quite problematical and, given the possibility of partial oxidation of these crystals, nearly impossible. Calculation of the Gladstone–Dale relationship yields results consistent with the presence of some Mn^{3+}, but we cannot offer a firm formula for this compound. Optical examination of these crystals indicated that they are optically inhomogeneous and some have an isotropic core. There is undulatory extinction of some zones, but not with a consistent pattern. The mean refractive index, measured in sodium light, is approximately 1.76. Inasmuch as chlorophoenicite is colorless, the dark reddish brown color of these crystals also suggests the presence of some Mn^{3+}.

Single-crystal X-ray photographs show broad, diffuse reflections whose appearance resembles those from crystals which have been subject to chemical and/or structural alteration. One crystal of average size for single-crystal diffraction studies gave barely observable intensities, indicating that only a portion of the crystal retained the translational periodicity reflected in the morphology.

The diffraction relations are dominated by a translation of ~ 3.3Å, parallel to the prism direction, as is true of both jarosewichite and chlorophoenicite. Zero-level photographs normal to this

Table 2. X-ray powder diffraction data for a chlorophoenicite-like phase

d (obs.)	d (calc.)	hkl	I/Io
10.90	10.90	200	100
3.74	3.74	501	5
3.62	3.64	002	10
	3.63	602	
3.49	3.45	202	5
3.23	——	——	2
3.02	3.02	402	30
2.95	——	——	1
2.86	2.86	701	5
	2.84	011	
	2.84	310	
2.509	2.517	510	20
	2.517	411	
2.330			20
2.184			2
2.120			10
1.814			15
1.684			5

translation were directly compared with corresponding photographs of jarosewichite and chlorophoenicite. There is a close relationship between those of this phase and of chlorophoenicite, but they are clearly different. However, the relations are similar enough to suggest that the full three-dimensional structures are very closely related.

Although the diffraction relations were not well-enough defined to lead to a determination of extinction relations and thus to the space group, they did lead to a determination of cell parameters. This phase is orthorhombic, Laue symmetry $2/m\ 2/m\ 2/m$, has a body-centered cell and lattice parameters $a = 21.80(8)$, $b = 3.08(1)$, $c = 7.27(2)$Å. The lattice parameters were determined through least-squares refinement of the powder diffraction data (Table 2), obtained utilizing a 114.6 mm diameter Gandolfi powder camera, a polycrystalline sample, and Si as an internal standard. Because the powder data can be indexed using the lattice parameters as determined through single-crystal diffraction relations (with the exception of two reflections which are so weak that their contribution by this phase is uncertain) and because the powder data were obtained using several crystals, there is a strong implication that at least portions of our material are crystalline and probably represent a distinct member of a family of phases related to chlorophoenicite.

The data given above clearly imply that the crystals are not of a homogeneous single-phase mineral. The unusual rounded shape of the crystals, heterogeneous optical properties, and diffuse, weak reflections on single-crystal diffraction photographs are compatible with this conclusion. On the other hand, the data imply that if this is a polyphase material, then it consists of a disordered, non-diffracting component, plus a well-defined phase which is closely related to chlorophoenicite. The only reason it cannot be completely characterized is that one cannot be entirely sure of a one-to-one correlation between electron microprobe analytical data and those portions of the sample which yield interpretable diffraction data. We can reasonably postulate, however, that this phase provides evidence for a large family of phases, all based on the structural scheme shown by Moore (1968) to exist for chlorophoenicite.

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