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Ferrisurite, the Fe^{3+} analogue of surite, from Inyo County, California

ANTHONY R. KAMPF
Mineralogy Section, Natural History Museum of Los Angeles County, 900 Exposition Blvd., Los Angeles, California 90007, U.S.A.
LARRY L. JACKSON, GARY B. SIDDER, EUGENE E. FOORD
U.S. Geological Survey, Denver Federal Center, Lakewood, Colorado 80225, U.S.A.
PAUL M. ADAMS
Aerospace Corporation, 2350 E. El Segundo Blvd., El Segundo, California 90245, U.S.A.

ABSTRACT

Ferrisurite is the Fe^{3+} analogue of surite. The type locality is the Shirley Ann claim, a small oxidized contact metamorphic lead-copper deposit west of Death Valley in Inyo County, California. The new mineral occurs as compact radial aggregates of forest green fibers embedded in quartz and cerussite and as tapering feathery yellow-green crystals in radiating groups in vugs. Crystal sizes range up to 2 mm along **a** × 0.01 mm along **b** × 0.04 mm along **c**. The {010} form is prominent and no others are measurable. Other associated minerals are galena, calcite, mimetite, wulfenite, pyrite, chalcopyrite, covellite, hematite, chalcocite, and malachite. Ferrisurite probably formed during the early stages of oxidation as a consequence of the alteration of silicates in close proximity to galena.

The mineral is transparent and has a greenish yellow to olive green streak and silky luster. The estimated Mohs hardness is 2–2½. $D_{meas} = 4.0(1)$ g/cm³ and $D_{calc} = 3.89$ g/cm³. Ferrisurite is biaxial (+), $\alpha = 1.757(3)$, $\beta = 1.763(3)$, $\gamma = 1.773(3)$, $2V_{calc} = 76°$; orientation (pleochroism): $X = c$ (yellow), $Y = b$ (brown), $Z = a$ (light green).

Single-crystal precession study showed the mineral to be monoclinic with space group $P2_1$ or $P2_1/m$. Cell parameters refined from powder data are $a = 5.241(1)$, $b = 9.076(5)$, $c = 16.23(1)$ Å, $\beta = 90.03(7)°$, and $V = 772(1)$ Å³ ($Z = 2$). The strongest X-ray powder diffraction lines are [d in angstroms $(I)(hkl)$] 16.1(40)(001), 5.40(25)(003), 4.53(100)(110,020), 3.727(35)(014,103), 3.240(90)(104,$\bar{1}$04,005), 2.612(80)(201,$\bar{2}$01,200,130), 2.272(50)(220,040), 1.715(25)(150,240,310).

The H_2O, CO_2, and FeO components were determined by Karl Fischer titration, coulometric titration, and potentiometric titration, respectively. Other constituents were determined by electron microprobe analysis yielding Na_2O 0.3, MgO 0.2, CaO 3.4, FeO 0.8, BaO 0.1, PbO 42.7, Al_2O_3 3.2, Fe_2O_3 10.5, SiO_2 26.6, F 0.8, CO_2 8.2, H_2O 3.5, sum 100.3, less O = F 0.3, total 100.0 wt%. The IR absorption spectrum supports the presence of CO_3, SiO_4, OH, and H_2O groups.

The structures of surite and ferrisurite probably consist of smectite-like layers between which are cerussite-hydrocerussite-like regions of variable composition. The following simplified formula is proposed for these minerals: $(Pb,Ca)_{2-3}(CO_3)_{1.5-2}(OH,F)_{0.5-1}[(Fe,Al)_2Si_4O_{10}(OH)_2]\cdot nH_2O$.

INTRODUCTION

In 1989, one of the authors (P.M.A.) found an unusual green fibrous mineral at the Shirley Ann mining claim west of Death Valley in Inyo County, California. Initial X-ray powder diffraction, energy dispersive X-ray analysis, and infrared spectroscopy indicated a likely relationship with the mineral surite. Hayase et al. (1978) described surite from the oxidation zone of a lead-zinc-copper deposit exploited by the Cruz del Sur mine in Argentina. They proposed a cerussite-smectite intercalate model for this mineral.

Subsequent study has shown the mineral from the Shirley Ann claim to be the Fe^{3+} analogue of surite, and the new mineral has been named ferrisurite in recognition of this relationship. The mineral and name have been approved by the Commission on New Minerals and Mineral Names, IMA. Holotype material is deposited in the mineral collections of the Natural History Museum of Los Angles County (LACMNH no. 37275) and the Smithsonian Institution, Washington, DC (NMNH no. 170288).

OCCURRENCE

The Shirley Ann claim is located 300 m southwest of Big Dodd Spring in the Ubehebe mining district, Inyo County, California. This is about 45 km due east of Lone

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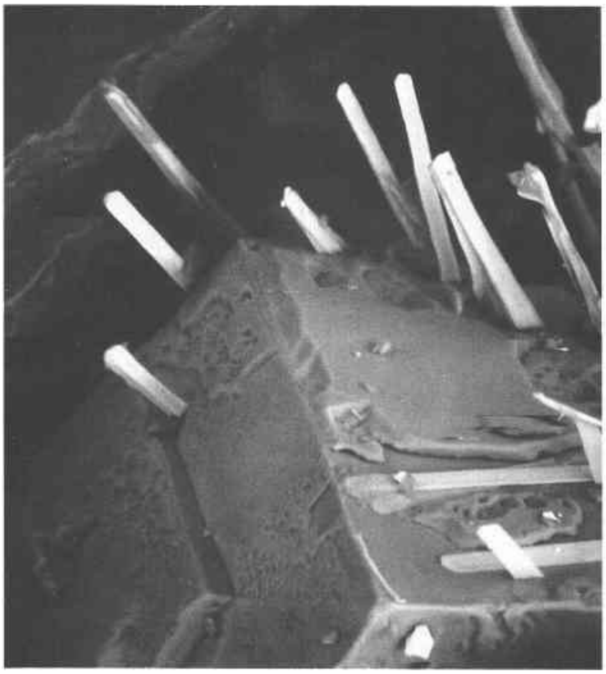

Fig. 1. Scanning electron photomicrograph of ferrisurite crystals on calcite (1300×).

Pine and 9 km west of the western boundary of Death Valley National Monument.

According to McAllister (1955), the Shirley Ann claim exploits an oxidized lead deposit in contact metamorphosed and faulted shaly and silty limestone. The deposit is notable for an abundance of Cu minerals and scarcity of Zn minerals relative to the larger mines in the area. The most prominent ore mineral is cerussite, which replaces galena. The mineral assemblage includes quartz, calcite, covellite, chalcocite, anglesite, wulfenite, hematite, limonite, malachite, and other supergene Cu minerals (McAllister, 1955).

Specimens containing ferrisurite were collected at the mine dump. Minerals associated with ferrisurite include galena, pyrite, chalcopyrite, covellite, chalcocite, quartz, calcite, hematite, cerussite, mimetite, wulfenite, and malachite. Ferrisurite probably formed during the early stages of oxidation as a consequence of the alteration of silicates in close proximity to galena.

PHYSICAL AND OPTICAL PROPERTIES

Ferrisurite occurs as compact radial aggregates of fibers embedded in quartz and cerussite and as tapering feathery crystals in radiating groups in vugs (Fig. 1). Crystals are flattened on {010}, the only measurable form, and elongate parallel to **a**. Maximum crystal dimensions are 2 mm along **a** × 0.01 mm along **b** × 0.04 mm along **c**. No twinning was observed.

Individual ferrisurite crystals are transparent to translucent with light yellow-green color and greenish yellow streak. Compact radial aggregates have a medium to dark forest green color and olive green streak. The mineral exhibits silky luster and perfect {010} cleavage. Fibers and individual crystals are very flexible. The Mohs hardness is approximately 2–2½. Ferrisurite effervesces in cold 1:1 HCl, leaving a gelatinous residue.

The density, determined by the method of sink-float in Clerici solution, is 4.0(1) g/cm³. The density calculated from the chemical and crystallographic data is 3.89 g/cm³, in fair agreement with the experimental value.

Optically, ferrisurite is biaxial (+). The indices of refraction measured in white light are $\alpha = 1.757(3)$, $\beta = 1.763(3)$, $\gamma = 1.773(3)$. Because of the unfavorable optical orientation relative to crystal morphology, $2V$ could not be measured and dispersion could not be observed. The optic angle ($2V$) calculated from the indices of refraction is 76°. The optical orientation is $X = c$, $Y = b$, $Z = a$. The mineral is pleochroic: X = yellow, Y = brown, Z = light green. No fluorescence in long- or short-wave ultraviolet radiation was observed.

TABLE 1. Cell parameters for ferrisurite and surite

	Surite*	Surite**	Ferrisurite
a (Å)	5.22	5.241(3)	5.241(1)
b (Å)	8.97	8.95(1)	9.076(5)
c (Å)	16.3	16.20(5)	16.23(1)
β (°)	96.1	90.0(1)	90.03(7)
V (Å³)	759	760(3)	772(1)

* Reported by Hayase et al. (1978).
** Refined using X-ray powder data of Hayase et al. (1978).

X-RAY CRYSTALLOGRAPHY

Ferrisurite crystals were studied by the X-ray precession method. Although diffraction spots were diffuse, they were sufficiently distinct for the determination of the space group and approximate cell parameters. As for many of the smectite-group minerals, the cell is pseudo-orthorhombic with β very close to 90°. The diffraction symmetry as evidenced by reflection intensities is $2/m$, indicating monoclinic symmetry. The only extinction criterion noted was $0k0$: $k = 2n$, showing the space group to be either $P2_1$ or $P2_1/m$. The cell parameters refined from the powder diffraction data are compared with those of surite in Table 1. The X-ray powder diffraction data for the two minerals (Table 2) are very similar.

The unit cells of surite and ferrisurite correspond closely except for a significant discrepancy in the angle β. Because the surite crystals studied by Hayase et al. (1978) were not of adequate quality to allow single-crystal X-ray study, they determined the surite cell by using electron diffraction patterns produced by oriented crystals on a colloidal membrane. They further correlated these results with the X-ray powder diffraction pattern. Because oblique texture patterns were used to determine β and this method is indirect, the accuracy of the resulting value is highly dependent upon the accuracy of the measured d values.

TABLE 2. X-ray powder diffraction data for ferrisurite and surite

Surite*		Ferrisurite			
I	d_{meas}	*I*	d_{meas}	d_{calc}	*hkl*
68	16.2	40	16.1	16.2	001
		5	8.15	8.11	002
71	5.4	25	5.40	5.41	003
20	4.48	100	4.53	4.54, 4.54	110, 020
12	4.35	10	4.36	4.37, 4.37, 4.37	021, 111, $11\bar{1}$
100	4.05	10	4.05	4.06	004
6b	3.705	35b	3.727	3.704, 3.763	014, 103
8b	3.573				
11b	3.463	10	3.470	3.476, 3.477, 3.478	113, 023, $\bar{1}13$
		<5	3.354	3.356, 3.357	121, $\bar{1}21$
60	3.240	90b	3.240	3.207, 3.209, 3.246	104, $\bar{1}04$, 005
8	3.035	10	3.025	3.024, 3.024, 3.025	024, 114, $\bar{1}14$
		<5	2.829	2.835	032
35	2.700	5	2.704	2.705	006
18	2.590	80b	2.612	2.587, 2.587, 2.620, 2.620	201, $\bar{2}01$, 200, 130
50	2.313	5	2.322	2.323, 2.323, 2.324	026, 116, $\bar{1}16$
14b	2.247	50	2.272	2.269, 2.269	220, 040
		10	2.199	2.201, 2.202	204, $\bar{2}04$
5b	2.079	15b	2.090	2.092, 2.092, 2.093	043, 223, $\bar{2}23$
5b	2.056				
7	2.024				
3b	1.984	20b	1.973	1.966–1.981	231, $\bar{2}31$, 018, 044, 224, $\bar{2}24$
3b	1.951				
		<5	1.864	1.859–1.860	225, $\bar{2}25$, 045, 233, $\bar{2}33$
5	1.800	5	1.811	1.803	009
4b	1.697	25	1.715	1.715, 1.715, 1.715	150, 240, 310
		<5	1.668	1.662–1.676	303, $\bar{3}03$, 029, 119, $\bar{1}19$
4b	1.618	5b	1.622	1.621–1.623	227, $\bar{2}27$, 047, 321, $\bar{3}21$, 0·0·10
3b	1.581	<5	1.541	1.538, 1.539	305, $\bar{3}05$
4b	1.497	20	1.512	1.513, 1.513	330, 060
4b	1.470				
		10	1.309	1.306, 1.306, 1.310, 1.310	401, $\bar{4}01$, 260, 400
		10	1.259	1.259, 1.259, 1.259	170, 350, 420

Note: Data obtained with 114.6-mm Gandolfi camera, Cu*Kα* (Ni filtered) radiation (λ = 1.54178), visually estimated intensities, indexed with the aid of single-crystal data.

* Data from Hayase et al. (1978).

Although Hayase et al. did not report uncertainties for their measured *d* values, comparison of their X-ray and electron diffraction results suggests that the uncertainty in their *d* values determined by electron diffraction is approximately ±0.02 Å. This uncertainty could readily account for a 6° error in their determination of β. The credibility of their β determination is compromised further by their failure to refine the surite cell parameters using the powder diffraction data.

A pseudo-orthorhombic cell ($\beta = 90°$) is, in fact, consistent with the X-ray powder diffraction data reported by Hayase et al. Least-squares refinement using their data with indexing similar to that employed for ferrisurite, 16.2 Å (001), 5.4 (003), 4.48 (020), 4.35 (111,$\bar{1}$11), 4.05 (004), 3.240 (005), 2.700 (006), 2.590 (201,$\bar{2}$01,130), 2.313 (026,116,$\bar{1}$16), yields the pseudo-orthorhombic cell data for surite provided in Table 1.

CHEMICAL COMPOSITION

Electron microprobe analysis was carried out using the following standards: albite (Na), phlogopite (Mg, F), diopside (Ca, Si), hyalophane (Ba), galena (Pb), orthoclase (Al), and hematite (Fe). H_2O was determined by Karl Fischer titration using a 15-mg sample. CO_2 was determined by coulometric titration using a 9-mg sample. Fe^{2+} was determined by potentiometric titration using a 23-mg sample. Because of the limited quantity of the mineral available and the difficulty in separating pure material, only one analysis each was conducted for H_2O, CO_2, and Fe^{2+}. Nevertheless, the reliability of the techniques used for these analyses is judged to be high.

Electron microprobe analysis totals varied considerably and were significantly lower than expected, largely because of the poor polish taken by the mineral and, to a lesser extent, to the thinness of the crystals. No other elements were detected using either the microprobe or inductively coupled plasma emission spectroscopy. Care was taken to avoid deterioration of the sample under the electron beam, and this effect is judged insignificant.

Because insufficient material was available for complete wet chemical analysis, the three microprobe analyses with highest totals (each with a total near 78 wt%) were averaged, and they were factored up by 13% to bring the total analysis including H_2O and CO_2 to 100%. This approach was used because all of the microprobe analyses, regardless of overall total, yielded very similar relative quantities of the individual oxides. Fe was allocated as FeO and Fe_2O_3 in accord with the Fe^{2+} analysis. Analytical results and ranges are given in Table 3.

The Gladstone-Dale compatibility index, $1 - (Kp/Kc)$,

TABLE 3. Chemical analytical data for ferrisurite and surite

	Surite*	Ferrisurite
Na_2O	0.77	0.3
MgO	1.29	0.2
CaO	4.75	3.4
CuO	0.07	—
FeO	—	0.8
BaO	—	0.1
PbO	45.32	42.7
Al_2O_3	11.27	3.2
Fe_2O_3	0.41	10.5
SiO_2	23.58	26.6
F	—	0.8
CO_2	9.45	8.2
H_2O	3.72	3.5

* Data from Hayase et al. (1978).

for ferrisurite is −0.059 (Mandarino, 1981), indicating good compatibility among the calculated density, average index of refraction, and composition.

INFRARED ABSORPTION SPECTRUM

The infrared absorption spectrum of ferrisurite is shown in Figure 2. Ferrisurite absorption bands at 1019, 878, 819, 491, and 425 cm^{-1} are comparable in position and relative intensity to bands in the spectrum of smectite (Salisbury et al., 1987) that can be assigned to silicate. Bands at 3452 and 1622 cm^{-1}, assigned to H_2O, and at 3543 cm^{-1}, assigned to OH, are also similarly represented in the smectite spectrum. Bands at 1422, 853, and 691 cm^{-1} compare with bands in the spectrum of cerussite (Ferraro, 1982) that are assignable to carbonate.

The infrared absorption spectrum of surite over the region of 2000–600 cm^{-1} (Hayase et al., 1978) is also shown in Figure 2. The spectra are seen to be very similar.

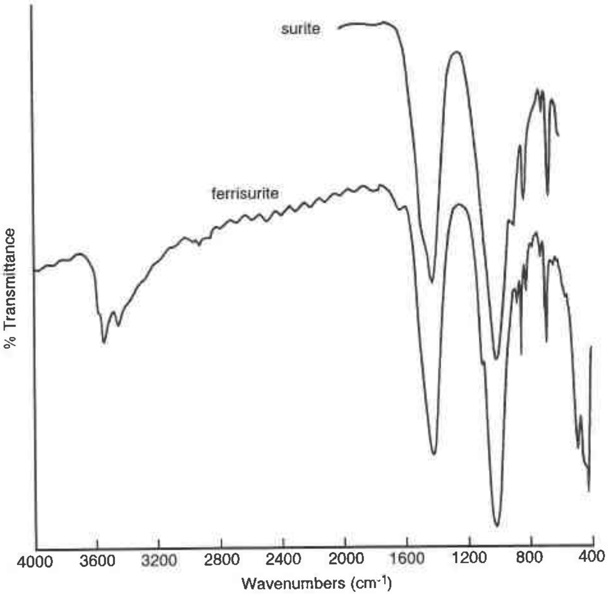

Fig. 2. Infrared absorption spectrum of ferrisurite compared with the surite spectrum of Hayase et al. (1978).

FORMULA AND RELATIONSHIP TO SURITE

In accord with the cerussite-smectite intercalate model proposed by Hayase et al. (1978) for surite, the empirical formula for ferrisurite based upon Si = 4 can be expressed as

$$(Pb_{1.73}Ca_{0.55}Na_{0.09}Ba_{0.01})_{\Sigma 2.38}(CO_3)_{1.68}(OH)_{0.51}F_{0.38}\cdot 0.50H_2O$$
$$(Fe^{3}_{1.19}Al_{0.57}Fe^{2}_{0.10}Mg_{0.05}\square_{0.09})_{\Sigma 2.00}Si_4O_{10}(OH)_2.$$

The first line of the formula corresponds to the interlayer region and the second line to the smectite layer. Assigning Si alone to the tetrahedral site yields the best agreement between the measured and calculated densities.

The deviation of the empirically derived subscripts from whole numbers is common in smectite-like minerals. The interlayer region can vary considerably in composition for a given species, and vacancies in the octahedral sheets are typical.

The empirical formula for surite provided by Hayase et al., $(Pb_{1.90}Cu_{0.01}Ca_{0.25})_{\Sigma 2.16}(CO_3)_2(Al_{1.75}Fe^{3}_{0.05}Mg_{0.30})_{\Sigma 2.10}$-$(Si_{3.68}Al_{0.32})O_{10}(OH)_2$, does not accurately reflect the chemical analyses or density which they report for the mineral. Using their measured density as a basis, their chemical analytical data yield an empirical formula similar to that of ferrisurite:

$$(Pb_{1.84}Ca_{0.77}Na_{0.23}Cu_{0.01})_{\Sigma 2.85}(CO_3)_{1.95}(OH)_{0.59}\cdot 0.58H_2O$$
$$(Al_{1.58}Mg_{0.29}Fe^{3}_{0.05}\square_{0.08})_{\Sigma 2.00}(Si_{3.57}Al_{0.43})O_{10}(OH)_2.$$

These formulae suggest that at least a portion of the cerussite-like layer may be more similar to hydrocerussite. Furthermore, the interlayer portion apparently deviates significantly from whole number stoichiometry. The difficulty in deriving ideal formulas for these compounds is additionally complicated by the substitution of Al for Si in the tetrahedral sheet (in surite) and vacancies and divalent cations for trivalent cations in the octahedral sheet, situations that require excess positive charge in the interlayer region for charge balance. Consequently, the following somewhat-variable simplified formula is proposed for these compounds:

$$(Pb,Ca)_{2-3}(CO_3)_{1.5-2}(OH,F)_{0.5-1}[(Fe,Al)_2(Si,Al)_4O_{10}(OH)_2]\cdot nH_2O.$$

Without more direct structural evidence or chemical data for other compounds of this type, the limits of variability in the cerussite-hydrocerussite-like layer remain poorly defined.

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