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New data on hemihedrite from Arizona

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ABSTRACT

Hemihedrite from the Florence Lead-Silver mine in Pinal County, Arizona, USA was first described and assigned the ideal chemical formula $Pb_{10}Zn(CrO_4)_6(SiO_4)_2F_2$, based upon a variety of chemical and crystal-structure analyses. The primary methods used to determine the fluorine content for hemihedrite were colorimetry, which resulted in values of F that were too high and inconsistent with the structural data, and infrared (IR) spectroscopic analysis that failed to detect OH or H_2O. Our reinvestigation using electron microprobe analysis of the type material, and additional samples from the type locality, the Rat Tail claim, Arizona, and Nevada, reveals the absence of fluorine, while the presence of OH is confirmed by Raman spectroscopy. These findings suggest that the colorimetric determination of fluorine in the original description of hemihedrite probably misidentified F due to the interferences from PO_4 and SO_4, both found in our chemical analyses. As a consequence of these results, the study presented here proposes a redefinition of the chemical composition of hemihedrite to the ideal chemical formula $Pb_{10}Zn(CrO_4)_6(SiO_4)_2(OH)_2$. Hemihedrite is isotypic with iranite with substitution of Zn for Cu, and raygrantite with substitution of Cr for S. Structural data from a sample from the Rat Tail claim, Arizona, indicate that hemihedrite is triclinic in space group $P\bar{1}$, $a = 9.4891(7)$, $b = 11.4242(8)$, $c = 10.8155(7)$ Å, $\alpha = 120.368(2)°$, $\beta = 92.017(3)°$, $\gamma = 55.857(2)°$, $V = 784.88(9)$ Å^3, $Z = 1$, consistent with previous investigations. The structure was refined from single-crystal X-ray diffraction data to $R_1 = 0.022$ for 5705 unique observed reflections, and the ideal chemical formula $Pb_{10}Zn(CrO_4)_6(SiO_4)_2(OH)_2$ was assumed during the refinement. Electron microprobe analyses of this sample yielded the empirical chemical formula $Pb_{10.05}(Zn_{0.91}Mg_{0.02})_{\sum = 0.93}(Cr_{5.98}S_{0.01}P_{0.01})_{\sum = 6.00}Si_{1.97}O_{34}H_{2.16}$ based on 34 O atoms and six (Cr + S + P) per unit cell.

Keywords: hemihedrite, Arizona, redefinition, electron microprobe analysis, single-crystal structure, iranite, OH, fluorine, Raman spectroscopy.

Introduction

Hemihedrite was first described by Williams and Anthony (1970) as a secondary lead mineral from the Florence Lead-Silver mine in the Tortilla mountains, Pinal County, Arizona, USA. At the type locality, hemihedrite forms euhedral crystals in vugs and fractures in association with wulfenite, cerussite, mimetite, minium, phoenicochroite, willemite and vauquelinite. These minerals occur in a secondary assemblage derived from the alteration of primary galena, sphalerite, pyrite and minor tennantite. Williams and Anthony (1970) also report a second occurrence of hemihedrite at the Rat Tail claim close to Wickenburg, Maricopa County, Arizona, USA with a similar mineral assemblage.

Multiple chemical analyses performed by Williams and Anthony (1970) on samples from Pinal and Maricopa Counties, Arizona, combined with structural data reported by McLean and Anthony (1970), lead to the idealized formula $Pb_{10}Zn(CrO_4)_6(SiO_4)_2F_2$. Despite the significant compositional variation observed in their chemical

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analyses, the major elements Pb, Zn, Cr and Si were consistent with the structural data. However, in the case of F, the amount determined by colorimetry (5.1%) greatly exceeded the amount indicated by the crystal structure (1.2%). This inconsistency led the authors to consider the latter value in the definition of the ideal chemical formula for hemihedrite. Additionally, their IR spectroscopic analyses failed to detect OH or H_2O.

In their study of several lead-bearing minerals, Cesbron and Williams (1980), hydrothermally synthesized both the OH-analogue of hemihedrite $Pb_{10}Zn(CrO_4)_6(SiO_4)_2(OH)_2$ and iranite $Pb_{10}Cu(CrO_4)_6(SiO_4)_2(OH)_2$ at 230°C and pH between 9 and 9.5. From the analysis of these synthetic materials and additional natural samples from Arizona (USA), New Mexico (USA), and Iran, they concluded that there probably existed a complete solid-solution between iranite and hemihedrite. Unfortunately, their chemical data did not report either fluorine or water contents. Similarly, the work by Frost (2004) on Raman microscopy of selected chromate minerals does not report the chemical composition of the samples used in their study, including hemihedrite. Moreover, the Raman spectrum for hemihedrite was reported only below 1000 cm^{-1}, and did not include the region where the O–H stretching modes would be detected (typically > 3000 cm^{-1}).

Subsequently, hemihedrite has been reported near Boulder City, Clark County, Nevada, USA (Anthony *et al.*, 1990) and in the Seh–Changi mine, near Nayband, Iran (Bariand and Poullen, 1980), but details on the fluorine content are lacking. Interestingly, Raman spectroscopic studies of an important English oil painting of the 18th Century (Edwards *et al.*, 2014) revealed hemihedrite in some red-pigmented areas of the painting. Given that hemihedrite is an uncommon mineral and that cerussite, a common natural white lead carbonate pigment, was present in the same areas where hemihedrite was found, those authors suggest that hemihedrite was probably associated with cerussite, as both minerals are typically found together. The study did not include a chemical analysis.

In the course of characterizing minerals for the RRUFF Project (http://rruff.info) (Lafuente *et al.*, 2015), electron microprobe analyses of four hemihedrite samples from both Pinal and Maricopa Counties, surprisingly, did not reveal the presence of fluorine in their chemistries. Subsequent Raman spectroscopic analyses did however indicate the presence of OH. As a consequence of these results, a fragment of the type material held by the Natural History Museum in London (Previously British Museum) was also studied. Its chemistry and Raman spectrum also indicate the absence of fluorine and the presence of OH, respectively.

This paper reports the chemical composition of type hemihedrite and RRUFF samples by means of electron microprobe. A sample labelled as hemihedrite from Nevada (USA) was also analysed, resulting in a chemical formula closer to that of iranite. A detailed crystal structure study of a sample from the Rat Tail claim (RRUFF sample R140134) is also given. Based on the results, this work provides evidence for a redefinition of the chemical composition of hemihedrite to the ideal formula $Pb_{10}Zn(CrO_4)_6(SiO_4)_2(OH)_2$. Note that hemihedrite from Iran was not studied here and its fluorine content might differ from those in our study. The findings of this study will be reviewed and announced in a forthcoming CNMNC Newsletter.

Experimental

Samples

Six samples were examined during the course of this study: a fragment of hemihedrite type material from the collection of the Natural History Museum, London, UK (NHM-London: BM 1968, 246); additional hemihedrite samples from the Florence Lead-Silver mine and the Rat Tail claim from the RRUFF project (deposit numbers: R050551, R140133, R140134 and R141184); and a sample from the Root mine, Good springs, Clark County, Nevada, USA, provided by Mr. Dick Thomssen of Tucson, Arizona, USA. The poor crystalline quality of the type material prevented its use for crystal structure analysis. Thus, RRUFF sample R140134 from the Rat Tail claim was selected for a detailed characterization, including X-ray data collection and structure analysis, electron microprobe analysis and Raman spectroscopy.

Chemical composition

The chemical compositions of the samples were determined using a CAMECA SX100 electron microprobe operating in wavelength dispersion (WDS) mode with an accelerating voltage of 20 kV, a beam current of 20 nA and beam diameter <1 μm. The following standards were used: Si, Mg: *K*α, forsterite; Pb: *L*α, NBS_K0229 synthetic glass (PbO 70%, SiO_2 30%); Cr: *K*α, chromite; Zn: *K*α,

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ZnO; S: *Kα*, baryte; P: *Kα*, apatite (syn.); As: *Lα*, NiAs; Cu: *Kα*, chalcopyrite. The average compositions were normalized on the basis of 34 O atoms and six (Cr + S + P) per unit cell. Analytical results are given in Table 1.

Fluorine content was not detected in any of the analysed samples. To confirm this, spectrometer scans of sample R140134, collected on the Cameca SX100 using the thallium acid phthalate (TAP) crystal, are displayed in Fig. 1. A WDS scan over the ~0.65–0.70 keV range failed to show any evidence of the F*Kα* peak. Similar results were found for the other hemihedrite samples.

The H_2O content was not determined directly, but was calculated so as to achieve 34 O atoms in the idealized empirical formula. The presence of OH was confirmed by Raman spectroscopic analyses. The Raman spectra of sample R140134 (Fig. 2) shows a broad band at ~3389 cm^{-1}, indicative of O–H stretching vibrations (υ_{OH}). The Raman spectra were collected from randomly oriented crystals on a Thermo Almega microRaman

TABLE 1. Composition (wt.%) and unit formula (apfu) for hemihedrite.

	(1)[a]	(2)[a]	(3)[a]	(4)[a]	(5)[a]	(6)[a]	(7)[b]	(8)[c]
PbO	72.63(42)	73.38(51)	72.21(37)	72.50(32)	72.54(39)	73.07(47)	70.5	73.0
ZnO	2.49(2)	2.29(10)	2.38(7)	2.43(7)	2.53(23)	0.882(270)	3.93	2.7
MgO	0.028(10)	0.091(59)	0.032(20)	0.027(9)	0.022(13)	b.d.l.		
CrO_3	19.25(24)	18.82(28)	19.24(17)	19.29(13)	19.29(14)	19.02(22)	19.5	19.7
SO_3	0.174(69)	0.225(129)	0.020(17)	0.200(73)	0.049(48)	0.091(51)		
P_2O_5	0.065(35)	0.159(133)	0.032(15)	0.034(18)	0.02(1)	0.159(17)		
SiO_2	3.62(10)	3.67(21)	3.81(6)	3.70(5)	3.92(8)	3.53(4)	3.2	3.9
As_2O_5	b.d.l.	0.513(450)	b.d.l.	0.077(57)	b.d.l.	0.384(101)		
CuO						1.65(24)		
H_2O[d]	1.37	0.73	1.08	1.31	0.93	0.81		
F							5.1	1.2
$O=F^-$							–2.1	–0.5
Σ	99.63	99.89	98.82	99.57	99.29	99.60	100.1	100.0
Pb	9.98	10.21	10.05	9.94	10.06	10.21	9.71	10
ΣA	9.98	10.21	10.05	9.94	10.06	10.21	9.71	10
Zn	0.94	0.88	0.91	0.91	0.96	0.34	1.37	1
Cu						0.65		
Mg	0.02	0.07	0.02	0.02	0.02			
ΣM	0.96	0.95	0.93	0.93	0.98	0.99	1.37	1
Cr	5.90	5.84	5.98	5.90	5.97	5.93	6.00	6
S	0.07	0.09	0.01	0.08	0.02	0.04		
P	0.03	0.07	0.01	0.02	0.01	0.07		
ΣT1	6.00	6.00	6.00	6.00	6.00	6.04	6.00	6
Si	1.85	1.90	1.97	1.88	2.02	1.83	1.66	2
As		0.14		0.02	0.00	0.10		
ΣT2	1.85	2.04	1.97	1.90	2.02	1.93	1.66	2
H	2.74	1.47	2.16	2.62	1.85	1.62		
F							8.25	2

b.d.l.: below detection limit.

Samples (Reference, locality, *n* = number analyses points): (1) This study (type material), Florence mine (AZ), *n* = 10; (2) This study (R140133), Florence mine (AZ), *n* = 18; (3) this study (R140134), Rat Tail claim (AZ), *n* = 13; (4) this study (R141184), Rat Tail claim (AZ), *n* = 12; (5) this study (R050551), Rat Tail claim (AZ), *n* = 15; (6) this study, Nevada, *n* = 8; (7–8) Williams and Anthony (1970), Florence mine (AZ).

[a]Unit formula (atoms per formula units) calculated based on 34 O atoms and six CrO_3 per unit cell.

[b]Average of all chemical analyses recalculated to 100%.

[c]Ideal chemical formula $Pb_{10}Zn(CrO_4)_6(SiO_4)_2F_2$.

[d]H_2O calculated to achieve 34 O atoms in the idealized empirical formulae.

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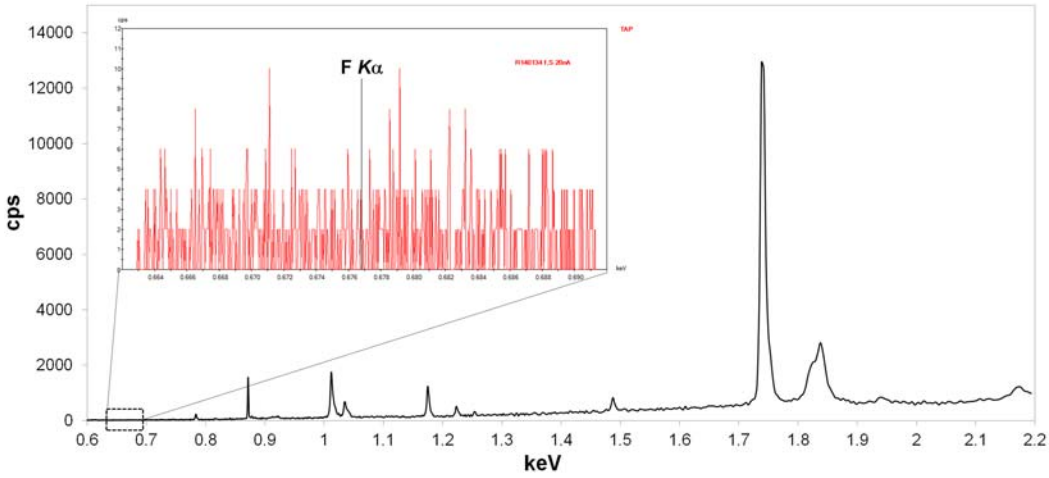


FIG. 1. Wavelength-dispersive spectrometry scans (TAP-crystal spectrometer) of the sample R140134. The scan focused in the region ~0.66–0.70 keV shows the absence of the F*K*α line.

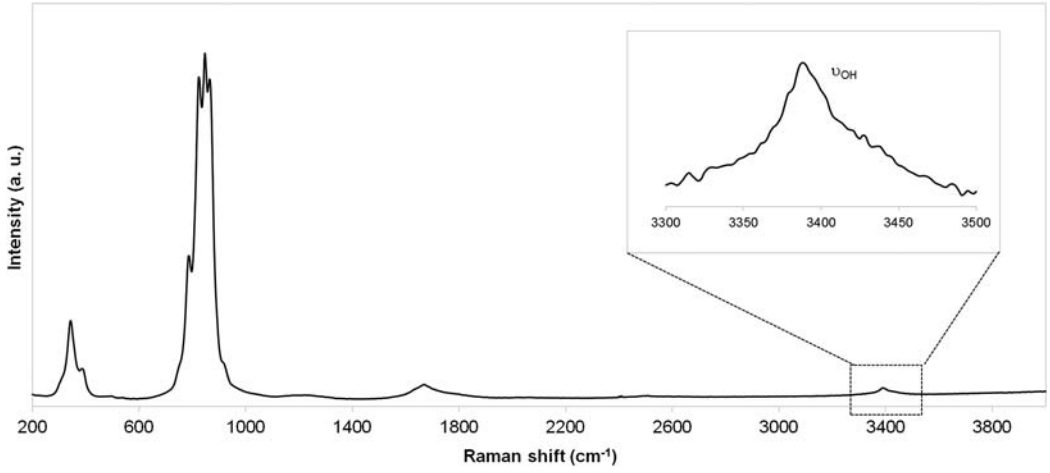


FIG. 2. Raman spectra of the sample R140134. The weak Raman band at ~3389 cm^{-1} is assigned to the OH stretching vibrations associated with the OH group (υ_{OH}).

system, using a 532 nm solid-state laser with a thermoelectric cooled CCD detector. The laser is partially polarized with 4 cm^{-1} resolution and spot size of 1 μm.

Crystal structure determinations

Single-crystal X-ray diffraction data of hemihedrite sample R140134 from the Rat Tail claim were collected on a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromated Mo*K*α radiation from a 0.05 mm × 0.05 mm × 0.04 mm crystal. The intensities of 22,054 reflections with $-14 < h < 14$, $-17 < k < 17$, $-16 < l < 16$ were collected to 65.42°2θ using frame widths of 0.5° in ω and 30 s counting time per frame; an empirical absorption correction (*SADABS*, Bruker, 2004) was applied (average redundancy ~4.5). The crystal is triclinic, space group $P\bar{1}$, $a = 9.4891(7)$, $b = 11.4242(8)$, $c = 10.8155(7)$ Å, $\alpha = 120.368(2)°$, $\beta = 92.017(3)°$,

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TABLE 2. Coordinates and displacement parameters of atoms in hemihedrite, sample R140134.

	x	*y*	*z*	U_{eq}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn	0	0.5	0	0.01025(14)	0.0121(4)	0.0098(3)	0.0103(4)	−0.0072(3)	−0.0038(3)	0.0063(3)
Pb1	0.25899(3)	0.11186(2)	0.25985(2)	0.01539(4)	0.01459(9)	0.01520(9)	0.01312(9)	−0.00990(8)	−0.00425(7)	0.00594(8)
Pb2	0.26117(2)	0.08673(2)	0.65721(2)	0.01157(4)	0.01000(8)	0.01094(8)	0.01254(9)	−0.00655(7)	−0.00316(7)	0.00624(7)
Pb3	0.93098(2)	0.24437(2)	0.03143(2)	0.01234(4)	0.01226(8)	0.01296(8)	0.01305(9)	−0.00864(7)	−0.00391(7)	0.00748(7)
Pb4	0.73123(3)	0.41635(3)	0.75114(2)	0.01711(5)	0.01861(10)	0.02038(10)	0.01929(10)	−0.01316(8)	−0.00913(8)	0.01452(9)
Pb5	0.31697(3)	0.45258(3)	0.53113(2)	0.01397(4)	0.01695(9)	0.02078(9)	0.01587(9)	−0.01517(8)	−0.01015(7)	0.01351(8)
Cr1	0.95935(11)	0.07509(10)	0.35577(9)	0.01095(14)	0.0128(4)	0.0127(3)	0.0104(4)	−0.0103(3)	−0.0044(3)	0.0058(3)
Cr2	0.56448(10)	0.17568(9)	0.15362(9)	0.00904(14)	0.0078(3)	0.0083(3)	0.0101(4)	−0.0044(3)	−0.0022(3)	0.0057(3)
Cr3	0.44657(10)	0.32502(10)	0.83679(9)	0.00931(14)	0.0079(3)	0.0103(3)	0.0120(4)	−0.0063(3)	−0.0036(3)	0.0071(3)
Si	0.02323(17)	0.45100(16)	0.65878(14)	0.0071(2)	0.0091(6)	0.0077(5)	0.0064(6)	−0.0060(5)	−0.0036(5)	0.0044(5)
O1	0.7537(5)	0.2224(5)	0.4835(5)	0.0245(9)	0.0156(19)	0.0182(19)	0.023(2)	−0.0089(17)	0.0023(16)	0.0046(18)
O2	0.1078(6)	0.0762(5)	0.4369(5)	0.0230(9)	0.030(2)	0.025(2)	0.027(2)	−0.0223(19)	−0.0218(19)	0.0169(18)
O3	0.9906(5)	0.1215(5)	0.7366(4)	0.0180(8)	0.0194(19)	0.0173(18)	0.0179(19)	−0.0150(16)	−0.0031(16)	0.0065(16)
O4	0.9689(6)	0.1151(6)	0.2326(5)	0.0253(9)	0.027(2)	0.040(2)	0.029(2)	−0.025(2)	−0.0131(19)	0.027(2)
O5	0.5103(5)	0.1383(5)	0.2690(4)	0.0158(7)	0.0162(18)	0.0190(18)	0.0173(18)	−0.0109(16)	−0.0039(15)	0.0134(16)
O6	0.4289(6)	0.2026(6)	0.0568(5)	0.0257(9)	0.020(2)	0.038(2)	0.024(2)	−0.019(2)	−0.0152(18)	0.020(2)
O7	0.7736(5)	0.0120(5)	0.0319(4)	0.0177(7)	0.0123(17)	0.0161(17)	0.0172(19)	−0.0042(15)	−0.0017(15)	0.0109(16)
O8	0.5379(5)	0.3572(5)	0.2658(4)	0.0184(8)	0.0174(18)	0.0127(17)	0.024(2)	−0.0098(15)	−0.0057(16)	0.0097(16)
O9	0.5984(5)	0.2939(6)	0.9156(5)	0.0258(9)	0.017(2)	0.034(2)	0.031(2)	−0.0165(19)	−0.0154(18)	0.022(2)
O10	0.4545(6)	0.3977(5)	0.7423(5)	0.0220(8)	0.032(2)	0.034(2)	0.023(2)	−0.027(2)	−0.0122(18)	0.0217(19)
O11	0.2372(5)	0.4832(5)	0.9738(4)	0.0145(7)	0.0110(16)	0.0131(16)	0.0174(18)	−0.0074(14)	−0.0017(14)	0.0080(15)
O12	0.4828(5)	0.1369(5)	0.7195(4)	0.0166(7)	0.0111(17)	0.0141(17)	0.022(2)	−0.0086(15)	−0.0049(15)	0.0081(16)
O13	0.2089(5)	0.3053(4)	0.5091(4)	0.0131(7)	0.0151(17)	0.0101(15)	0.0081(16)	−0.0077(14)	0.0010(13)	0.0022(14)
O14	0.0416(5)	0.3854(4)	0.7660(4)	0.0118(6)	0.0160(17)	0.0121(15)	0.0104(16)	−0.0092(14)	−0.0038(14)	0.0077(14)
O15	0.9928(5)	0.3747(5)	0.2595(4)	0.0148(7)	0.025(2)	0.0142(16)	0.0125(17)	−0.0152(16)	−0.0074(15)	0.0088(15)
O16	0.8463(5)	0.4793(5)	0.6143(4)	0.0138(7)	0.0132(17)	0.0190(17)	0.0180(18)	−0.0119(15)	−0.0092(14)	0.0138(16)
OH	0.1438(4)	0.2500(4)	0.9322(4)	0.0101(6)	0.0100(16)	0.0101(15)	0.0098(16)	−0.0061(13)	−0.0038(13)	0.0061(14)

TABLE 3. Selected bond distances for hemihedrite, sample R140134.

Cr(1) – O(2)	1.636(4)	Pb(1)–O(13)	2.294(4)	Pb(4)–O(16)	2.444(3)
Cr(1) – O(4)	1.631(4)	Pb(1)–O(15)	2.625(4)	Pb(4)–O(8)	2.506(4)
Cr(1) – O(1)	1.644(4)	Pb(1)–O(4)	2.740(4)	Pb(4)–O(1)	2.522(4)
Cr(1) – O(3)	1.684(4)	Pb(1)–O(5)	2.559(4)	Pb(4)–O(11)	2.669(4)
Ave.	1.649	Pb(1)–O(12)	2.630(4)	Pb(4)–O(10)	2.746(4)
		Pb(1)–O(7)	2.822(4)	Pb(4)–O(3)	2.759(4)
Cr(2) – O(6)	1.623(4)	Pb(1)–O(2)	2.744(4)	Pb(4)–O(14)	2.772(4)
Cr(2) – O(7)	1.643(4)	Pb(1)–O(6)	3.120(4)	Pb(4)–O(6)	3.038(4)
Cr(2) – O(8)	1.651(4)	Pb(1)–O(9)	3.342(4)	Pb(4)–O(9)	3.292(4)
Cr(2) – O(5)	1.683(3)	Pb(1)–O(6)	3.595(4)	Pb(4)–O(2)	3.366(4)
Ave.	1.650	Ave.	2.847	Pb(4)–O(9)	3.371(4)
				Ave.	2.862
Cr(3) – O(9)	1.605(4)	Pb(2)–O(14)	2.346(3)		
Cr(3) – O(10)	1.635(4)	Pb(2)–OH	2.420(3)	Pb(5)–O(16)	2.279(3)
Cr(3) – O(12)	1.670(4)	Pb(2)–O(3)	2.480(4)	Pb(5)–O(13)	2.335(3)
Cr(3) – O(11)	1.697(4)	Pb(2)–O(12)	2.463(4)	Pb(5)–O(5)	2.641(4)
Ave.	1.652	Pb(2)–O(2)	2.734(4)	Pb(5)–O(15)	2.665(4)
		Pb(2)–O(5)	2.765(4)	Pb(5)–O(10)	2.763(4)
Si – O(14)	1.629(3)	Pb(2)–O(1)	3.149(4)	Pb(5)–O(8)	2.918(4)
Si – O(16)	1.627(4)	Pb(2)–O(13)	3.412(4)	Pb(5)–O(8)	3.125(4)
Si – O(13)	1.637(4)	Pb(2)–O(12)	3.463(4)	Pb(5)–O(1)	3.302(4)
Si – O(15)	1.631(4)	Ave.	2.808	Pb(5)–O(4)	3.312(4)
Ave.	1.631			Pb(5)–O(1)	3.471(4)
		Pb(3)–OH	2.367(3)	Ave.	2.881
Zn – OH	2.034(3) x2	Pb(3)–O(7)	2.407(4)		
Zn – O(14)	2.102(3) x2	Pb(3)–O(15)	2.411(3)		
Zn – O(11)	2.165(4) x2	Pb(3)–O(11)	2.614(3)		
Ave.	2.100	Pb(3)–O(3)	2.678(4)		
		Pb(3)–O(4)	2.106(4)		
		Pb(3)–O(10)	3.132(4)		
		Pb(3)–O(4)	3.412(4)		
		Pb(3)–O(9)	3.206(4)		
		Ave.	2.785		

$\gamma = 55.857(2)°$, $V = 784.88(9)$ Å^3, $Z = 1$, consistent with the values reported by McLean and Anthony (1970). The crystal structure was solved and refined using *SHELX97* (Sheldrick, 2008) to $R_1 = 0.022$ with Goof value of 1.022 for 4976 independent reflections (247 refined parameters). While the electron microprobe analysis revealed minor Mg, P and S, incorporation of these elements in the structure refinement produced no significant improvement in terms of *R* factors or displacement parameters. Hence, the ideal chemical formula $Pb_{10}Zn(CrO_4)_6(SiO_4)_2(OH)_2$was assumed during the refinement. The position of all the non-H atoms were refined with anisotropic displacement parameters. Final coordinates and displacement parameters are given in Table 2 and selected bond distances in Table 3. Bond-valence calculations show that certain O atoms are underbonded, and thus are probably OH groups (Table 4). In the Fourier map, several peaks (<2.5 *e*/Å^3) were noted within 1 Å of the Pb atoms. The presence of these 'ghost' peaks, commonly associated with heavy atoms, prevent the location of H atoms in the structure.

Discussion

The colorimetric analysis performed by Williams and Anthony (1970) to determine the fluorine content in their hemihedrite samples from Arizona resulted in values too high, $F_{8.25}$, and inconsistent with the ideal formula $Pb_{10}Zn(CrO_4)_6(SiO_4)_2F_2$. Colorimetric determination of fluorine in rock and mineral samples has been described in numerous studies (Evans and Sergeant, 1967; Huang and

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TABLE 4. Calculated bond-valence sums for hemihedrite, sample R140134.

	Zn	Pb1	Pb2	Pb3	Pb4	Pb5	Cr1	Cr2	Cr3	Si	Sum
O1			0.061		0.330	0.040	1.502				1.957
						0.025					
O2		0.181	0.186		0.034		1.534				1.935
O3			0.370	0.217	0.174		1.346				2.106
O4		0.183		0.068		0.039	1.554				1.906
				0.062							
O5		0.299	0.171			0.239		1.349			2.058
O6		0.018			0.082			1.588			1.754
		0.066									
O7		0.147		0.450				1.506			2.103
O8					0.345	0.113		1.473			1.996
						0.065					
O9		0.036		0.052	0.033				1.668		1.830
					0.041						
O10				0.063	0.180	0.172			1.539		1.955
O11	0.287↓2×			0.257	0.222				1.301		2.068
O12		0.246	0.387						1.397		2.054
			0.024								
O13		0.611	0.030			0.547				0.965	2.152
O14	0.342↓2×		0.532		0.168					0.987	2.028
O15		0.250		0.446		0.225				0.981	1.902
O16					0.408	0.637				0.993	2.038
OH	0.410↓2×		0.435	0.502							1.347
Sum	2.079	2.036	2.195	2.118	2.018	2.102	5.934	5.916	5.905	3.926	

Jackson, 1967; Huang and Johns, 1967; Hall and Walsh, 1969; Fuge, 1976). Most of these descriptions imply the need for preliminary separation of fluorine from other elements likely to cause interference. Fuge (1976) mentioned aluminum as well as phosphate and sulfate ions as potential interfering elements in colorimetric determinations of fluorine. Ferrari *et al.* (1961) also refer to the interference by phosphate and sulfate ions in their study of colorimetric determination of fluorine in organic compounds.

Although the chemical data in Williams and Anthony (1970) did not include phosphate or sulfate ions in hemihedrite, our electron microprobe results of the type material and additional samples confirm SO_3 in the range 0.02–0.23 wt.% and P_2O_5 in the range 0.02–0.16 wt.% (Table 1). In addition, our chemical analyses failed to detect fluorine in any of the samples. These results, together with the confirmation of the presence of OH by Raman spectroscopy, lead us to propose that the colorimetric determination of fluorine performed by Williams and Anthony (1970) probably misidentified F due to the interference of the PO_4 and SO_4 moieties. Unfortunately, Williams and Anthony (1970) did not provide enough detail on their IR study to permit an evaluation of their reasons for the lack of OH or H_2O.

Excluding the data reported by Williams and Anthony (1970) in their description of the hemihedrite from the Florence Lead-Silver mine and the Rat Tail claim, fluorine contents of hemihedrite samples have not been reported in other studies of the mineral (e.g. Bariand and Poullen, 1980; Cesbron and Williams, 1980; Frost, 2004). It is also interesting to note that none of the other mineral species found at the Florence Lead-Silver mine or the Rat Tail claim contain fluorine, with the exception of fluorite (CaF_2), reported in the latter locality (from www.mindat.org, retrieved January 28, 2016).

Similarly, the other reported hemihedrite localities in Nevada and Iran do not host minerals containing fluorine (from www.mindat.org, retrieved January 28, 2016). Our own electron microprobe analyses of the sample labelled as hemihedrite from Clack County, Nevada, USA, yielded the empirical chemical formula $Pb_{10.21}(Cu_{0.65}Zn_{0.34})_{\sum = 0.99}(Cr_{5.93}P_{0.07}S_{0.04})_{\sum = 6.03}(Si_{1.83}As_{0.10})_{\sum = 1.93}O_{34}H_{1.62}$ (Table 1), which

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TABLE 5. Comparison of crystallographic data for the iranite group of minerals.

	Raygrantite	Hemihedrite	Hemihedrite	Iranite
Reference	Yang *et al.* (2016)	McLean and Anthony (1970)	This work	Yang *et al.* (2007)
Ideal chemical formula	$ZnPb_{10}(SO_4)_6(SiO_4)_2(OH)_2$	$ZnPb_{10}(CrO_4)_6(SiO_4)_2F_2$	$ZnPb_{10}(CrO_4)_6(SiO_4)_2(OH)_2$	$CuPb_{10}(CrO_4)_6(SiO_4)_2(OH)_2$
Crystal symmetry	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$.
a (Å)	9.3175(4)	9.497(3)	9.4891(7)	9.5416(4)
b (Å)	11.1973(5)	11.443(5)	11.4242(8)	11.3992(5)
c (Å)	10.8318(5)	10.841(4)	10.8155(7)	10.7465(4)
α (°)	120.374(2)	120.50(4)	120.368(2)	120.472(2)
β (°)	90.511(2)	92.10(4)	92.017(3)	92.470(2)
γ (°)	56.471(2)	55.84(3)	55.857(2)	55.531(2)
V (Å^3)	753.13(6)	787.183	784.88(9)	780.08(6)
Z	1	1	1	1
ρ_{cal} (g/cm^3)	6.374	6.42	6.456	6.49
2θ range for data collection	≤65.24		≤65.42	≤69.3
No. of reflections collected	32,373		22,054	14,248
No. of independent reflections	5286	2790	5705	6319
No. of reflection with $I > 2\sigma(I)$	4543	2428	4976	5022
No. parameters refined	243		242	242
R (int)	0.042		0.033	0.036
Final R_1, wR_2 factors [$I > 2\sigma(I)$]	0.031, 0.073	0.041	0.022, 0.045	0.034, 0.062
Final R_1, wR_2 factors (all data)	0.041, 0.076		0.028, 0.045	0.050, 0.070
Goodness-of-fit	1.093		1.022	1.013

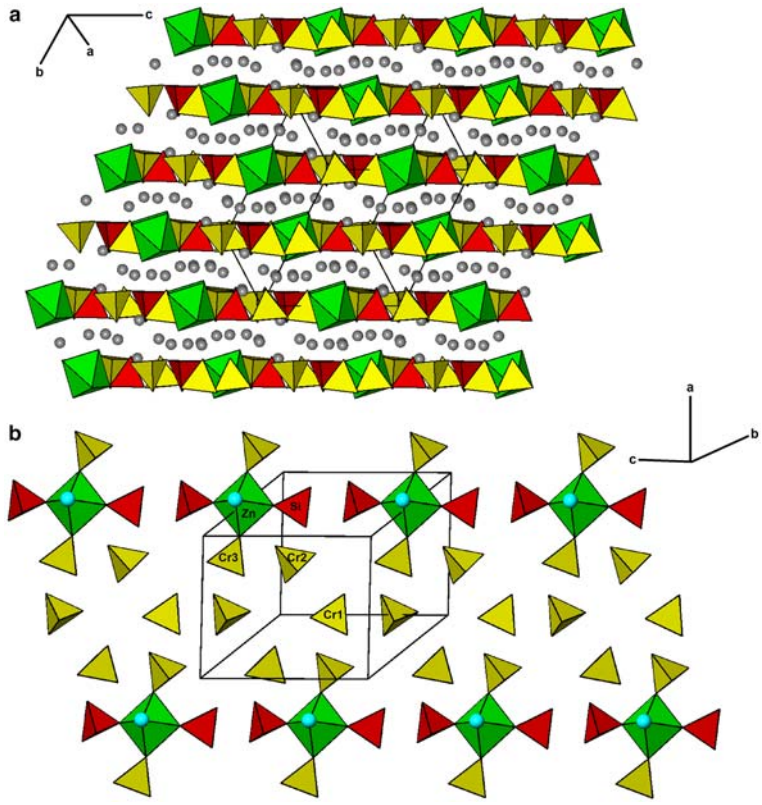


FIG. 3. (*a*) Crystal structure of hemihedrite. The yellow and red tetrahedra, green octahedra, and grey spheres represents CrO_4, SiO_4, $ZnO_4(OH)_2$, and Pb, respectively; (*b*) a polyhedral layer in hemihedrite. The Zn atoms are in octahedra that are corner-linked to the SiO_4 and $Cr3O_4$ tetrahedra. The $Cr1O_4$ and $Cr2O_4$ tetrahedra are isolated. Yellow and red tetrahedra and green octahedra represents CrO_4, SiO_4, and $ZnO_4(OH)_2$ groups, respectively. The aquamarine spheres represent the OH groups.

is closer to that of iranite. No traces of F were found.

Hemihedrite is part of the iranite group of minerals which includes iranite $[Pb_{10}Cu(CrO_4)_6(SiO_4)_2(OH)_2]$ (Yang *et al.*, 2007), with substitution of Zn for Cu, and raygrantite $[Pb_{10}Zn(SO_4)_6(SiO_4)_2(OH)_2]$ (Yang *et al.*, 2016), with substitution of Cr for S (Table 5). A continuous solid-solution between hemihedrite and iranite varying the Zn:Cu ratio was proposed by Cesbron and Williams (1980) while Bariand and Poullen (1980), in their study of rare chromates from Seh–Changi, Iran, found crystals of iranite–hemihedrite with variable Zn:Cu ratios. Yang *et al.* (2016) predict the possible existence of a Cu-analogue for raygrantite.

Hemihedrite $Pb_{10}Zn(CrO_4)_6(SiO_4)_2(OH)_2$ can be defined as a layered structure where CrO_4 and SiO_4 tetrahedra, together with $ZnO_4(OH)_2$ octahedra, form layers stacked along (120). These layers are linked by five symmetrically-independent Pb^{2+} cations (Fig. 3*a*). The $ZnO_4(OH)_2$ octahedra are linked, by opposite corners, to two CrO_4 and two SiO_4 tetrahedra, while the two OH groups are oriented towards the Pb layer. Two additional nonequivalent CrO_4 groups are isolated (Fig. 3*b*). The major differences with the structure reported by McLean and Anthony (1970) are that anisotropic thermal parameters were determined for all non-H atoms, and, of course, F is replaced by OH.

The number and location of the OH groups were determined from bond-valence sum calculations (Brese and O'Keeffe, 1991) (Table 4). The results show that O17 (bond-valence sum of 1.347 valence units (vu)) represents an OH group with a hydrogen bond to O6 (bond-valence sum of 1.754 vu) [O17–

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O6 = 2.874 Å]. This is similar to that reported for iranite (Yang *et al.*, 2007) and raygrantite (Yang *et al.*, 2016), with O17–O6 distances of 2.852 Å and 3.108 Å, respectively. The O17 site is also where the F atom was proposed in the structure reported by Williams and Anthony (1970) [F–O6 = 2.912 Å]. According to the correlation of O–H IR stretching frequencies with O–H···O hydrogen-bond lengths in minerals (Libowitzky, 1999), the distance 2.874 Å would correspond to an O–H stretching frequency of ~3401 cm^{-1}, which is close to the value 3389 cm^{-1} from the Raman spectrum.

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