

Iranite, $\text{CuPb}_{10}(\text{CrO}_4)_6(\text{SiO}_4)_2(\text{OH})_2$,
isomorphous with hemihedriteHexiong Yang,* Jennifer L. Sano, Carla Eichler, Robert T.
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This study presents the first structural report of iranite, ideally $\text{CuPb}_{10}(\text{CrO}_4)_6(\text{SiO}_4)_2(\text{OH})_2$ [copper decalead hexachromate bis(orthosilicate) dihydroxide], based on single-crystal X-ray diffraction data. Iranite is isomorphous with hemihedrite, with substitution of Cu for Zn and OH for F. The Cu atom is situated at the special position with site symmetry $\bar{1}$. The CrO_4 and SiO_4 tetrahedra and $\text{CuO}_4(\text{OH})_2$ octahedra form layers that are parallel to (120) and are linked together by five symmetrically independent Pb^{2+} cations displaying a rather wide range of bond distances. The $\text{CuO}_4(\text{OH})_2$ octahedra are corner-linked to two CrO_4 and two SiO_4 groups, while two additional CrO_4 groups are isolated. The mean Cr—O distances for the three nonequivalent CrO_4 tetrahedra are all slightly shorter than the corresponding distances in hemihedrite, whereas the $\text{CuO}_4(\text{OH})_2$ octahedron is more distorted than the ZnO_4F_2 octahedron in hemihedrite in terms of octahedral quadratic elongation.

Comment

Iranite was first discovered in Sébarz, Anarak (central Iran), and incorrectly described as a lead chromate with chemical formula $\text{PbCrO}_4 \cdot \text{H}_2\text{O}$ (Bariand & Herpin, 1963). Adib & Ottemann (1970) reported several new lead chromates from Iran, one of which was called khuniite, with chemical formula $(\text{Pb}_{1.6}\text{Zn}_{0.2}\text{Cu}_{0.2})\text{CrO}_5$. However, further studies of khuniite by Adib *et al.* (1972) suggested a new chemical formula, *viz.* $\text{Pb}_5(\text{Cu,Zn})(\text{CrO}_4)_3\text{SiO}_4$, for this mineral. Concurrently, the new mineral hemihedrite, $\text{ZnPb}_{10}(\text{CrO}_4)_6(\text{SiO}_4)_2\text{F}_2$, was discovered (Williams & Anthony, 1970) and its crystal structure reported (McLean & Anthony, 1970). Fleischer (1973) noted that the chemical formula given by Adib *et al.* (1972) for khuniite was not charge-balanced and that this mineral might be isostructural with hemihedrite on the basis of similar X-ray powder diffraction data. A re-examination of the type mineral of iranite by Williams (1974) showed that it was probably the Cu analog of hemihedrite and that khuniite was misidentified

and is actually iranite. A synthetic hydroxide analogue of iranite and synthetic hemihedrite were found to have the formulae $\text{CuPb}_{10}(\text{CrO}_4)_6(\text{SiO}_4)_2(\text{OH})_2$ and $\text{ZnPb}_{10}(\text{CrO}_4)_6(\text{SiO}_4)_2(\text{OH})_2$, respectively, and analyses of natural materials indicated that there is probably a solid solution between the two minerals (Cesbron & Williams, 1980; Bariand & Poullen, 1980). While the crystal structure of hemihedrite was determined by McLean & Anthony (1970), the crystal structure of iranite remained undetermined until now. This paper reports the first structural refinement of natural iranite based on single-crystal X-ray diffraction data.

Iranite is isotypic with hemihedrite, with substitution of Cu for Zn and OH for F. The view down the $[2\bar{1}\bar{1}]$ direction (Fig. 1) demonstrates that iranite can be regarded as a layered structure of CrO_4 and SiO_4 tetrahedra, along with $\text{CuO}_4(\text{OH})_2$ octahedra that lie parallel to (120) and are linked together by five symmetrically independent Pb^{2+} cations. Within a polyhedral layer, each $\text{CuO}_4(\text{OH})_2$ octahedron shares opposite corners with two SiO_4 tetrahedra as well as opposite corners with two CrO_4 tetrahedra, while the two OH groups are oriented towards the Pb layer. The Cr1O_4 and Cr2O_4 tetrahedra are isolated in the polyhedral layer (Fig. 2). Owing mostly to the Jahn–Teller effect of Cu^{2+} , the Cu1—O11 bond length [2.290 (5) Å] in iranite is longer than the Zn—O11 length (2.17 Å) in hemihedrite, whereas the Cu1—O17 bond distance [1.950 (5) Å] is shorter than the Zn—F distance (2.05 Å). As a consequence, the $\text{CuO}_4(\text{OH})_2$ octahedron in iranite is more distorted (1.0150) than the ZnO_4F_2 octahedron (1.0075) in hemihedrite in terms of the octahedral quadratic elongation (Robinson *et al.*, 1971). The mean Cr—O distances for the Cr1, Cr2 and Cr3 tetrahedra are 1.640, 1.650 and 1.648 Å, respectively, which are all slightly shorter than the corresponding mean distances (1.659, 1.662 and 1.658 Å) in hemihedrite (McLean & Anthony, 1970) but are comparable to most values in the literature, such as those reported for tarapacaite (K_2CrO_4 ; 1.643 Å; McGinnety, 1972), lopezite

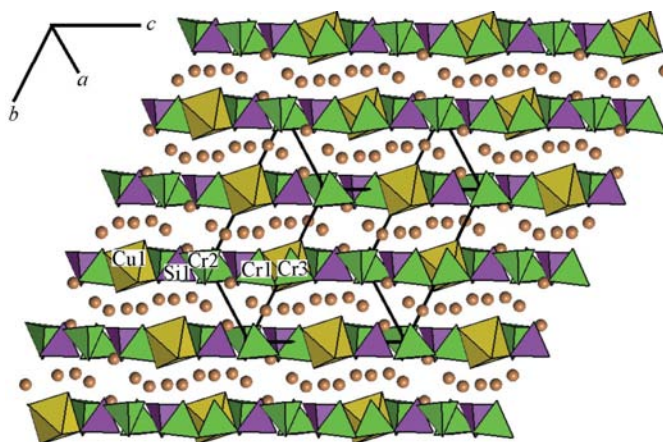


Figure 1

The crystal structure of iranite viewed down $[2\bar{1}\bar{1}]$. The spheres represent Pb atoms. Atom Cu1 is in an octahedral coordination and atoms Si1, Cr1, Cr2 and Cr3 are in tetrahedral coordinations.

($K_2Cr_2O_7$; ~ 1.65 Å; Brunton, 1973), dietzeite [$Ca_2(IO_3)_2 \cdot CrO_4 \cdot H_2O$; 1.647 Å; Burns & Hawthorne, 1993] and edoylerite ($Hg_3CrO_4S_2$; 1.643 Å; Burns, 1999). Within 3.2 Å, the coordination numbers of the five nonequivalent Pb^{2+} cations vary from 7 to 9.

There have been considerable discussions about the effects of F–OH substitution on the crystal structures and properties of minerals (e.g. Groat *et al.*, 1990; Cooper & Hawthorne, 1995; Yang *et al.*, 2007). For some minerals, the OH and F members may form a complete solid solution, such as for the amblygonite [$LiAl(PO_4)F$]–montebrasite [$LiAl(PO_4)(OH)$] and fluorapatite [$Ca_5(PO_4)_3F$]–hydroxylapatite [$Ca_5(PO_4)_3(OH)$] series. However, there are also many examples in which F–OH substitution results in structural transformations or symmetry changes, such as the cases between $C2/c$ tilasite [$CaMg(AsO_4)F$] and $P2_12_12_1$ adelite [$CaMg(AsO_4)(OH)$], and between $C2/c$ triplite [$Mn_2(PO_4)F$] and $P2_1/c$ triploidite [$Mn_2(PO_4)(OH)$]. Although a number of studies (e.g. Bariand & Poullen, 1980; Cesbron & Williams, 1980) have shown that OH-rich iranite and hemihedrite constitute a continuous series varying the Zn/Cu ratio, Frost (2004) reported that the Raman spectra of F-rich iranite and hemihedrite are remarkably different in the Cr–O stretching region (between 750 and 900 cm^{-1}) and suggested that the two minerals may not be homologous. The presence of Pb atoms in iranite prevented the location of the H atom. However, bond-valence considerations show that only atom O17 can accommodate H as an OH group. The O17 site is also where the F atom is located in hemihedrite. It appears that atom O17 may form an O–H \cdots O linkage with one of the two closest O atoms, *viz.* O6 [2.852 (6) Å away from O17] or O7 [2.881 (6) Å away from O17]. The possibility of the O17–H \cdots O7 linkage can be ruled out on the basis of the Pb3–O17–O7 angle being equal to 53 (3)°. When the O17–H \cdots O6 linkage is considered, the environment around atom O17 is tetrahedral, with Pb3–O17–O6 = 117.6 (2)°, Pb2–O17–O6 = 108.6 (2)°,

Cu1–O17–O6 = 104.4 (2)°, and an average angle of 110°. According to Libowitzky (1999), an O–H \cdots O distance of 2.85 Å would correspond to an O–H stretching frequency of ~ 3399 cm^{-1} , which is close to what we measured (~ 3387 cm^{-1}) for our sample with Raman spectroscopy (<http://rruff.info>). A comparison of the environment around atom O17 in iranite with that around the F atom in hemihedrite indicates that the bonding topologies of these two ions are similar, leading us to suggest that there is no impediment to a complete solid solution between OH and F in the hemihedrite–iranite series.

Experimental

The iranite specimen used in this study is from Chapacase mine, Sierra Cerillos district, Tocopilla, Chile, and is in the collection of the RRUFF project (deposition No. R060781; <http://rruff.info>), donated by Mike Scott. The average chemical composition of the studied sample, *viz.* $CuPb_{10}\{(Cr_{0.99}[O_{0.01}]_{\Sigma=1}[O_{3.82}(OH)_{0.18}]_{\Sigma=4})_6(SiO_4)_2(OH)_2$, was determined with a CAMECA SX50 electron microprobe (<http://rruff.info>).

Crystal data

$CuPb_{10}(CrO_4)_6(SiO_4)_2(OH)_2$	$\gamma = 55.531$ (2)°
$M_r = 3049.64$	$V = 780.08$ (6) Å ³
Triclinic, $P\bar{1}$	$Z = 1$
$a = 9.5416$ (4) Å	Mo $K\alpha$ radiation
$b = 11.3992$ (5) Å	$\mu = 56.58$ mm ⁻¹
$c = 10.7465$ (4) Å	$T = 293$ (2) K
$\alpha = 120.472$ (2)°	$0.05 \times 0.05 \times 0.04$ mm
$\beta = 92.470$ (2)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	14248 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2005)	6319 independent reflections
$T_{min} = 0.083$, $T_{max} = 0.104$	5022 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	242 parameters
$wR(F^2) = 0.070$	H-atom parameters not defined
$S = 1.01$	$\Delta\rho_{max} = 3.68$ e Å ⁻³
6319 reflections	$\Delta\rho_{min} = -3.50$ e Å ⁻³

The H atoms were not located in the final difference Fourier syntheses. The chemical analysis showed a little deficiency in Cr when compared with the ideal value of six per chemical formula, but the refinement assumed an ideal chemistry, as the overall effects of such a small amount of vacancy on the final structure results are negligible. The highest residual peak in the difference Fourier map was located 0.71 Å from atom Pb4 and the deepest hole was located 0.88 Å from Pb2.

Data collection: APEX2 (Bruker, 2003); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: Xtal-Draw (Downs & Hall-Wallace, 2003); software used to prepare material for publication: SHELXTL (Bruker, 1997).

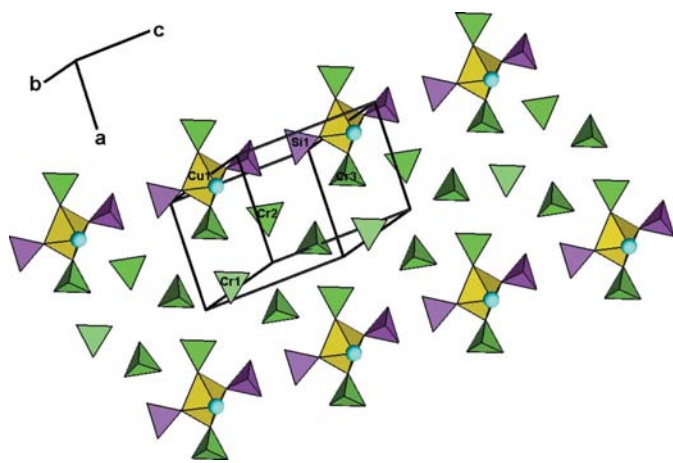


Figure 2

The polyhedral layer in iranite. The Cu1 atoms are in octahedra that are corner-linked to the SiO_4 and Cr_3O_4 tetrahedra. The Cr_1O_4 and Cr_2O_4 tetrahedra are isolated. The spheres represent the OH groups. The coordinates of atom Cr1 are at $(-x, -y, -z)$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3032). Services for accessing these data are described at the back of the journal.

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