Redetermination of the mixed-valence manganese arsenate flinkite, $Mn_2^{II}Mn^{III}(OH)_4(AsO_4)$

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The crystal structure of the rare mixed-valence manganese(II,III) arsenate mineral flinkite [dimanganese(II) manganese(III) arsenate tetrahydroxide], $Mn_2^{II}Mn^{III}(OH)_4(AsO_4)$ has been redetermined from single-crystal X-ray data. The previously unknown positions of both H atoms could be identified. Flinkite contains one unique $Mn^{III}O_2(OH)_4$ polyhedron with a Jahn–Teller-distorted [4+2]-coordination of Mn^{III}, one $Mn^{II}O_3(OH)_3$ octahedron, and one fairly regular AsO_4 tetrahedron. Atoms on special sites are Mn1 (site symmetry $\bar{1}$), As, O4 and O5 (all with site symmetry $.m.$). The structure is based upon pyrochroite $[Mn(OH)_2]$-type sheets of edge-sharing $Mn(O,OH)_6$ octahedra parallel to (100). Some $Mn(O,OH)_6$ octahedra are omitted to allow AsO_4 tetrahedra to connect the sheets via shared corners. Additional strong hydrogen bonds between the sheets provide further strengthening. Relations to the structures of antlerite, $Cu_3(SO_4)(OH)_4$, synthetic $Cu_3(SeO_4)(OH)_4$, synthetic $Cu_3(CrO_4)(OH)_4$, and szenicsite, $Cu_3(MoO_4)(OH)_4$, are pointed out.

Comment

Flinkite is a very rare basic arsenate mineral containing both di- and trivalent manganese. It was originally described from the Harstigen mine, Pajsberg (near Filipstad), Värmland, Sweden. The orthorhombic crystal symmetry and unit-cell parameters were determined by Culver & Berry (1963), who reported space group *Pnna*, based on a single-crystal study.

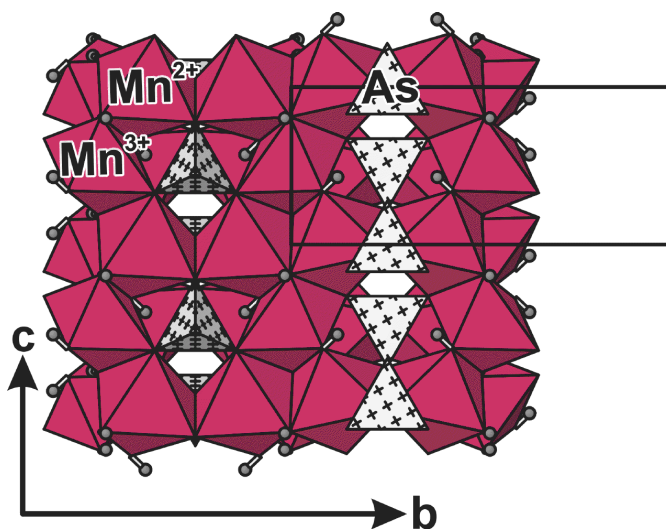**Figure 1**
View of the sheet-based structure of flinkite along [100], *i.e.* perpendicular to the $Mn(OH)_2$-based polyhedral sheet. $Mn(O,OH)_6$ octahedra are shown in red, AsO_4 tetrahedra are pale grey and marked with crosses. H atoms are represented by small spheres. The unit cell is outlined.
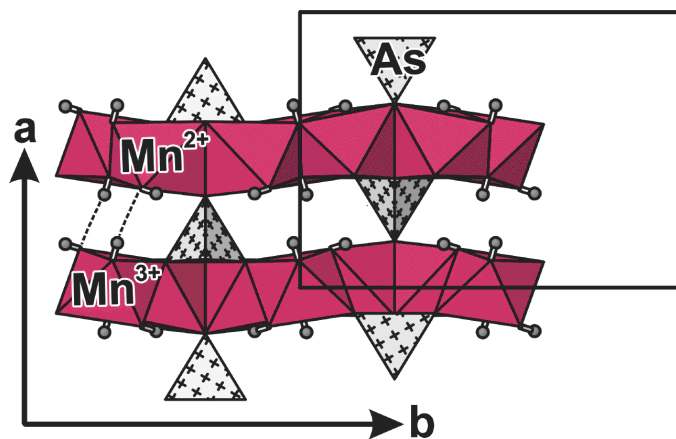
Figure 2
View of the structure of flinkite along [001]. Designations are as in Fig. 1. The octahedral sheets parallel to (100) are connected by AsO₄ tetrahedra and hydrogen bonds (dashed lines).

The crystal structure was subsequently solved in space group *Pnma* by Moore (1967), albeit from $hk0$ and $h0l$ intensity data only, resulting in a relatively high discrepancy factor (R = 0.144) and large uncertainties for the structure model. The present reinvestigation of the structure was carried out to verify the space group and provide a more accurate picture of the atomic arrangement, including the Jahn–Teller-distortion of the Mn^{III}–O_6 octahedron and the character of the hydrogen-bonding system (H atoms were not found in the previous structure study).

The flinkite studied was taken from an old specimen from the type locality (Museum of Natural History, Vienna, Austria; collection No. F9361). It shows mm-sized aggregates of dark brownish tabular crystals arranged in a subparallel radiating way. The aggregates are grown on whitish barite (which, in turn, is grown on caryopilite) and partly overgrown by a thin colourless crust of an unknown mineral. Semiquantitative energy-dispersive X-ray analyses of flinkite revealed no elements except Mn, As and O.

The structure of flinkite is based upon infinite sheets of $Mn(O,OH)_6$ octahedra. These sheets are connected to each other *via* AsO₄ tetrahedra. There are two non-equivalent Mn atoms that form distinctly different Mn-(O,OH)₆ polyhedra. Mn1 exhibits four short equatorial Mn1—OH bonds and two long apical Mn—O bonds, thus forming an elongated distorted $Mn1O_2(OH)_4$ octahedron. This [4+2]-distortion is typical of the Jahn–Teller-effect shown by trivalent Mn. By comparison to reported average equatorial and apical Mn^{III}—O distances, 1.93 and 2.24 Å, respectively (Burns *et al.*, 1994), the Jahn–Teller-distortion in flinkite is fairly strong. The average Mn1—(O,OH) distance, 2.032 Å, is within the range commonly observed for Mn^{III}–O₆ polyhedra, 1.99–2.08 Å (Burns *et al.*, 1994; see also Foley *et al.*, 1997). Moore (1967) reported the following Mn1—(O,OH) distances for flinkite: 1.80 (5), 1.91 (5) and 2.29 (5) Å (each 2 ×); however, a recalculation gives the values 1.83, 1.87 and 2.29 Å.
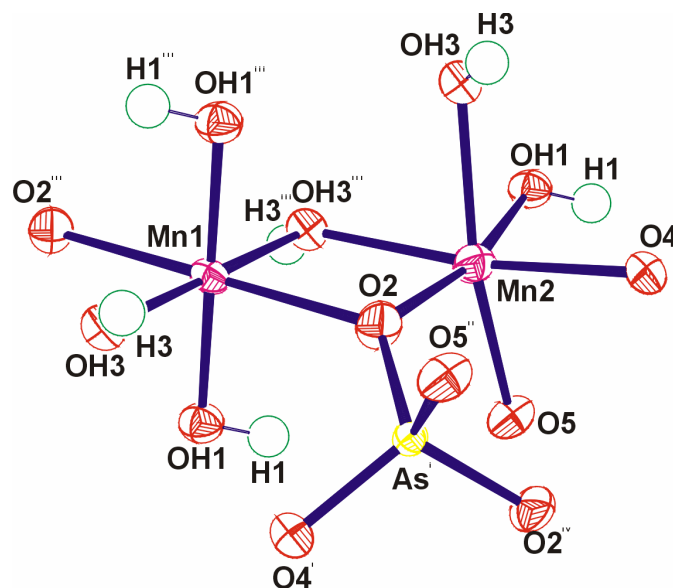

Figure 3
Anisotropic displacement ellipsoids (90% probability level) of the atoms in the flinkite structure. [Symmetry codes: (i) x, $y+1/2$, $-z$; (ii) $x+1/2$, $-y+1/2$, $-z+1/2$; (iii) $-x$, $-y$, $-z$; (iv) x, $-y+1/2$, z.]

The Mn2 atom is also octahedrally coordinated by six (O,OH) ligands, but in a more regular manner. The Mn2—O distances in the resulting $Mn2O_3(OH)_3$ octahedron are longer and range from 2.1280 (14) to 2.2399 (15) Å. The average Mn2—(O,OH) distance, 2.179 Å, is close to the literature value for Mn^{II} (2.205 Å; Baur, 1981). Calculated bond-valence sums for Mn1 and Mn2, 3.16 and 2.11 v.u. (valence units), respectively, are close to theoretical values (calculations were performed using the parameters of Brese & O'Keeffe, 1991). The value for As amounts to 4.93 v.u.

The distorted $Mn1O_2(OH)_4$ octahedra share edges to form infinite chains parallel to the *b* axis. The chains are linked to the $Mn2O_3(OH)_3$ octahedra by edge-sharing to form dense octahedral sheets parallel to (100). These sheets are topologically identical to the close-packed octahedral sheets in pyrochroite, $Mn(OH)_2$ (Christensen & Ollivier, 1972), and brucite, $Mg(OH)_2$, except that in flinkite some of the octahedra are missing to make space for the interconnecting AsO₄ tetrahedra (Figs. 1–3). The AsO₄ tetrahedra are connected to the sheets *via* common corners; their geometry is fairly regular. Unlike in pyrochroite (brucite), the sheets in flinkite are not perfectly planar but are curved in a wave-like manner along the *b* axis (Fig. 2).

The two H atoms in flinkite are bonded to the OH1 and OH3 atoms, whose bond-valence sums are 1.02 and 1.34 v.u., respectively, if one neglects the H contributions. H3 is involved in a fairly strong hydrogen bond, with a donor–acceptor distance O3···O1 of 2.670 (2) Å, thus providing an efficient linkage between two parallel $Mn(O,OH)_6$ octahedral sheets (Fig. 2). H1, on the other hand, may only be involved in very weak, if any, hydrogen bonding (the closest oxygen neighbour is O5, at 3.28 Å and with an O—H···O angle of *ca* 109°). The OH1—H1 bond vector points in the void space

below the base of the AsO_4 tetrahedron.

Flinkite has no isostructural analogue among minerals or synthetic compounds. Among the very few compounds with identical stoichiometry, there are four copper oxysalts: antlerite $Cu_3(SO_4)(OH)_4$ (Hawthorne *et al.*, 1989), synthetic $Cu_3(CrO_4)(OH)_4$ (Pollack, 1985), synthetic $Cu_3(SeO_4)(OH)_4$ (Giester, 1991) and szenicsite $Cu_3(MoO_4)(OH)_4$ (Burns, 1998; Stolz & Armbruster, 1998). All four are orthorhombic and show very closely related structures and space groups. Their unit-cell parameters bear some similarity to those of flinkite, if one neglects the different labelling of the orthorhombic axes. The copper oxysalts are all characterized by triple chains of edge-sharing CuO_6 octahedra running parallel to ~ 6 Å axes. The triple chains are linked by MO_4- tetrahedra ($M = $ S, Cr, Se, Mo). To demonstrate the relation to flinkite, two alternative descriptions of the common topology of the copper oxysalts are possible. Firstly, the structure can be described as incomplete pyrochroite-like sheets of CuO_6 octahedra which are connected by CuO_6 octahedra and MO_4 tetrahedra. Secondly, the description can be based on two intersecting, incomplete pyrochroite-like sheets of CuO_6 octahedra which are connected by MO_4 tetrahedra only.

Although flinkite also shares the same overall stoichiometry with retzian, $Mn^{II}_2 REE^{3+}(AsO_4)(OH)_4$ ($REE = $ Ce, Nd, La) (Moore, 1967; Dunn & Sturman, 1982) and although both exhibit octahedral sheets held together by AsO_4 tetrahedra, the two structures are only remotely related (Moore, 1967). Chantalite, $CaAl_2SiO_4(OH)_4$, is isoelectronic with retzian, but is tetragonal and characterized by edge-sharing $AlO_2(OH)_4$ octahedra forming chains linked by isolated SiO_4 tetrahedra and $CaO_4(OH)_4$ polyhedra (Liebich *et al.*, 1979). Cahnite, $Ca_2B(AsO_4)(OH)_4$, is also unrelated to the above sheet structures because of the different structural role of the very small, tetrahedrally coordinated B^{3+} cation; cahnite is tetragonal with a zircon-related structure (Prewitt & Buerger, 1960).

Experimental

The title compound is a natural sample (see above).

Crystal data

$Mn_3(OH)_4(AsO_4)$	Mo $K\alpha$ radiation
$M_r = 371.77$	Cell parameters from 1212
Orthorhombic, $Pnma$	reflections
$a = 9.483$ (2) Å	$\theta = 2.5$–$29.9°$
$b = 13.030$ (3) Å	$\mu = 10.64$ mm^{-1}
$c = 5.339$ (1) Å	$T = 293$ (2) K
$V = 659.7$ (2) Å^3	Fragment, red–brown
$Z = 4$	$0.10 \times 0.06 \times 0.05$ mm
$D_x = 3.743$ Mg m^{-3}	

Data collection

Nonius KappaCCD diffractometer	1002 independent reflections
φ and ω scans	969 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.011$
(*HKL SCALEPACK*; Otwi-	$\theta_{max} = 30.0°$
nowski & Minor, 1997)	$h = -13 \rightarrow 13$
$T_{min} = 0.416$, $T_{max} = 0.618$	$k = -18 \rightarrow 18$
1785 measured reflections	$l = -7 \rightarrow 7$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.03P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.018$	$+ 1.50P]$
$wR(F^2) = 0.055$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} < 0.001$
1002 reflections	$\Delta\rho_{max} = 0.81$ e Å^{-3}
70 parameters	$\Delta\rho_{min} = -0.52$ e Å^{-3}
H atoms restrained	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.0084 (6)

Table 1
Selected geometric parameters (Å, °).

Mn1—OH3^i	1.9085 (14)	Mn2—OH3^{iii}	2.1977 (15)
Mn1—OH1^i	1.9158 (14)	Mn2—OH3	2.1999 (15)
Mn1—O2^{ii}	2.2709 (15)	Mn2—O4^{iv}	2.2399 (15)
Mn2—O5	2.1280 (14)	As—O2^{iv}	1.6858 (14)
Mn2—O2	2.1430 (15)	As—O4^{ii}	1.692 (2)
Mn2—OH1	2.1702 (15)	As—O5^v	1.695 (2)
OH3^i—Mn1—OH3	180	O5—Mn2—OH3^{iii}	105.73 (6)
OH3^i—Mn1—OH1^i	86.94 (6)	O2—Mn2—OH3^{iii}	78.97 (5)
OH3—Mn1—OH1^i	93.06 (6)	OH1—Mn2—OH3^{iii}	89.65 (6)
OH1^i—Mn1—OH1	180	O5—Mn2—OH3	164.11 (7)
OH3^i—Mn1—O2^{ii}	82.18 (6)	O2—Mn2—OH3	99.30 (5)
OH3—Mn1—O2^{ii}	97.82 (6)	OH1—Mn2—OH3	74.03 (5)
OH1^i—Mn1—O2^{ii}	90.79 (6)	OH3^{iii}—Mn2—OH3	77.85 (6)
OH1—Mn1—O2^{ii}	89.21 (6)	O5—Mn2—O4^{iv}	85.46 (6)
O2^{ii}—Mn1—O2^{iii}	180	O2—Mn2—O4^{iv}	95.63 (7)
O5—Mn2—O2	96.59 (7)	OH1—Mn2—O4^{iv}	94.76 (7)
O5—Mn2—OH1	90.39 (7)	OH3^{iii}—Mn2—O4^{iv}	167.98 (6)
O2—Mn2—OH1	167.90 (6)	OH3—Mn2—O4^{iv}	92.59 (6)

Symmetry codes: (i) $-x, -y, -z$; (ii) $x, y, z - 1$; (iii) $-x, -y, 1 - z$; (iv) $-x, 1 - y, 1 - z$; (v) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$.

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
OH3—H3$\cdots$OH1^i	0.844 (18)	1.845 (19)	2.670 (2)	165 (3)

Symmetry code: (i) $x - \frac{1}{2}, y, \frac{1}{2} - z$.

H atoms were constrained to have a U_{iso} value of 0.03 Å^2. O—H distances were restrained to a length of 0.90 (2) Å.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: ATOMS (Shape Software, 1999) and *ORTEP*-3 for Windows (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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