

The crystal structure of saleeite, $\text{Mg}[\text{UO}_2\text{PO}_4]_2 \cdot 10\text{H}_2\text{O}$

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Crystal structure / $\text{Mg}[\text{UO}_2\text{PO}_4]_2 \cdot 10\text{H}_2\text{O}$

Abstract. Saleeite, $\text{Mg} [\text{UO}_2\text{PO}_4]_2 \cdot 10\text{H}_2\text{O}$, is monoclinic, space group $P2_1/c$, with $a = 6.951(3)$, $b = 19.947(8)$, $c = 9.896(4)$ Å, $\beta = 135.17(2)^\circ$, $Z = 2$, $U = 967.4$ Å³ and $D_c = 3.21$ g/cm³, $F_{000} = 844$, $\mu = 161$ cm⁻¹, $\lambda = 0.7107$ Å (MoK α), at 298 K. Least-squares refinement of the structure with 1324 single reflexions gave $R = 0.053$. The structure consists of UO_2PO_4 sheets, similar to those in threadgoldite, between which are located Mg^{2+} ions and water molecules. The Mg^{2+} ions are octahedrally coordinated to six of the 10 interlayer waters, but the last four water molecules are not bound to Mg. Saleeite is pseudotetragonal, the last few water molecules distorting it from true tetragonal symmetry. Previous assignments of saleeite as tetragonal appear to be incorrect; the other fully hydrated members of the autunite series may also have symmetry lower than the tetragonal symmetry assumed in the literature.

Introduction

The autunite series of minerals is usually written as $\text{A}[\text{UO}_2\text{XO}_4]_2 \cdot 10\text{H}_2\text{O}$, where A is generally an alkaline earth cation and X is P or As. Members of the autunite group have always been reported as tetragonal (Beintema, 1938; Frondel, 1951; Heinrich, 1958; Mrose, 1950, 1953; Takano, 1961; Weigel and Hoffmann, 1976; Wyckoff, 1965). There are also lower hydrates (Weigel and Hoffmann, 1976) with less than 10 water molecules (the metaphases).

It was noted (Beintema, 1938) that autunite is “anomalously” biaxial in the polarizing microscope, a sensitive technique able to distinguish between tetragonal and lower symmetries. Saleeite has elsewhere been reported as biaxial (Heinrich, 1958). However, no detailed three-dimensional X-ray structure determinations has been made on the autunite series to clarify

the finer details of these structures. When saleeite crystals were obtained from the Ranger I mine, Northern Territory (Australia), we were able to undertake a full structural determination of this member.

Experimental and analysis

The colour of crystals in the saleeite specimen varied from straw to greenish yellow. An electron microprobe analysis indicated the presence of the elements U, Mg, and P but not As, together with a small amount of Al (Mg:Al = 4:1). A crystal was selected which gave no disorder streaking on Weissenberg photographs, and found to have monoclinic symmetry, with space group $P2_1/c$, and $a = 6.951(3)$, $b = 19.947(8)$, $c = 9.896(4)$ Å, $\beta = 135.17(2)^\circ$ (cell dimensions from least-squares refinement of 20 angles to $2\theta = 50^\circ$).

The crystal data are given in the Abstract. .

The wafer-shaped morphology is as follows:

(hkl)	Distance from crystal centre (cm)
(010)	0.0026
(0 $\bar{1}$ 0)	0.0026
(10 $\bar{1}$)	0.0082
(001)	0.0106
($\bar{3}$ 02)	0.0082
(103)	0.0116

The intensities of 2395 reflections were measured on a locally made 4-circle diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.7107$ Å), giving 1324 single unique reflections to $\sin\theta/\lambda = 0.50$ on merging (merging $R = 0.064$) ($-7 < h < 4$; $0 < k < 20$; $0 < l < 10$). The data were reduced and absorption corrected (Elcombe et al., 1971) ($\mu_{\text{MoK}\alpha} = 161 \text{ cm}^{-1}$). A standard reflection showed no significant decline over the experiment. The structure was solved by Patterson and Fourier methods; hydrogens atoms were not located. Refinement with the program SHELX (Sheldrick, 1976) with unit weights gave $R = \Sigma\{(|F_o| - |F_c|)\} / \Sigma|F_o| = 0.053$ for $F_o > 4\sigma(F_o)$. The final difference synthesis showed that the interlayer atoms were not disordered; the only significant peak, $4 \text{ e}/\text{Å}^3$, 1.3 Å from uranium, could be given no structural significance and was considered to arise from systematic errors. The small amount of Al was assumed to go replace Mg in the 2(d) sites; some of the water sites must then be OH^- groups for charge balance. On the basis of the atoms located in the structure, the ideal formula is $\text{Mg}[\text{UO}_2\text{PO}_4]_2 \cdot 10\text{H}_2\text{O}$. The final structural parameters are given in Table 1. The Table of F_o and F_c data has been deposited¹.

¹ Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 52500, the names of the authors and the title of the paper.

Table 1. Atomic positions ($\times 10^3$) and thermal parameters ($\times 10^3$) in saleeite.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
4U	-72.2(1)	791.6(1)	-21.2(2)	15.1(5)	25.9(5)	8.6(4)	0.8(4)	9.1(4)	0.4(4)
2Mg	500	0	500	31(7)	24(6)	25(6)	0	17(6)	0
4P	421(1)	752(1)	474(1)	22(3)	30(3)	18(3)	2(3)	18(3)	1(3)
4O(1)	-81(3)	879(1)	-26(2)	24(9)	59(12)	30(9)	-9(10)	20(8)	-11(10)
4O(2)	-64(4)	703(1)	-18(2)	36(10)	54(11)	48(10)	-14(11)	35(9)	-15(11)
4O(3)	212(3)	798(1)	309(2)	24(8)	36(10)	20(8)	-3(8)	16(7)	-3(8)
4O(4)	-456(3)	793(1)	-79(2)	14(7)	30(9)	4(7)	-2(7)	-1(6)	-8(7)
4O(5)	-368(3)	797(1)	-352(2)	15(8)	46(10)	10(7)	-3(7)	7(7)	-6(8)
4O(6)	294(3)	794(1)	24(2)	18(8)	24(9)	45(10)	-15(9)	20(8)	-4(8)
4O(7)	259(4)	81(1)	428(2)	39(10)	47(11)	27(9)	-2(9)	23(9)	9(9)
4O(8)*	267(4)	586(1)	240(2)	34(10)	50(12)	32(10)	-7(9)	23(9)	-8(9)
4O(9)	203(3)	570(1)	-74(2)	34(10)	32(10)	22(9)	1(8)	18(8)	2(8)
4O(10)*	-425(4)	574(1)	-361(3)	57(3)	55(13)	37(11)	15(10)	30(11)	-4(11)
4O(11)	321(4)	997(1)	224(3)	46(11)	32(10)	38(10)	-9(9)	30(10)	-8(9)

* not bound to Mg.

Discussion

The structure

Saleeite, $\text{Mg}[\text{UO}_2\text{PO}_4]_2 \cdot 10\text{H}_2\text{O}$, is built up of UO_2PO_4 layers, similar to those found in the lower hydrates metatorbernite (Makarov and Tobelko, 1960), $\text{Cu}[\text{UO}_2\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$, meta-autunite (Makarov and Ivanov, 1960), $\text{Ca}[\text{UO}_2\text{PO}_4]_2 \cdot 6\text{H}_2\text{O}$, metazeunerite (Hanic, 1960), $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$ and threadgoldite (Piret et al., 1979), $\text{Al}[\text{UO}_2\text{PO}_4]_2 \cdot \text{OH} \cdot 8\text{H}_2\text{O}$. These layers consist of corner-shared UO_6 octahedra and PO_4 tetrahedra (Fig. 1). The UO_6 octahedra have uranyl bonds of length 1.75 and 1.76 Å normal to the layers, and longer U–O bonds of ≈ 2.30 Å in the layers (Table 2). The layers are puckered, as in the other sheet structures discussed above. The Mg^{2+} ions and water molecules lie between the layers. Of the 10 water molecules in the formula, six are octahedrally coordinated to Mg^{2+} , forming $\text{MgO}(\text{H}_2\text{O})_6$ groups; the other four are uncoordinated and more loosely bound in the structure. The Mg–O distances lie between 2.04 and 2.15 Å and the O(water) . . . O distances of 2.8–3.2 Å given in Table 2 are possible hydrogen bonds. As the hydrogen atoms have not been directly observed, hydrogen bond schemes are not proposed. The complete structure is shown in a stereoview (Fig. 2).

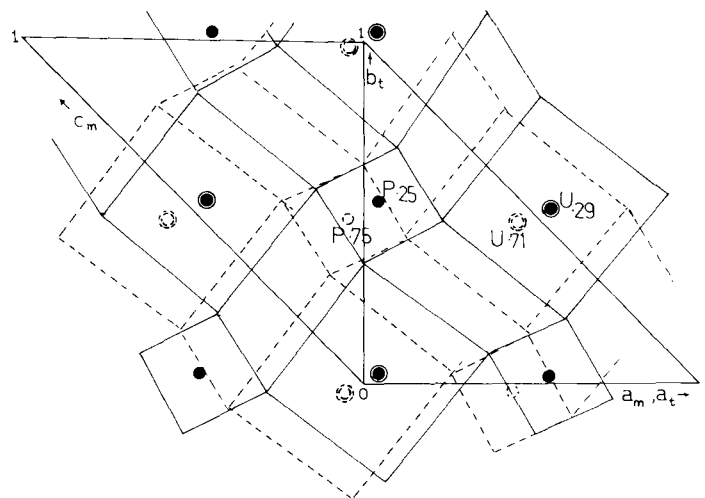


Fig. 1. View down b of the saleeite structure, showing the UO_2PO_4 layers only, and the pseudotetragonal a_t and b_t cell edges. Sheet oxygens are at the corners of the PO_4 tetrahedra and UO_6 octahedra. The layers would conform to tetragonal $I4/mmm$ symmetry only if adjacent layers were exactly superposed in projection, and the polyhedral edges were lined up parallel to a_t and b_t .

Table 2. Interatomic distances (Å) and angles (degrees) in salecite.

<i>Uranium coordination distances</i>		<i>Uranium octahedral angles</i>	
U—O(1)	1.75(2)	O(1)—U—O(2)	179.9(2)
U—O(2)	1.76(2)	—O(3)	87.7(7)
U—O(3)	2.34(2)	—O(4)	88.2(7)
U—O(4)	2.30(2)	—O(5)	86.6(7)
U—O(5)	2.32(2)	—O(6)	89.7(7)
U—O(6)	2.25(2)	O(2)—U—O(3)	92.5(7)
		—O(4)	91.8(7)
		—O(5)	93.3(7)
		—O(6)	90.3(7)
		O(3)—U—O(4)	91.5(5)
		—O(6)	90.4(5)
		O(4)—U—O(5)	86.4(5)
		O(5)—U—O(6)	91.4(5)
<i>Phosphate group distances</i>		<i>Phosphorous tetrahedral angles</i>	
P—O(3)	1.49(2)	O(3)—P—O(4)	108.9(8)
—O(4)	1.57(2)	—O(5)	107.0(9)
—O(5)	1.52(2)	—O(6)	112.2(9)
—O(6)	1.58(2)	O(4)—P—O(5)	113.5(8)
		—O(6)	108.1(8)
		O(5)—P—O(6)	107.2(8)
<i>Magnesium-water distances (× 2)</i>		<i>Magnesium octahedral angles</i>	
Mg—O(7)	2.06(2)	O(7)—Mg—O(9)	92.5(6)
—O(9)	2.15(2)	—O(11)	89.2(7)
—O(11)	2.04(2)	O(9)—Mg—O(11)	89.9(7)
		<i>Around O(9)</i>	
		O(9)—O(2)	3.50
		O(9)—O(1)	3.52
		O(9)—O(8)	2.82
		O(9)—O(3)	2.89
		O(9)—O(5)	3.39
		<i>Around O(10)</i>	
		O(10)—O(8)	2.88, 3.30
		O(10)—O(11)	2.81
		O(10)—O(7)	3.56
		O(10)—O(4)	3.34
		O(10)—O(6)	2.98
		O(10)—O(2)	3.53
		O(10)—O(10)	3.64
		<i>Around O(11)</i>	
		O(11)—O(1)	3.11, 2.85
		O(11)—O(10)	2.81
		O(11)—O(8)	3.17
<i>Water oxygen environment distances</i>			
O(7)—O(1)	3.33		
—O(2)	3.20		
—O(5)	2.81		
—O(10)	3.56		
O(8)—O(2)	2.99		
—O(4)	2.80		
—O(6)	3.59		
—O(9)	2.82		
—O(10)	2.88, 3.30		
—O(11)	3.17		
O(9)—O(2)	3.50		
—O(1)	3.52		
—O(8)	2.82		
—O(3)	2.89		
—O(5)	3.39		
O(10)—O(8)	2.88, 3.30		
—O(11)	2.81		
—O(7)	3.56		
—O(4)	3.34		
—O(6)	2.98		
—O(2)	3.53		
—O(10)	3.64		
O(11)—O(1)	3.11, 2.85		
—O(10)	2.81		
—O(8)	3.17		

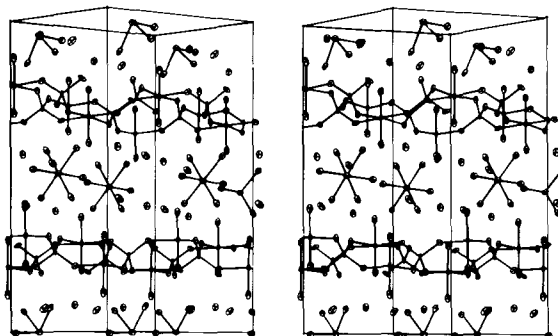


Fig. 2. Stereoview of the complete saleeite structure, showing the MgO(water) octahedra and loosely bound water oxygen atoms between the UO_2PO_4 layers.

The pseudosymmetry of saleeite

The uncoordinated water molecules [O(8) and O(10) are their oxygen atoms] distort the structure from tetragonal symmetry. The pseudotetragonal cell edges (Fig. 2) are obtained from the monoclinic cell by the transformation $a_t = a_m$, $b_t = a_m + c_m$, $c_t = b_m$. The dimensions of the pseudo cell are $a_t = 6.951(3)$, $b_t = 6.978(3)$, $c_t = 19.947(8)$ Å, $\alpha_t = 89.91(3)$, $\beta_t = 89.99(2)$, $\gamma_t = 89.45(3)^\circ$. The significant differences between a_t and b_t , and the deviation of γ from 90° reveal the lower monoclinic symmetry, whereas in the structure deviations from tetragonal are even more marked.

Members of the autunite series, including saleeite, have always been described as tetragonal (Weigel and Hoffmann, 1976; Heinrich, 1958), they have been assigned various tetragonal symmetries such as $P4/nmm$, $P4_222$, $P4/n$, $P4_2/n$, and $I4/mmm$. By transforming our systematic absences to a pseudotetragonal cell we have obtained the pseudo space group $P4_222$ for saleeite, but the symmetry elements of the latter are difficult to reconcile with our structure. Beintema (1938) gave the space group $I4/mmm$ for autunite; our UO_2PO_4 layers can be made to conform with this by moving the adjacent layers in Figure 1 until they superpose, and their polyhedral edges so that they are parallel to a_t and b_t . This, however, requires a considerable adjustment to the structure, and even more movement would be necessary for the interlayer atoms. Consequently, our pseudo-systematic absences do not agree with I-centering, and the structure obviously deviates greatly from tetragonal symmetry.

Conclusion

On the basis of the present study, the earlier assignments of saleeite, $\text{Mg}[\text{UO}_2\text{PO}_4]_2 \cdot 10\text{H}_2\text{O}$, as tetragonal are incorrect. Optical evidence

(Beintema, 1938) suggests that autunite also has a symmetry lower than the tetragonal symmetry presently assumed. Probably more three-dimensional X-ray studies of other members are needed to resolve uncertainties about the crystal systems in the autunite series.

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