

Ab initio X-ray powder structure determination of parascorodite, $\text{Fe}(\text{H}_2\text{O})_2\text{AsO}_4$

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Abstract: The crystal structure of parascorodite, $\text{Fe}(\text{H}_2\text{O})_2\text{AsO}_4$, has been solved *ab-initio* from powder data. The mineral is trigonal, with space group $P\bar{3}c1$, $Z = 6$, $a = 8.9232(2)$ Å, $c = 9.9296(3)$ Å. The Rietveld refinement was led up to $R_p = 4.5$ %. The structure is built up by the same coordination polyhedra found in its dimorph scorodite, namely slightly distorted Fe-centred octahedra and As-centred tetrahedra, but their connection lead to quite different crystal structures for the two polymorphs. Parascorodite structure can be described in terms of mixed octahedral-tetrahedral “columns” including Fe2 and As polyhedra, running along c , similar to those found in ferrinaitrite and kaatialaite. These columns are interconnected in a three-dimensional framework by the sharing of the O1 oxygen between $[\text{AsO}_4]$ tetrahedra and Fe1 octahedra, and by the strong hydrogen bond $\text{OW}\cdots\text{O2}$.

Key-words: parascorodite, Kaňk, powder data, *ab-initio*, structural solution.

Introduction

Parascorodite was described by Ondruš *et al.* (1999) from the medieval dumps of the Kuntery mine, located in the Kaňk ore district (Central Bohemia, Czech Republic), neighbouring the worldwide famous Kutná Hora ore district. The formation of parascorodite is due to the natural weathering of arsenopyrite and pyrite, and to its subsequent precipitation from the iron-arsenic-bearing solutions in a subaerial environment. Parascorodite represents one of the youngest iron arsenates at Kaňk ore deposit, where occurs as earthy pale green-gray aggregates, most frequently associated with scorodite, bukovskýite, kaňkite, zýkaite, gypsum, jarosite and amorphous ferric hydroxides (Trdlička & Hoffman, 1965; Novák *et al.*, 1967; Čech *et al.*, 1976, 1978). Ondruš *et al.* (1997) identified parascorodite also in the vein Geschieber of the Svornost mine in the Jáchymov (Joachimsthal) ore district, where it is found in a quartz gangue associated to scorodite, kaňkite, vajdakite, pyrite, arsenic, and proustite.

In these two finding localities, parascorodite is invariably associated with its dimorph scorodite. Its rarity, compared with scorodite, suggests that parascorodite most probably forms as a transitional metastable phase during crystallization of iron arsenates, in restricted conditions of supergene zone, moreover favourable for its preservation.

SEM/TEM observations (Ondruš *et al.*, 1999) showed that the crystals are prismatic, typically up to 0.5 µm in length, rarely up to 1 µm. Therefore, a single-crystal study was impracticable, and the crystal structure of parascorodite has been solved and refined from powder data *ab initio*.

Experimental

A preliminary scan, performed with $\text{CuK}\alpha$ radiation, allowed to detect the presence of a considerable (near 5 %) amount of scorodite in our powder. Moreover, the high background, due to the fluorescence of iron, advised to select a suitable radiation, such as Co, to get a high quality data collection. Powder diffraction data were collected with a Stoe STADI P diffractometer, in transmission $\theta - 2\theta$ geometry at the Bayerisches Geoinstitut, Bayreuth University, Bayreuth, Germany. A primary Ge (111) monochromator was tuned to provide monochromatic $\text{CoK}\alpha_1$ radiation. A Braun linear PSD detector was utilized. The powder sprayed on a mylar foil was spun during the data acquisition. This arrangement allowed to use a very low amount of material, as well as reducing a possible preferred orientation. Powder data were collected in the range $7.5 - 124.98^\circ 2\theta$, with a 0.02 step size and 35 s counting time. Details of the experimental conditions and of the structure solution are given in Table 1.

Structure determination and refinement

The crystal structure was solved through the EXPO package (Altomare *et al.* 1999), checking all the possible space groups for parascorodite (Ondruš *et al.*, 1999). A reasonable crystal-chemical model, giving the lowest R factor among the whole set, was obtained for the $P\bar{3}c1$ space group. Trials were made to refine the structure as non-centrosymmetric,

and to verify the existence of possible supercells, but we did not get any compelling evidence for these possibilities. This model was therefore assumed as a starting one for the subsequent Rietveld refinement, performed through the FullProf (Rodríguez-Carvajal, 2004) program. Background was prepared in advance and read from a file. In the final stages of the refinement, the background was transformed *via* a 4 parameter filtering (see the FullProf manual for details). For scorodite, a scale factor only was refined, keeping instead fixed its cell parameters, together with its atomic positional and displacement parameters (Hawthorne, 1976). In the final stages of the refinement, anisotropic displacement factors were introduced for the heavier Fe and As atoms. Final agreement factors were $R_p = 4.5\%$, $R_{\text{Bragg}} = 4.6\%$. A plot, displaying the observed, calculated and difference curves is given in Fig. 1. Refined atomic and displacement parameters for parascorodite are reported in Table 2, and selected interatomic distances and angles are given in Table 3.

Structure description

In parascorodite, two independent octahedrally coordinated Fe^{3+} sites, denoted as Fe1 and Fe2, are present. Three symmetry equivalent oxygens and three symmetry equivalent water molecules, denoted as O1 and OW respectively, make up a moderately asymmetric Fe1 octahedron, $\langle \text{Fe1-O} \rangle = 2.036 \text{ \AA}$, distortion 5.17×10^{-4} defined according to Rodríguez-Carvajal (2004). Likewise scorodite, in parascorodite Fe1-O1 ($1.990 \text{ \AA}$) bonds are distinctly shorter than the Fe1-OW ($2.082 \text{ \AA}$) ones. The distortion of Fe1 octahedra is very similar in scorodite ($\langle \text{Fe1-O} \rangle = 2.015 \text{ \AA}$, distortion: 7.62×10^{-4}) and in parascorodite. Site Fe2, being placed on a ternary rotoinversion axis, makes six symmetry equivalent bonds with O2, yielding a perfectly symmetric octahedron ($\langle \text{Fe2-O2} \rangle = 2.049 \text{ \AA}$). Comparing the $[\text{AsO}_4]$ tetrahedra in the two polymorphs, we found slight variations for both the As-O

Table 1. Crystal data, experimental conditions and refinement of parascorodite from Kaňk. R agreement factors defined according to McCusker *et al.* (1999) and Rodríguez-Carvajal (2001).

Crystal data	
Formula	$\text{Fe}(\text{H}_2\text{O})_2\text{AsO}_4$
M_r	231.08
Symmetry	trigonal, $P\bar{3}c1$
a (Å)	8.9232(2)
c (Å)	9.9296(3)
V (Å ³)	684.71(3)
Z	6
D_c (g/cm)	3.358
$F(000)$	666
Program packages used	EXPO (Altomare <i>et al.</i> , 1999); Fullprof (Rodríguez-Carvajal <i>et al.</i> , 2004)
Data collection	
Diffractionmeter	Stoe STADI P
Scan mode	Transmission $\theta - 2\theta$ arrangement
Monochromator	primary Ge (111)
Radiation, λ (Å)	$\text{CoK}_{\alpha 1}$, 1.788920
Start, end angle, step size ($^\circ 2\theta$)	7.5, 124.98, 0.02
Refinement	
Parascorodite, scorodite (wt. %)	97.9(4), 2.1(1)
Halfwidth parameters	$U = 0.079(4)$, $V = -0.059(4)$, $W = 0.0386(8)$
ν Pseudovoigt	0.44(2)
η angular variation	0.0035(4)
No. of observed reflections	252
No. of parameters	37
R_p (%)	4.5
wR_p (%)	6.0
R_F	4.8
χ^2	1.05
Bragg R (%)	4.6
Largest diff. peak and hole ($\text{e.\AA}^{-3}$)	1.0 / -0.4

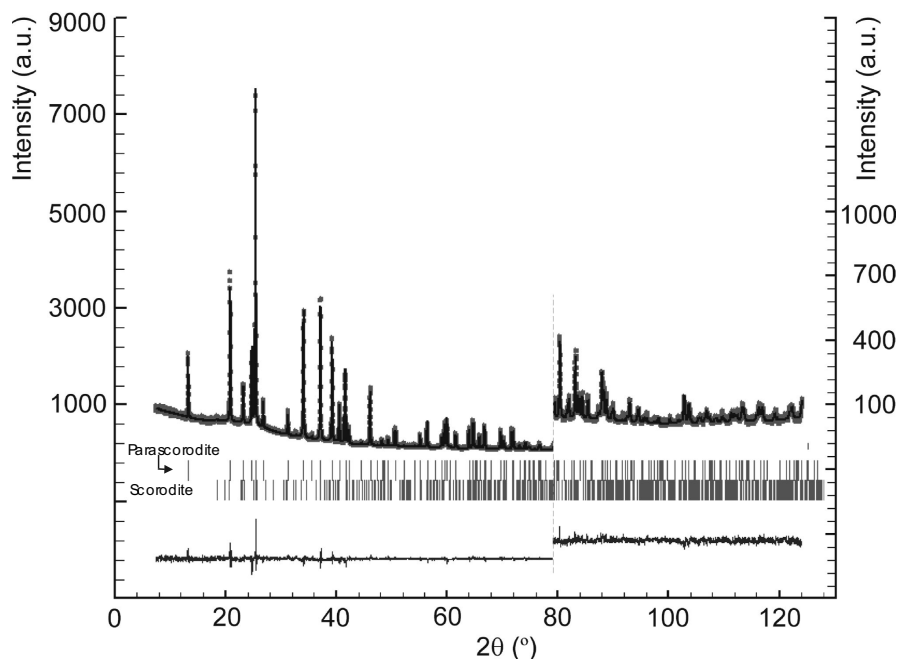


Fig. 1. Observed, calculated and difference curve for the Rietveld refinement of parascorodite. Reflection position for both parascorodite and scorodite are marked by vertical bars.

Table 2a. Atomic coordinates and isotropic displacement factors ($\text{\AA}^2$); U_{iso} are marked as asterisks.

Name	Site	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
Fe1	4d	1/3	2/3	0.3070(4)	0.056(3)
Fe2	2b	0	0	0	0.038(2)
As1	6f	0.2735(2)	0	1/4	0.020(1)
O1	12g	0.4621(6)	0.1664(6)	0.2999(5)	0.012(2)*
O2	12g	0.2136(6)	0.0695(8)	0.1175(5)	0.017(2)*
Ow	12g	0.8615(7)	0.5046(7)	0.0642(5)	0.014(2)*

Table 2b. Anisotropic displacement factors ($\text{\AA}^2$) for Fe and As atoms in parascorodite.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe1	0.058(3)	0.058(3)	0.051(3)	0.029(3)	0	0
Fe2	0.048(3)	0.048(3)	0.017(1)	0.024(3)	0	0
As1	0.019(1)	0.021(1)	0.017(1)	0.010(1)	-0.0001(16)	-0.0003(16)

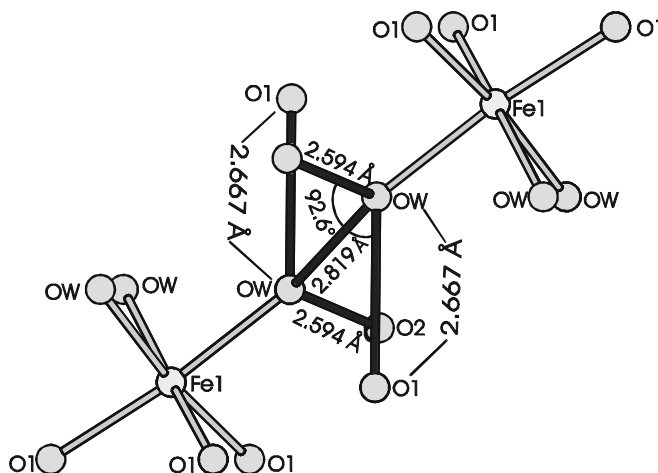


Fig. 2. Close-up of the crystal structure of parascorodite showing the hydrogen bond system. Every water molecule in parascorodite structure forms a single bond with the O2 oxygen and a bifurcated bond with O1 and OW anions.

bonds and for the polyhedral distortion (parascorodite $\langle \text{As-O} \rangle$ 1.661 Å, distortion: 0.22×10^{-4} ; scorodite and $\langle \text{As-O} \rangle$ 1.692 Å, distortion: 0.27×10^{-4}). Each of the two independent oxygen atoms in parascorodite, O1 and O2, are connected to one As and one Fe, whereas the water molecule is connected to the Fe1 cation only. The hydrogen bond contribution is therefore essential to maintain the charge balance on both O1 and O2.

A hydrogen bonding scheme (Fig. 2) has been derived by checking all the O-O distances shorter than 3.2 Å, involving oxygens not belonging to the same coordination polyhedron. The water molecule OW acts as donor, engaging the O1 and O2 oxygens as acceptors, with O...O distances of 2.667 Å and 2.594 Å respectively, the O1-OW-O2 angle being 92.6°. An additional hydrogen bond, involving water molecules, OW...OW = 2.819 Å, is moreover present. It is remarkable how this bond distance is shorter than the OW-OW edge (2.847 Å) of the Fe1 octahedron. Every water molecule forms therefore three strong hydrogen bonds, two of them with O1 and O2 oxygens and one just between water molecules.

Table 3. Selected interatomic distances and angles for coordination polyhedra and O...O bonds in parascorodite (Å and degrees).

Fe1	-O1 (x3)	1.990(6)	O1-Fe1-O1	94.2(2)
	-Ow (x3)	2.082(6)	O1-Fe1-Ow	173.6(2)
			O1-Fe1-Ow	87.6(2)
			O1-Fe1-Ow	91.8(2)
			Ow-Fe1-Ow	86.2(2)
$\langle \text{Fe1-O} \rangle$		2.036	distortion: 5.17×10^{-4}	
Fe2	-O2 (x6)	2.049(6)	O2-Fe2-O2	180.0(2)
			O2-Fe2-O2	89.2(2)
			O2-Fe2-O2	90.8(2)
$\langle \text{Fe2-O} \rangle$		2.049	distortion: $< 0.01 \times 10^{-4}$	
As1	-O2 (x2)	1.653(5)	O1-As1-O1	111.4(2)
	-O1 (x2)	1.668(6)	O2-As1-O1	105.9(2)
			O2-As1-O1	107.6(3)
			O2-As1-O2	118.6(3)
$\langle \text{As1-O} \rangle$		1.661	distortion: 0.22×10^{-4}	
Ow	-O1 ^a	2.667(7)	O2-Ow-O1 ^a	92.6(2)
	-O2	2.594(9)		

Symmetry codes: ^a1-y, 1-x, -0.5+z

Two hypotheses can be made to explain such a configuration. In parascorodite structure there could be the simultaneous presence of H_3O^+ and H_2O , randomly distributed over the water position, coupled with a contemporaneous substitution of Fe^{3+} by Fe^{2+} . Alternatively, the water molecules could form a single and a bifurcated hydrogen bond, engaging as acceptors, respectively, O2 and the couple O1, OW. The presence of hydronium in phases isostructural with scorodite was hypothesized by Mooney-Slater (1961) in his structural study of $\text{InPO}_4 \cdot 2\text{H}_2\text{O}$, and supported by the IR studies by Tarte & Pasques-Ledent (1968). The natural counterpart of this synthetic compound, yanomanite, belongs together with scorodite, mansfieldite, strengite and variscite to a group of orthorhombic isostructural phases, also embedding various synthetic compounds, with general formula $^{\text{VI}}\text{Me}^{3+\text{IV}}\text{X}^{5+}\text{O}_4 \cdot 2\text{H}_2\text{O}$, where Me = Al, P, V, Ga and X = As, P, which can be denoted as variscite group. Many of these compounds possess monoclinic polymorphs, which can be grouped in the metavariscite group. Subsequent studies on the phases of the variscite and metavariscite groups, did not confirm the presence of H_3O^+ . Salvador & Fayos (1972), on the basis of IR studies, pointed out the presence of two neutral H_2O molecules in variscite, this result being confirmed by the following structural study by Kniep *et al.* (1977). Other studies on the variscite group phases were performed on scorodite (Hawthorne, 1976) and mansfieldite, $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$ (Harrison, 2000), both excluding the presence of hydronium and confirming the presence of neutral water molecules. A structural study of metavariscite is due to Kniep & Mootz (1973), who report the presence of two neutral water molecules, the first one forming two single hydrogen bonds, the second one forming instead two bifurcated hydrogen bonds. An examination of the hydrogen bond system in metastrengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, Moore, 1966) leads to the conclusion that two neutral water molecules are present in this phase. Finally, a recent structural study of the orthorhombic and monoclinic polymorphs of $\text{InPO}_4 \cdot 2\text{H}_2\text{O}$

Table 4. Bond valences and their sums (v.u.) for parascorodite. $\Sigma_c v$ and $\Sigma' v$ indicate respectively sums of bond strengths non corrected and after correction for hydrogen bond contributions. O...O distances (Å) and associated hydrogen bond strengths (v.u.) are given in the last row of the table.

	O1	O2	OW	Σa_v
Fe1	0.536(x3)		0.417(x3)	2.859
Fe2		0.457(x6)		2.742
As1	1.305(x2)	1.361(x2)		5.332
$\Sigma_c v$	1.841	1.818	0.417	
$\Sigma' v$	2.085	2.109	-0.118	
OW-O1	2.667	0.244		
OW-O2		2.594	0.291	

is due to Tang *et al.* (2001). On the basis of crystal structural determinations and of IR studies they conclude that in both the polymorphs neutral water molecules, involved in both single and bifurcated hydrogen bonds, are present.

On these grounds, it seems straightforward to assume the presence of two water molecules in parascorodite, forming a single OW...O2 bond and a bifurcated OW...O1, OW...OW bond.

A bond valence balance is reported in Table 4, where $\Sigma_c v$ row shows the sums of bond strengths calculated following Brese & O'Keeffe (1991); in $\Sigma' v$ row these sums are corrected for hydrogen bond contributions, evaluated according to Ferraris & Ivaldi (1988). The balance can be considered as satisfactory.

No striking relationships exist between the structures of the two $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ polymorphs. According to Hawthorne (1976), in the crystal structure of scorodite, the sharing of each oxygen between an As tetrahedron and an Fe octahedron give rise to a three-dimensional network, with resulting composition $\{\text{FeAsO}_4\}_\infty$. The two independent water molecules are each linked to one Fe cation only, and give rise to a hydrogen bond system. The crystal structure of parascorodite can be better described (Fig. 3–4) in terms of

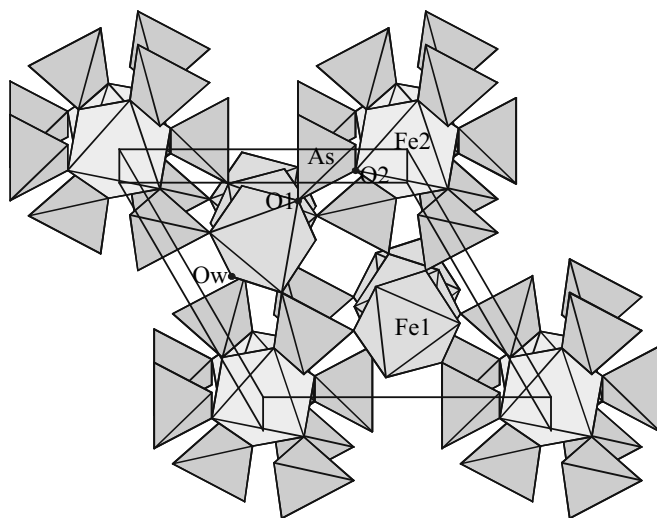


Fig. 3. The crystal structure of parascorodite, as seen 5° away from [0001]. The mixed octahedral-tetrahedral “columns” made of Fe2 octahedra (light shadow) and As tetrahedra, are connected by the Fe1 octahedra (heavier shadow) in a three-dimensional framework.

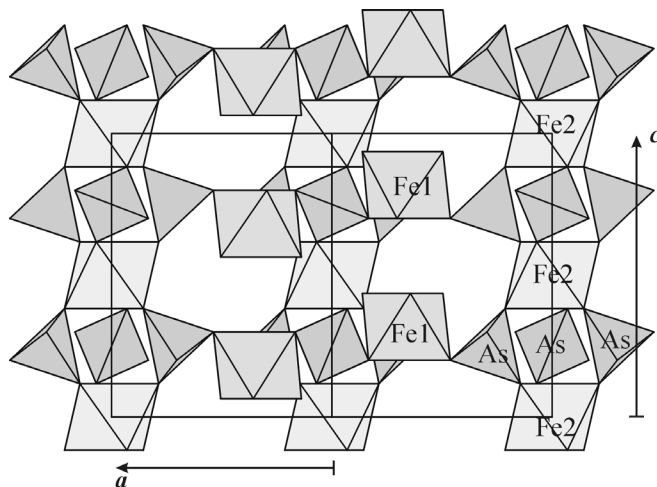


Fig. 4. The polyhedral connections in the crystal structure of parascorodite, as seen along [110].

“columns”, built up by Fe2 octahedra, stacked along c with As tetrahedra, each $[\text{AsO}_4]$ tetrahedron sharing two O2 oxygens with alternating Fe2 octahedra. Fe1 octahedra are just located between these mixed octahedral-tetrahedral “columns”, and are interconnected by the OW...OW = 2.818 Å hydrogen bonds, formed between water molecules of neighbouring Fe1 octahedra stacked along c . The mixed octahedral-tetrahedral “columns” are interconnected to form a three-dimensional framework (Fig. 4), by sharing of O1 oxygens between the As centred tetrahedra and the Fe1 octahedra, and by the strong hydrogen bond OW...O2.

In the classification scheme of Hawthorne *et al.* (2000), both scorodite and parascorodite are consequently to be placed among the group of structures based on tetrahedra and divalent and/or trivalent cation octahedra, subgroup “structures with infinite frameworks”.

Mixed octahedral-tetrahedral “columns”, close to those found in parascorodite, are present in ferrinaitrite, $\text{Na}_3(\text{H}_2\text{O})_3\text{Fe}(\text{SO}_4)_3$ (Scordari, 1977) and in kaatialaite, $\text{Fe}(\text{AsO}_2(\text{OH})_2) \cdot 5\text{H}_2\text{O}$ (Boudjada & Guitel, 1981). In these two phases, zeolite-like channels are present, hosting Na^+ and water molecules in ferrinaitrite, and water molecules only in kaatialaite. Adjacent columns are linked together by the “zeolitic” content, namely sodium polyhedra and hydrogen bonds in ferrinaitrite and by a hydrogen bond system in kaatialaite.

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