The crystal structure of kastningite
(Mn, Fe, Mg) $(H_2O)_4[Al_2(OH)_2(H_2O)_2(PO_4)_2]$ · 2 H_2O
— a new hydroxyl aquated orthophosphate hydrate mineral

G. Adiwidjaja[I], K. Friese[*,II], K.-H. Klaska[I] and J. Schlüter[I]

[I] Universität Hamburg, Mineralogisch-Petrographisches Institut, Grindelallee 48, D-20146 Hamburg, Germany
[II] Universidad del País Vasco, Facultad de Ciencias, Departamento de Física de la Materia Condensada, Apdo. 644, E-48080 Bilbao, Spain

Abstract. The crystal structure of kastningite, a new mineral from Waidhaus, Bavaria, Germany, has been determined. Ideal formula from X-ray structure analysis is $Mn(H_2O)_4[Al_2(OH)_2(H_2O)_2(PO_4)_2]$ · 2 H_2O. Lattice parameters are $a = 10.205(1)$ Å, $b = 10.504(1)$ Å, $c = 7.010(1)$ Å, $\alpha = 90.38(1)°$, $\beta = 110.10(1)°$, $\gamma = 71.82(1)°$ (space group $P\bar{1}$, $Z = 2$).

Kastningite is isostructural to stewartite $Mn(H_2O)_4$ · $[Fe_2^{3+}(OH)_2(H_2O)_2(PO_4)_2]$ · 2 H_2O. Chains of corner sharing octahedra run in the [102] direction. Within the chain, octahedra of composition $[Al(OH)_2(O_P)_2(H_2O)_2]^{3-}$ alternate with others of composition $[Al(OH)_2(O_P)_4]^{7-}$ (with O_P designating oxygen atoms which form part of a phosphate group). The resulting chain composition is $[Al(O_P)_3(OH)(H_2O)]^{4-}$. Symmetry equivalent chains are bridged by $[PO_4]^{3-}$ tetrahedra and sheets parallel to {010} of composition $[Al_2(OH)_2(H_2O)_2(PO_4)_2]^{2-}$ are formed. $[Mn(H_2O)_4(O_P)_2]^{2-}$ octahedra link these sheets in the direction of [010] thus resulting in a three dimensional structure. The structure is further held together by a complex system of hydrogen bonds.

Chains of corner-sharing octahedra which are further connected to $[PO_4]^{3-}$ tetrahedra are a common feature within other aquated orthophosphate hydrate minerals. Yet there are differences with respect to the number of symmetrically equivalent octahedra within the chain, their composition as well as to the way they are connected to the tetrahedra. A brief comparison of kastningite to these other minerals is given.

1. Introduction

The new mineral kastningite was found in Waidhaus, Bavaria, Germany. It occurred in a phosphate-rich assemblage associated with other minerals like variscite and paravauxite in the aplite of the Waidhaus pegmatite. The crystals attain 2 mm and are tabular on [001]. For a closer description see [1]. The mineral was approved by the I.

M. A. Commission on New Minerals and Mineral Names in 1998.

The ideal formula of kastningite from X-ray structure analysis is $Mn^{2+}(H_2O)_4[Al_2(OH)_2(H_2O)_2(PO_4)_2]$ · 2 H_2O. It is isostructural with stewartite and polymorphic to mangangordonite. These minerals are closely related to other aquated orthophosphate hydrate minerals like laueite, gordonite, mangangordonite, paravauxite etc.. The dominant feature within the structures of these compounds are chains of corner sharing octahedra with a chain repeat distance of approximately 7 Å.

We determined the crystal structure of kastningite to gain insight about the relationship of it to other aquated orthophosphate hydrate minerals.

2. Experimental and structure refinement

Crystal data as well as details concerning the measurement and refinement are given in Table 1.

Positions of the hydrogen atoms were found using difference Fourier synthesis. Their coordinates were refined while there isotropic displacement parameters were fixed. Final atomic coordinates are given in Tables 2 and 3. Selected bond lengths are given in Table 4[1].

3. Description of the structure and comparison to other related minerals

Kastningite is isostructural with the mineral stewartite. It is also a polymorph of mangangordonite and has close relationship to several aquated hydroxyl orthophosphate hydrate minerals. Lattice parameters of related compounds are given in Table 6.

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* Correspondence author (e-mail: wmbfrxxk@lg.ehu.es)

Table 1. Experimental conditions and structure refinement.

Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	10.205(1)
b [Å]	10.504(1)
c [Å]	7.010(1)
α [°]	90.38(1)
β [°]	110.10(1)
γ [°]	71.82(1)
Lattice parameters from	25 reflections
V [Å^3]	666.2(1)
μ [mm^{-1}]	13.205
Diffractometer	Cad4
Wavelength [Å]	1.54184
Scan	$\omega - 2\theta$
θ range	$2° < \theta < 75°$
$hkl_{min} - hkl_{max}$	0, $\overline{11}$, $\overline{13}$ − 8, 12, 13
2 standard reflections	every 120 min
Absorption correction	Gauss
with program	MOLEN [4]
Crystal size	0.036 mm × 0.1 mm × 0.12 mm
Measured reflections	2737
Reflections $\geq 4\sigma$	2389
$R(F^2)_{int}$	0.030
Structure solution	Sir92 [5]
Structure refinement	SHELX93 [6]
$R(F)$ reflections $\geq 4\sigma$	0.056
$R(F)$ all reflections	0.065
$wR(F^2)$ all reflections	0.186
Extinction correction	SHELXL93 [6]
Extinction coefficient	0.0088(14)
Weighting scheme	$w = 1/[\sigma^2(F_{obs})^2 + (0.1212 \cdot P)^2 + 1.5684P]$
with	$P = (\text{Max}\,(F_{obs}^2) + 2F_{calc}^2)/3$

Table 2. Positional and isotropic atomic displacement parameters for the atoms with e.s.d.'s in parenthesis.

Atom	x	y	z	U_{eq} [Å^2]
Mn	0.27053(9)	0.48833(8)	0.6504(1)	0.0270(3)
Al1	0	0	0	0.0171(4)
Al2	$^1/_2$	0	0	0.0196(4)
Al3	0.2511(1)	0.9947(1)	0.5099(2)	0.0157(3)
P1	0.9082(1)	0.1807(1)	0.3411(2)	0.0181(3)
P2	0.4595(1)	0.1719(1)	0.5967(2)	0.0186(3)
O1	0.8731(4)	0.3322(3)	0.2976(5)	0.0236(7)
O2	0.0656(3)	0.1192(3)	0.4956(5)	0.0211(7)
O3	0.8015(4)	0.1570(3)	0.4354(5)	0.0233(7)
O4	0.8893(4)	0.1167(3)	0.1389(5)	0.0224(7)
O5	0.4311(4)	0.3226(3)	0.6066(6)	0.0280(8)
O6	0.5376(4)	0.0956(4)	0.8107(5)	0.0245(7)
O7	0.3132(4)	0.1475(3)	0.4870(5)	0.0228(7)
O8	0.5602(4)	0.1263(3)	0.4723(5)	0.0225(7)
OH1	0.1747(4)	−0.0107(3)	0.2217(5)	0.0217(7)
OH2	0.3257(4)	−0.0018(4)	0.7986(5)	0.0225(7)
OW1	0.0190(4)	0.1519(4)	0.8693(6)	0.0259(8)
OW2	0.3894(4)	0.1674(4)	0.0789(6)	0.0292(8)
OW3	0.6335(5)	0.5574(5)	0.0265(6)	0.0379(9)
OW4	0.8567(5)	0.6392(4)	0.3364(7)	0.0372(10)
OW5	0.8531(5)	0.4561(4)	0.6770(6)	0.0344(9)
OW6	0.5888(4)	0.3909(4)	0.3585(7)	0.0332(8)
H2O1	0.0977(5)	0.3241(4)	0.1494(6)	0.0320(8)
H2O2	0.7045(5)	0.3413(4)	0.8388(7)	0.0355(9)

Table 3. Positional parameters for the hydrogen atoms.

Atom	x	y	z	U_{iso} [Å^2]
H1	0.771(10)	0.012(8)	0.83(1)	0.050
H2	1.023(9)	0.146(8)	0.76(1)	0.050
H3	0.049(9)	0.200(9)	0.93(1)	0.050
H4	0.286(9)	−0.035(8)	0.85(1)	0.050
H5	0.430(10)	0.172(9)	0.18(1)	0.050
H6	0.353(9)	0.252(9)	0.01(1)	0.050
H7	0.670(9)	0.469(8)	0.95(1)	0.050
H8	0.559(10)	0.602(9)	0.97(1)	0.050
H9	0.855(9)	0.708(8)	0.41(1)	0.050
H10	0.932(10)	0.614(8)	0.30(1)	0.050
H11	0.877(9)	0.519(8)	0.78(1)	0.050
H12	0.823(9)	0.415(8)	0.78(1)	0.050
H13	0.655(9)	0.304(9)	0.40(1)	0.050
H14	0.547(9)	0.373(8)	0.46(1)	0.050
H15	0.017(9)	0.343(8)	0.21(1)	0.050
H16	0.168(10)	0.264(9)	0.23(1)	0.050
H17	0.640(10)	0.323(8)	0.78(1)	0.050
H18	0.753(9)	0.270(9)	0.92(1)	0.050

The dominant feature of the structure are chains of corner sharing octahedra which run along the direction [102] (Fig. 1c). Three symmetry independent octahedra can be observed within the chain. Designating the oxygen atoms which also form part of the $[PO_4]^{3-}$ tetrahedra as O_P, two of the octahedra (around Al1 and Al2) have composition $[Al(O_P)_2(OH)_2(H_2O)_2]^{3-}$ while the third (around Al3) has composition $[Al(O_P)_4(OH)_2]^{7-}$. Different octahedra are connected via OH$^-$ groups. The composition of the chain of octahedra is $[Al(O_P)_3(OH)(H_2O)]^{4-}$.

The $[PO_4]^{3-}$ tetrahedra bridge different chains, forming layers of composition $[Al_2(OH)_2(H_2O)_2(PO_4)_2]^{2-}$ parallel

Mn	O5	2.090(4)	P1	O1	1.526(4)	P2	O5	1.523(4)
	O1^i	2.114(3)		O2^{ii}	1.528(3)		O6	1.524(4)
	OW3^i	2.125(4)		O3	1.533(3)		O7	1.527(3)
	OW4^i	2.159(4)		O4	1.542(3)		O8	1.533(3)
	OW5^i	2.183(4)						
	OW6^i	2.207(4)			1.532			1.527
		2.147						
Al1	O4^{iv}	1.898(3)	Al2	OH2^{vi}	1.858(3)	Al3	OH1^x	1.886(4)
	O4^v	1.898(3)		OH2^{viii}	1.858(3)		O3^{ix}	1.906(4)
	OW1^{vi}	1.939(3)		O6^{vi}	1.878(3)		OH2^{ix}	1.906(4)
	OW1^{vii}	1.939(3)		O6^{viii}	1.878(3)		O8^i	1.910(4)
	OH1	1.956(3)		OW2	1.962(4)		O3^i	1.913(3)
	OH1^{iii}	1.956(3)		OW2^v	1.962(4)		O7^{ix}	1.927(3)
		1.931			1.899			1.908

Table 4. Bond distances in Å in the coordination polyhedra with e.s.d.'s in parentheses.

Symmetry code: (i) $1-x$, $1-y$, $1-z$ (ii) $1+x$, y, z (iii) $-x$, $-y$, $-z$ (iv) $-1+x$, y, z, (v) $1-x$, $-y$, $-z$ (vi) x, y, $-1+z$ (vii) $-x$, $-y$, $1-z$ (viii) $1-x$, $-y$, $1-z$ (ix) $1+x$, y, $1+z$, (x) x, $1+y$, z
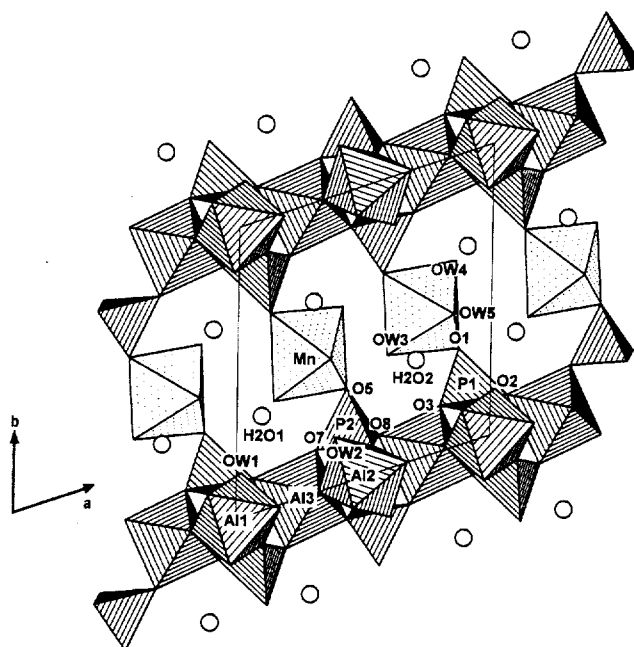
Fig. 1. a-b-projection of the crystal structure of kastningite; octahedra and tetrahedra around Mn, Al and P are shown. Oxygen atoms forming part of water molecules appear as open circles; hydrogen atoms are not drawn for reasons of clearness; drawn with STRUPLO84 [14].

to the the {010} plane. These layers are corner-connected via $[Mn(O_P)_2(H_2O)_4]^{2-}$ octahedra in the direction of [010] to form the three dimensional structure (see Fig. 1).

Two water molecules are incorporated into cavities within the structure and a complex system of hydrogen bonds further binds the structure together. The corresponding O–O distances are generally in good agreement with the ones observed in stewartite (see Table 5).

The chain repeat distance of 2×7.113 Å in kastningite compares nicely with the one observed in Mn-gordonite (7.088 Å). In stewartite where the centers of the octahedra are occupied by Fe^{3+} ions the chain repeat distance is considerably larger (2×7.39 Å; see Table 6).

Table 5. Hydrogen bond system: O–H⋯O distances and O–H–O angles. Corresponding distances for stewartite are given in parenthesis.

	O–O distance [Å]	O–H–O-angle [°]
H_2O1 —1.00— H15 ·1.82· O1	2.80 (2.83)	164.7
OW6 —0.93— H13 ·1.73· O2	2.63 (2.64)	163.4
OW1 —0.79— H2 ·2.040· O3	2.82 (2.85)	171.5
H_2O2 —0.84— H18 ·2.01· O4	2.85 (2.90)	170.8
OH2 —0.77— H4 ·2.24· O4	2.96 (2.93)	157.2
H_2O2 —0.74— H17 ·2.05· O5	2.77 (2.82)	165.1
OW6 —0.98— H14 ·2.00· O5	2.97 (2.91)	167.1
OH1 —0.72— H1 ·2.23· O6	2.89 (2.77)	152.2
H_2O1 —0.81— H16 ·2.01· O7	2.80 (2.86)	160.7
OW4 —0.89— H9 ·2.23· O7	2.93 (2.88)	135.8
OW2 —0.68— H5 ·2.00· O8	2.66 (2.67)	163.3
OW1 —0.74— H3 ·2.02· H_2O1	2.75 (2.84)	165.7
OW3 —1.09— H7 ·1.56· H_2O_2	2.65 (2.69)	174.0
OW4 —0.87— H10 ·2.03· OW5	2.85 (2.94)	157.9
OW5 —1.02— H11 ·1.78· H2O1	2.71 (2.76)	150.3
OW5 —1.01— H12 ·1.79· H2O2	2.72 (2.76)	152.1
OW2 —0.91— H6 ·2.08· OW3	2.91 (2.91)	151.5
OW3 —0.73— H8 ·2.25· OW6	2.79 (2.93)	131.4

The average bond distance within the Mn–O octahedron is 2.147 Å and agrees well with the one in mangangordonite (2.155 Å). In stewartite on the other hand the average bond distance is significantly larger (2.180 Å). Accordingly bond valence calculations lead to the high values of 2.3 v.u. and 2.24 v.u. for the Mn^{2+} ion in kastningite and mangangordonite while in stewartite the value is closer to the ideal value (2.11 v.u.) This is presumably due to the fact that in kastningite and mangangordonite a considerable amount of the smaller Fe^{2+} ion is incorporated into the octahedra while in stewartite the site is fully occupied by Mn^{2+}.

As pointed out by Moore [2, 3] chains of edge-linked octahedra are a dominant feature in a group of aquated orthophosphate hydrate minerals (see Table 6, Fig. 2). Yet there are basic differences with respect to the composition
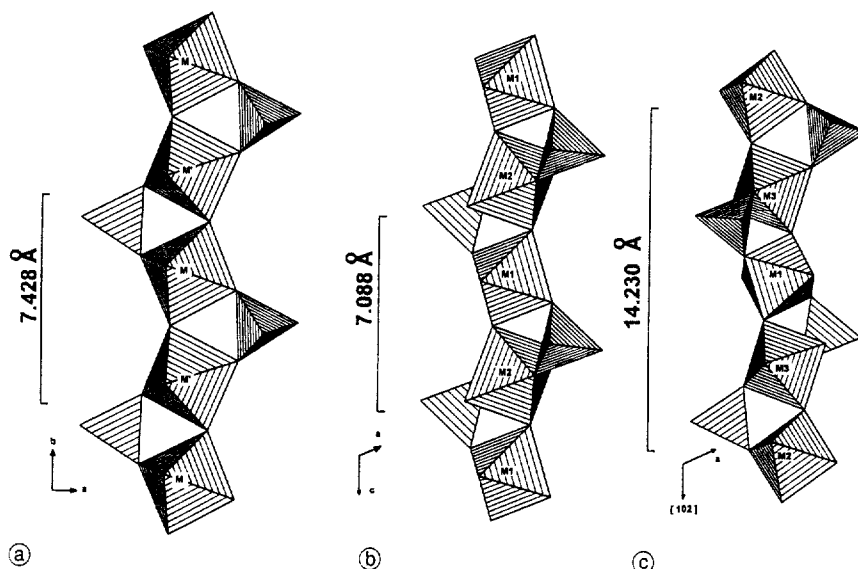

Fig. 2. part of the chain of edge linked octahedra in (a) pseudolaueite (b) mangangordonite and (c) kastningite; only tetrahedra which are bonded to two octahedra of the chain are shown; drawn with STRUPLO84 [14].

Table 6. Lattice parameters and chemical composition of related compounds.

Mineral / composition	a	b	c	V	S.G.	Z	Ref.
Kastningite (Mn, Fe, Mg)$(H_2O)_4[Al_2(OH)_2(H_2O)_2(PO_4)_2] \cdot 2\,H_2O$	$a = 10.205(1)$ Å; $\alpha = 90.38(1)°$	$b = 10.504(1)$ Å; $\beta = 110.10(1)°$	$c = 7.010(1)$ Å [102]: 14.226 Å chain direction; $\gamma = 71.82(1)°$	$V = 666.2$ Å³	$P\bar{1}$	$Z = 2$	this work
Stewartite $Mn(H_2O)_4[Fe_2(OH)_2(H_2O)_2(PO_4)_2] \cdot 2\,H_2O$	$a = 10.398(2)$ Å; $\alpha = 90.10(3)°$	$b = 10.672(3)$ Å; $\beta = 109.10(2)°$	$c = 7.223(3)$ Å [102]: 14.78 Å chain direction; $\gamma = 71.82(2)°$	$V = 715.1$ Å³	$P\bar{1}$	$Z = 2$	[7]
Metavauxite $Fe^{2+}(H_2O)_4[Al_2(OH)_2(H_2O)_2(PO_4)_2] \cdot 2\,H_2O$	$b = 9.586$ Å	$a = 10.248$ Å; $\beta = 97.87°$	$c = 6.962$ Å	$V = 677.5$ Å³	$P2_1/c$	$Z = 2$	[8]
Pseudolaueite $Mn(H_2O)_4[Fe_2(OH)_2(H_2O)_2(PO_4)_2] \cdot 2\,H_2O$	$a = 9.647$; $\alpha = 90°$	$c = 10.194$ Å; $\beta = 104.63°$	$b = 7.428$ Å; $\gamma = 90.0°$	$V = 706.8$ Å³	$P2_1/a$	$Z = 2$	[9]
Laueite $Mn(H_2O)_4[Fe_2(OH)_2(H_2O)_2(PO_4)_2] \cdot 2\,H_2O$	$a = 5.28$ Å; $\alpha = 107.55°$	$b = 10.66$ Å; $\beta = 110.59°$	$c = 7.14$ Å; $\gamma = 71.07°$	$V = 347.8$ Å³	$P\bar{1}$	$Z = 1$	[10]
Gordonite $Mn(H_2O)_4[Al_2(OH)_2(H_2O)_2(PO_4)_2] \cdot 2\,H_2O$	$a = 5.246(2)$ Å; $\alpha = 107.51(3)°$	$b = 10.532(5)$ Å; $\beta = 111.03(3)°$	$c = 6.975(3)$ Å; $\gamma = 72.21(3)°$	$V = 334.5$ Å³	$P\bar{1}$	$Z = 1$	[11]
Mangangordonite $Mn(H_2O)_4[Al_2(OH)_2(H_2O)_2(PO_4)_2] \cdot 2\,H_2O$	$a = 5.251(2)$ Å; $\alpha = 105.45(4)°$	$b = 10.368(5)$ Å; $\beta = 113.05(3)°$	$c = 7.088(3)$ Å; $\gamma = 78.65(4)°$	$V = 340.4$ Å³	$P\bar{1}$	$Z = 1$	[11]
Paravauxite $Fe^{2+}(H_2O)_4[Al_2(OH)_2(H_2O)_2(PO_4)_2] \cdot 2\,H_2O$	$a = 5.233$ Å; $\alpha = 106.9°$	$b = 10.541$ Å; $\beta = 110.8°$	$c = 6.962$ Å; $\gamma = 72.1°$	$V = 334.4$ Å³	$P\bar{1}$	$Z = 1$	[12]
Sigloite $Fe^{3+}(H_2O)_4[Al_2(OH)_2(H_2O)_2(PO_4)_2] \cdot 2\,H_2O$	$a = 5.190(2)$ Å; $\alpha = 105.00(3)°$	$b = 10.419(4)$ Å; $\beta = 111.31(3)°$	$c = 7.033(3)$ Å; $\gamma = 70.87(3)°$	$V = 330.5$ Å³	$P\bar{1}$	$Z = 1$	[13]

of the octahedra, the number of symmetrically independent octahedra and the linkage to the $[PO_4]^{3-}$ tetrahedra.

In pseudolaueite and metavauxite there exists only one type of symmetry independent octahedron within the chain (see Fig. 2a). In pseudolaueite, it has composition $[Fe^{3+}(O_P)_3(OH)_2(H_2O)]^{5-}$ while in metavauxite the center of the octahedra is occupied by Al^{3+}.

In laueite (and isostructural minerals like gordonite, mangangordonite, paravauxite, sigloite), two different symmetry independent octahedra are observed (see Fig. 2b). In laueite these octahedra have compositions $[Fe^{3+}(O_P)_4(OH)_2]^{7-}$ and $[Fe^{3+}(O_P)_2(OH)_2(H_2O)_2]^{3-}$. In the isostructural minerals, the centers of the octahedra are occupied by Al^{3+}.

As pointed out before in kastningite and stewartite, three different types of octahedra are found. In kastningite two of them have composition $[Al(OH)_2(O_P)_2(H_2O)_2]^{3-}$ while the third has composition $[Al(O_P)_4(OH)_2]^{7-}$, where in stewartite the centers of the octahedra are occupied by Fe^{3+}.

The chain composition for all these minerals taking into account only the octahedra thus results in $[M^{3+}(O_P)_3(OH)H_2O]^{4-}{}_n$ (with $M^{3+} = Fe^{3+}$, Al). The linkage of the chains of octahedra in the three structure types to the tetrahedra can be observed in Fig. 2.

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