Senegalite, Al$_2$(OH)$_3$(H$_2$O)(PO$_4$), a novel structure type

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Abstract

Senegalite, Al$_2$(OH)$_3$(H$_2$O)(PO$_4$), $Z = 4$, orthorhombic, space group $P2_1nb$, $a = 7.675(4)$, $b = 9.711(4)$, $c = 7.635(4)$A, is a new structure type based on chains of composition $^1_\infty[^{[5]}$Al$^{[6]}$Al(OH)$_3$(H$_2$O)(Op)$_4]$ or $^1_\infty[^{[5]}$Al$^{[6]}$Al$\phi_8]$ where ϕ is a coordinating oxygen and Op is phosphate oxygen. $R = 0.024$ for 1288 independent reflections.

Two symmetry-equivalent chains run parallel to [101] and [$\bar{1}$01], each based on distorted Al(OH)$_3$(H$_2$O)(Op)$_2$ octahedral and Al(OH)$_3$(Op)$_2$ trigonal bipyramidal edge-sharing dimers which further corner-link to complete the chain. Corner-linking (PO$_4$) tetrahedra knit neighboring chains to form an open sheet parallel to (010). Further tetrahedral corner-links to chains related by the b-axial glide form an open polyhedral framework structure.

Hydrogen bonds including OH $\cdots$ OW, OH $\cdots$ O and OW $\cdots$ O ranging from 2.73 to 3.24A are proposed. Bond-distance averages are $^{[5]}$Al(1)–O = 1.848A, $^{[6]}$Al(2)–O = 1.899A, and $^{[4]}$P–O = 1.534A.

Introduction

Senegalite, a new and relatively uncommon mineral, was first described by Johan (1976). He reported the composition Al$_2$PO$_4$(OH)$_3 \cdot$ H$_2$O, based on chemical analyses of material from the type locality at the Komondiako Iron Mine (magnetite ore) in the Falémé River Basin of east Senegal, Africa. It occurs in the oxidation zone of the deposit, associated with turquoise, augelite, wavellite, and crandallite. Our investigation was undertaken to determine the crystal structure, ascertain the role of water in the species, and discern the relationship of this mineral to other phosphate hydrate structures involving Al^{3+}.

Experimental section

A single crystal was obtained from a type-locality specimen, provided by the Mineralogical Research Company of San Jose, California. All parameters were redetermined utilizing calibrated precession photographs, yielding the results in Table 1. Extinction criteria, in agreement with the earlier study, hemimorphic development of the crystals, and the success of the structure refinement established the acentric group $P2_1nb$. Careful measurement of the crystal and application of the Gaussian integral method (Burnham, 1966) permitted application of absorption correction which, owing to low linear absorption coefficient and favorable crystal shape, was

a small effect. Symmetry-equivalent reflection pairs were then averaged, and after applying Lorentz and polarization corrections, 1288 independent F_o were obtained. Experimental details are summarized in Table 1.

Solution and refinement of the structure

A three-dimensional Patterson map $P(u, v, w)$ allowed derivation of three independent atomic positions assumed to be Al and P atoms, which constituted the basis of the weighted β-general synthesis (Ramachandran and Srinivasan, 1970, p. 96–119). All independent atomic positions excepting hydrogens thus obtained were then applied to full-matrix least-squares refinement, the first two cycles with isotropic temperature factors and the subsequent four cycles with anisotropic thermal parameters. The final refinement converged to $R = 0.024$ and $R_w = 0.038$, where

$$R = \frac{\Sigma ||F_o| - |F_c||}{\Sigma |F_o|} \quad \text{and} \quad R_w = \left[\frac{\Sigma_w(|F_o| - |F_c|)^2}{\Sigma_w|F_c|^2}\right]^{1/2}$$

with $w = \sigma^{-2}$ of F_o. Refinement minimized $w(F_o - F_c)^2$.

Scattering curves for Al^{3+}, P^0 and O$^-$ were obtained from Ibers and Hamilton (1974, p. 149), and anomalous dispersion corrections, $\Delta f''$, for Al and P from Cromer and Liberman (1970). Positions of hy-

Table 1. Experimental details for senegalite

(A) Crystal Cell Data

a, Å	7.675(4)
b, Å	9.711(4)
c, Å	7.635(4)
Space group	$P2_1nb$
Z	4
Formula	$Al_2(OH)_3(H_2O)(PO_4)$

(B) Intensity Measurements

Crystal size, mm	0.37($\parallel a$), 0.104($\parallel b$), 0.28($\parallel c$)
Rotation axis	a[100]
Max $(\sin\theta)/\lambda$	0.80
Scan speed, deg per min	1.0
Base scan width, deg	3.2, widening to 6.8 at higher levels
Background counts	Stationary, 20 s at beinning and end of scan
Reciprocal space coverage	$hk\ell$ and $h\bar{k}\ell$ with h = 0–11
Radiation	MoKα_1 (λ 0.7093 Å), graphite monochromator
Independent F_o	1288

(C) Absorption Correction

μ, cm^{-1}	8.11
Gaussian integral interval	7
Transmission factor range	0.857–0.925

Table 2. Senegalite. Atomic coordinate parameters †

Atom	x	y	z
Al(1)	½	0.19887(7)	0.5229(1)
Al(2)	0.8832(1)	0.34948(8)	0.6620(1)
P	0.5193(1)	0.48252(6)	0.68687(8)
O(1)	0.7179(3)	0.4818(2)	0.7206(3)
O(2)	0.4311(3)	0.5615(2)	0.8375(3)
O(3)	0.4465(3)	0.3349(2)	0.6882(3)
O(4)	0.4845(3)	0.5502(2)	0.5116(3)
OH(1)	0.7255(3)	0.2552(2)	0.5134(3)
OH(2)	0.0423(3)	0.4254(2)	0.8294(2)
OH(3)	0.8310(3)	0.2452(2)	0.8698(2)
OW	0.0521(3)	0.2018(2)	0.6050(3)

†Estimated standard errors in parentheses refer to the last digit.

drogen atoms were sought on difference Fourier maps after final refinement, but residual peaks were interpreted for OH(1) and OH(2), the others remaining ambiguous. Table 2 presents the refined atomic coordinates, Table 3 the polyhedral interatomic distances and angles, Table 4 the anisotropic thermal vibration parameters, Table 5 the parameters for the ellipsoids of vibration, and Table 6[1] the structure factors.

[1] To obtain a copy of Table 6, order Document AM-79-111 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D. C. 20009. Please remit $1.00 in advance for the microfiche.

Table 3. Senegalite. Bond distances and angles †

Al(1)			Al(2)			P	
Al(1)-O(2)[(1)]	1.788(2)		Al(2)-O(4)[(2)]	1.820(2)		P-O(4)	1.514(2)
Al(1)-OH(1)	1.816(2)		Al(2)-O(1)	1.860(2)		P-O(2)	1.539(2)
Al(1)-OH(3)[(3)]	1.828(2)		Al(2)-OH(1)	1.895(2)		P-O(3)	1.539(2)
Al(1)-O(3)	1.872(2)		Al(2)-OH(2)	1.915(2)		P-O(1)	1.546(2)
Al(1)-OH(2)[(3)]	1.935(2)		Al(2)-OH(3)	1.924(2)		average	1.534
average	1.848 Å		Al(2)-OW	1.981(2)			
			average	1.899			
apical-equatorial		O–Al–O′ (°)					O-P-O′ angles (°)
OH(2)[(3)]-OH(3)[(3)]	2.406(3)*	79.4(1)				O(2)-O(3)	2.481(3) 107.4(1)
O(3)-OH(1)	2.639(3)	91.3(1)	OH(2)-OH(3)	2.406(3)*	77.6(1)	O(1)-O(4)	2.489(3) 108.8(1)
OH(1)-OH(2)[(3)]	2.651(3)	89.9(1)	O(4)[(2)]-OW	2.620(3)	87.0(1)	O(1)-O(2)	2.498(3) 108.2(1)
O(2)[(1)]-O(3)	2.665(3)	93.4(1)	O(4)[(2)]-OH(2)	2.652(3)	90.4(1)	O(3)-O(4)	2.505(3) 110.3(1)
O(2)[(1)]-OH(2)[(3)]	2.685(3)	92.2(1)	OH(1)-OW	2.654(3)	86.4(1)	O(2)-O(4)	2.524(3) 111.5(1)
O(3)-OH(3)[(3)]	2.702(3)	93.8(1)	OH(3)-OW	2.673(3)	86.4(1)	O(1)-O(3)	2.526(3) 110.6(1)
average	2.625 Å	90.0	O(1)-OH(2)	2.681(3)	90.5(1)	average	2.504 109.5
			O(1)-OH(3)	2.707(3)	91.3(1)		
equatorial			O(1)-OH(1)	2.710(3)	92.4(1)	Hydrogen bonds	
O(2)[(1)]-OH(3)[(3)]	3.018(3)	113.1(1)	O(1)-O(4)[(2)]	2.725(3)	95.5(1)	OH(2)···>OW[(1)]	2.731(3)
O(2)[(1)]-OH(1)	3.153(3)	122.0(1)	O(4)[(2)]-OH(1)	2.750(3)	95.5(1)	OH(3)[(1)]···>O(1)	2.789(3)
OH(1)-OH(3)[(3)]	3.220(3)	124.1(1)	OH(2)-OW	2.767(3)	90.5(1)	OW[(1)]···>OH(3)[(2)]	2.840(3)
average	3.130	119.7	OH(1)-OH(3)	2.841(3)	96.1(1)	OH(1)[(2)]···>O(3)[(1)]	3.132(3)
			average	2.682	90.0	OW[(1)]···>O(2)	3.242(3)
apical							
O(3)-OH(2)[(3)]		172.5(1)				Angles with OW	
						OH(2)-OW[(1)]-O(2)	105.7(1)
						OH(2)-OW[(1)]-OH(3)[(2)]	105.7(1)
						O(2)-OW[(1)]-OH(3)[(2)]	122.2(1)

†Estimated standard errors refer to the last digit. The equivalent positions (referred to Table 2) as superscripts are
(1) = x, ½+y, ½−z; (2) = ½+x, −y, −z; (3) = ½+x, ½−y, ½+z. *Shared edge between polyhedra.

Table 4. Senegalite. Anisotropic thermal vibration parameters (×10³)†

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al(1)	2.4(1)	1.16(5)	2.8(1)	0.1(1)	-0.3(1)	0.0(1)
Al(2)	2.2(1)	1.35(6)	2.8(1)	0.1(1)	-0.3(1)	-0.1(1)
P	2.24(8)	1.11(5)	2.69(7)	0.1(1)	-0.2(8)	0.0(1)
O(1)	2.1(3)	1.7(1)	6.5(3)	-0.1(2)	-0.8(2)	0.4(2)
O(2)	4.0(3)	1.7(1)	4.6(2)	-0.1(2)	-0.8(2)	1.0(2)
O(3)	3.8(3)	1.5(2)	4.7(3)	-0.6(2)	0.9(2)	-0.3(2)
O(4)	5.7(3)	2.8(2)	4.0(3)	0.8(2)	0.7(2)	-1.1(2)
OH(1)	2.6(3)	2.7(2)	4.3(3)	0.7(2)	-0.2(2)	1.2(2)
OH(2)	2.4(3)	1.8(1)	4.0(2)	-0.3(2)	-0.4(2)	0.4(2)
OH(3)	3.1(3)	1.5(1)	3.8(2)	0.5(2)	-0.6(2)	-0.5(2)
OW	4.3(2)	2.1(2)	6.0(3)	0.4(2)	1.2(2)	0.1(2)

†Coefficients in the expression exp$-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell]$. Estimated standard errors refer to the last digit.

Description of the structure

Senegalite is based on two kinds of aluminum–oxygen coordination polyhedra which alternately share edges and corners to form infinite Al–O polyhedral chains. Two orientations of symmetry-equivalent chains run parallel to [101] and [$\bar{1}$01].

Figure 1 illustrates the chain parallel to [101] and its circumjacent phosphate tetrahedra. The Al–O polyhedra include a distorted Al(OH)$_3$(H$_2$O)(Op)$_2$ octahedron (Op = phosphate oxygen) and a distorted Al(OH)$_3$(Op)$_2$ trigonal bipyramid. The two polyhedra share the OH(2)–OH(3) edge to form dimers which further corner-link at OH(1) to complete the chain. The chain composition is thus $^1_\infty$[$^{[5]}$Al$^{[6]}$Al(OH)$_3$(H$_2$O)(Op)$_4$], or $^1_\infty$[$^{[5]}$Al$^{[6]}$Alϕ_8] where ϕ is a coordinating oxygen.

As seen in Figure 1 the associated tetrahedra corner-link to neighboring chains to form an open sheet parallel to (010). The tetrahedra further link to chains related by the b-axial glide to form an open polyhedral framework structure. Johan (1976) reports an imperfect (010) cleavage. Each tetrahedron is associated with three chains, sharing two of its corners within one chain as seen in Figures 1 and 2.

All hydroxyl groups are the points of linkage within a chain. The water (OW) of senegalite coordinates to one $^{[6]}$Al and is therefore not zeolitic in nature; it probably accounts for the endothermic reaction at 250°C reported by Johan.

Bond distances and angles

Bond distances and angles are presented in Table 3. The average P–O = 1.534A is typical for values found for mineral phosphates. Average P–O = 1.519A was found in the chemically-related augelite (Araki et al., 1968). The Al–O octahedral distances average 1.899A, close to 1.891A average in augelite. The distorted trigonal bipyramidal average is 1.848A (1.832A in augelite).

The Al–O trigonal bipyramid is substantially distorted, but the polyhedron is not regular and lies between the trigonal bipyramid and square pyramid (see Stephenson and Moore, 1968, for a discussion on five-coordinate polyhedra). With fixed Al–O distances the trigonal bipyramid would have one apical O–Al–O' angle of 180°, three equatorial angles of 120°, and six apical–equatorial angles of 90°. The most significant angular distortion, OH(2)–Al–OH(3) = 79.4° arises from the OH(2)–OH(3) shared edge between Al(1) and Al(2), an edge distance OH(2)–

Table 5. Senegalite parameters for the ellipsoids of vibration*

Atom	i	μ_i	θ_{ia}	θ_{ib}	θ_{ic}	B, $8\pi^2A^2$	Atom	i	μ_i	θ_{ia}	θ_{ib}	θ_{ic}	B, $8\pi^2A^2$
Al(1)	1	0.074(2)	74(9)	162(10)	84(6)	0.56(1)	O(4)	1	0.085(5)	110(4)	51(4)	46(4)	1.11(3)
	2	0.082(2)	144(8)	107(10)	121(6)			2	0.128(4)	112(16)	54(12)	136(4)	
	3	0.095(2)	121(6)	93(4)	32(6)			3	0.137(4)	149(13)	121(12)	88(13)	
Al(2)	1	0.078(2)	31(26)	117(37)	76(16)	0.56(1)	OH(1)	1	0.076(5)	40(7)	122(6)	68(6)	0.88(3)
	2	0.080(2)	110(35)	149(34)	112(12)			2	0.101(4)	51(8)	63(6)	130(6)	
	3	0.095(2)	113(5)	103(5)	27(5)			3	0.132(3)	81(4)	44(4)	48(5)	
P	1	0.071(2)	70(7)	159(7)	84(4)	0.52(1)	OH(2)	1	0.082(5)	26(20)	64(22)	86(12)	0.72(3)
	2	0.082(2)	152(8)	111(7)	107(8)			2	0.090(4)	111(24)	35(20)	116(7)	
	3	0.090(1)	109(8)	90(4)	19(8)			3	0.113(3)	105(6)	69(7)	26(7)	
O(1)	1	0.076(5)	10(3)	89(17)	80(4)	0.88(3)	OH(3)	1	0.076(5)	112(11)	25(7)	79(9)	0.72(2)
	2	0.089(4)	90(17)	8(4)	98(4)			2	0.092(4)	140(10)	101(12)	127(8)	
	3	0.140(3)	100(3)	82(3)	13(3)			3	0.115(4)	121(7)	112(5)	40(7)	
O(2)	1	0.076(5)	80(6)	149(5)	61(4)	0.88(3)	OW	1	0.096(4)	121(14)	32(16)	81(8)	1.07(3)
	2	0.104(4)	152(7)	111(7)	108(7)			2	0.108(4)	43(12)	59(16)	117(6)	
	3	0.130(3)	116(7)	68(4)	35(4)			3	0.141(3)	63(5)	83(4)	28(5)	
O(3)	1	0.080(5)	66(8)	24(8)	89(7)	0.86(3)							
	2	0.100(4)	43(8)	109(10)	127(6)								
	3	0.127(4)	57(6)	105(4)	37(6)								

*i = ith principal axis; μ_i = rms amplitude; θ_{ia}, θ_{ib}, θ_{ic} = angles (deg) between the ith principal axis and the cell axes a, b and c.
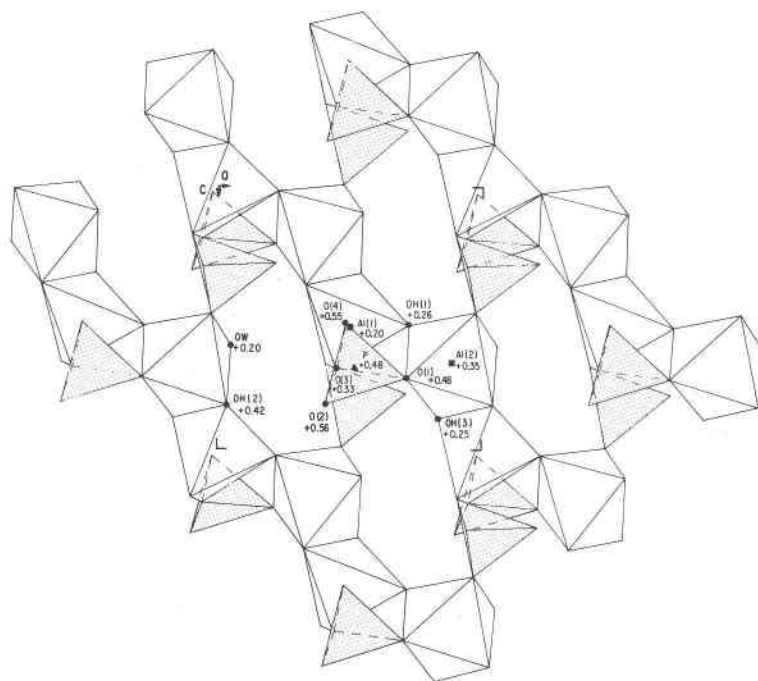
Fig. 1. Polyhedral diagram of the senegalite structure down the *b* axis. Note the Al–O polyhedral chains running parallel to [101]. The PO$_4$ tetrahedra are stippled and link above and below to Al–O chains running parallel to [$\bar{1}$01]. Atom heights are given as fractional coordinates in *y*. The atoms are labelled according to Table 2.
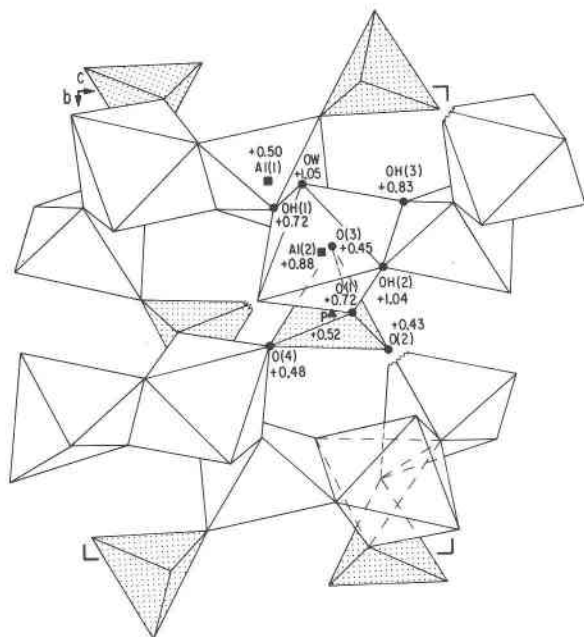

Fig. 2. Polyhedral diagram of the senegalite structure down the *a* axis. Atom heights are given as fractional coordinates in *x* and are labelled according to Table 2. Polyhedral vertices which link at the next level are broken. The PO$_4$ tetrahedra are stippled.

OH(3) = 2.406A corresponding to the shortest edge distance found in the structure.

Hydrogen bonds

Since the hydrogen positions could not be located by difference synthesis, geometrical considerations were used. The hydrogen-bonding criteria of Baur (1970) suggested five candidates for hydrogen-bond participation. These bonds are featured in Figure 3 and are complicated by the fact that it is not possible to select a specific projection owing to within-layer and interlayer bonds. Table 7 outlines the bond length–bond strength relationships following the guidelines of Baur. The most serious deviations from electrostatic neutrality, O(4), $\Delta p_o = -0.250$; and OW, $\Delta p_o = +0.333$, are manifested in net bond shortening and lengthening respectively, compared with polyhedral averages.

The (PO$_4$) oxygens, O(1) and O(3), receive bonds from OH(3) and OH(1) respectively, since OH(1) ⋯ O(3) = 3.13 and OH(3) ⋯ O(1) = 2.79A. O(2) receives one bond from the water molecule, OW, which donates a second bond to OH(3) and receives one bond from OH(2). This arrangement creates a network of hydrogen bonds and contributes

Fig. 3. Local environment of proposed hydrogen bonds in senegalite shown as a portion of Fig. 2. Since bonds link to levels above and below, alternate atom heights are given as well. The $Al_2\phi_9$ edge-sharing dimer is emphasized.

Table 7. Senegalite. Relations in bond strength–bond length*

Anions	Coordinating Cations					Δp_O	Bond Length Deviations		
	Al(1)	Al(2)	P	H_d	H_a		Al(1)	Al(2)	P
O(1)	-	1	1	-	1	-0.083	-	-0.039	+0.012
O(2)	1	-	1	-	1	+0.017	-0.060	-	+0.005
O(3)	1	-	1	-	1	+0.017	+0.024	-	+0.005
O(4)	-	1	1	-	-	-0.250	-	-0.079	-0.020
OH(1)	1	1	-	1	-	-0.067	-0.032	-0.004	-
OH(2)	1	1	-	1	-	-0.067	+0.087	-0.066	-
OH(3)	1	1	-	1	1	+0.100	-0.020	+0.025	-
OW	-	1	-	2	1	+0.333	-	+0.082	-

*Δp_O is the deviation of the bond strength sum from neutrality ($p_O = 2.000$). A bond length deviation is the polyhedral average subtracted from the individual bond distance.

A curious octahedral–tetrahedral corner-sharing tetramer $[^{[6]}Al_2(OH)(H_2O)_2F_4(PO_4)_2]$ has been noted for morinite by Hawthorne (1979). He showed a complex structure genealogy which related many distinct structure types, including augelite, but there does not appear to be any analogy with senegalite.

Acknowledgments

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to increased rigidity between and within two symmetry-equivalent polyhedral chains.

Discussion

Senegalite is a new structure type and demonstrates the significance of structure analysis in classifying crystal structures and expressing a sensible structural formula. The chemically-similar augelite, $Al_2(OH)_3(PO_4)$ was formerly believed to be a dehydrated version of senegalite, $Al_2(OH)_3(H_2O)(PO_4)$, but, aside from the presence of 5- and 6-coordinated Al^{3+} by oxygens, the structural principles of the two are quite different. Araki et al. (1968) demonstrated that augelite is based on an edge-sharing tetramer of composition $[^{[5]}Al_2{}^{[6]}Al_2(OH)_6(Op)_8]$ with an Al:ϕ ratio of 1:3.5, and is locally more condensed than senegalite with the M:ϕ ratio of 1:4. It appears that rearrangement through breaking numerous bonds is necessary to establish any structural similarity between the two minerals, and senegalite is hardly a hydrated version of augelite.