

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

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Abstract

Senegalite, $\text{Al}_2(\text{OH})_3(\text{H}_2\text{O})(\text{PO}_4)$, $Z = 4$, orthorhombic, space group $P2_1nb$, $a = 7.675(4)$, $b = 9.711(4)$, $c = 7.635(4)\text{\AA}$, is a new structure type based on chains of composition $\infty [^{15}\text{Al}^{16}\text{Al}(\text{OH})_3(\text{H}_2\text{O})(\text{Op})_4]$ or $\infty [^{15}\text{Al}^{16}\text{Al}\phi_8]$ 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 $\text{Al}(\text{OH})_3(\text{H}_2\text{O})(\text{Op})_2$ octahedral and $\text{Al}(\text{OH})_3(\text{Op})_2$ 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 $\text{OH} \cdots \text{OW}$, $\text{OH} \cdots \text{O}$ and $\text{OW} \cdots \text{O}$ ranging from 2.73 to 3.24\AA are proposed. Bond-distance averages are $^{15}\text{Al}(1)\text{-O} = 1.848\text{\AA}$, $^{16}\text{Al}(2)\text{-O} = 1.899\text{\AA}$, and $^{14}\text{P-O} = 1.534\text{\AA}$.

Introduction

Senegalite, a new and relatively uncommon mineral, was first described by Johan (1976). He reported the composition $\text{Al}_2\text{PO}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$, based on chemical analyses of material from the type locality at the Komondiako Iron Mine (magnetite ore) in the Falemé 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

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

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 6. Senegalite. Observed and calculated structure factors.

6/23/77		SENEGAL		ITE		SHEET NO.		1		PART		1					
H	K	L	FO	FC	ALPH	H	K	L	FO	FC	ALPH	H	K	L	FO	FC	ALPH
0	0	0	9.06	1.01	7.01	0	1	8	25.05	25.35	180.66	1	1	5	45.01	45.08	125.01
0	0	0	78.07	77.08	0.02	0	2	8	35.04	35.34	180.66	1	1	5	38.08	38.66	124.30
0	0	0	31.09	34.00	0.09	0	3	8	5.03	5.03	-2.05	1	1	5	11.08	11.05	117.03
0	0	0	8.01	8.09	179.02	0	4	8	16.09	16.09	181.04	1	1	5	18.09	18.09	83.09
0	0	0	11.03	11.03	0.00	0	5	8	25.05	25.35	180.66	1	1	5	29.01	28.09	118.01
0	0	0	59.02	58.04	0.09	0	6	8	6.06	6.06	182.02	1	1	5	10.03	10.03	110.03
0	0	0	42.05	41.03	180.03	0	7	8	14.05	14.05	180.03	1	1	5	18.09	18.09	110.03
0	0	0	8.03	8.03	180.03	0	8	8	2.02	2.02	180.03	1	1	5	13.03	13.03	125.03
0	0	0	14.03	14.03	180.03	0	9	8	5.05	5.05	190.00	1	1	5	13.03	13.03	133.06
0	0	0	56.03	55.00	180.04	0	10	8	10.04	10.04	180.04	1	1	5	17.03	17.03	133.06
0	0	0	10.05	10.05	181.00	0	11	8	15.05	15.05	180.04	1	1	5	25.07	25.07	126.07
0	0	0	15.06	15.06	181.00	0	12	8	22.04	22.04	179.07	1	1	5	34.07	34.07	126.07
0	0	0	10.08	10.08	180.07	0	13	8	20.04	20.04	180.07	1	1	5	39.01	39.01	126.07
0	0	0	20.08	20.08	180.07	0	14	8	6.04	6.04	180.07	1	1	5	5.01	5.01	126.07
0	0	0	35.08	36.06	180.06	0	15	8	22.04	22.04	179.07	1	1	5	9.01	9.01	126.07
0	0	0	24.02	24.02	180.05	0	16	8	22.04	22.04	179.07	1	1	5	12.01	12.01	126.07
0	0	0	93.00	91.04	180.02	0	17	8	6.04	6.04	181.00	1	1	5	14.01	14.01	126.07
0	0	0	19.05	18.04	180.02	0	18	8	13.05	13.05	181.00	1	1	5	17.01	17.01	126.07
0	0	0	18.06	18.04	180.02	0	19	8	13.05	13.05	181.00	1	1	5	21.01	21.01	126.07
0	0	0	53.05	54.05	180.01	0	20	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	54.06	54.05	180.01	0	21	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	11.09	11.09	181.00	0	22	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	15.02	15.02	181.00	0	23	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	22.04	22.04	180.07	0	24	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	11.08	11.08	180.07	0	25	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	15.08	15.08	180.07	0	26	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	24.07	24.07	180.07	0	27	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	19.08	19.08	180.07	0	28	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	22.08	22.08	180.07	0	29	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	19.09	19.09	180.07	0	30	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	24.09	24.09	180.07	0	31	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	19.09	19.09	180.07	0	32	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	37.09	36.06	180.04	0	33	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	47.09	46.06	180.04	0	34	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	12.09	12.09	180.04	0	35	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	73.09	72.09	180.04	0	36	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	78.09	77.09	180.04	0	37	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	61.04	61.04	180.03	0	38	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	3.07	3.07	180.06	0	39	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07
0	0	0	14.09	15.06	180.04	0	40	8	13.05	13.05	179.08	1	1	5	21.01	21.01	126.07

0	34	77	16:24	16:01	180:59	11	57	44	36:00	36:06	-84:07	22	11	30:57	17:02	235:07
0	5	77	16:07	17:05	180:06	11	9	44	37:55	37:01	-24:02	22	11	20:27	20:05	177:55
0	6	77	18:33	6:02	0:02	11	10	44	13:03	19:08	72:09	22	11	14:02	14:07	174:54
0	7	77	6:03	8:02	0:09	11	3	44	9:33	7:08	210:08	22	11	20:01	19:07	168:02
0	8	77	25:09	6:03	181:01	11	9	44	22:11	22:01	260:09	22	11	38:08	47:08	158:09
0	9	77	9:06	9:02	180:55	11	12	44	15:05	18:04	252:02	22	11	55:03	36:01	68:04
0	10	77	15:04	15:06	182:55	11	13	44	18:05	15:04	220:04	22	11	19:01	19:04	268:08
0	11	77	12:06	11:06	181:55	11	4	45	35:05	15:08	109:03	22	11	36:02	36:06	259:01

H	K	L	FD	FC	ALPH	H	K	L	FD	FC	ALPH	H	K	L	FD	FC	ALPH
N	7	N	28.5	28.5	148.0	2	1	11	16.4	15.9	-4.7	3	7	7	11.0	11.2	141.9
N	8	N	32.1	32.0	183.5	2	2	11	10.9	10.1	-32.0	3	8	7	11.0	11.0	205.5
N	9	N	22.6	23.0	164.6	2	3	11	14.9	15.1	-23.8	3	9	7	11.0	11.0	256.8
N	0	N	26.5	26.8	138.0	2	4	11	11.0	11.3	147.2	3	0	7	11.0	11.0	114.8
N	1	N	12.7	27.0	237.3	2	5	11	14.0	13.5	-36.4	3	1	7	11.0	11.0	76.4
N	2	N	10.7	27.0	233.9	2	6	11	10.9	11.0	195.5	3	2	7	11.0	11.0	52.5
N	3	N	9.7	27.0	120.1	2	7	11	8.4	8.7	-201.0	3	3	7	11.0	11.0	75.8
N	4	N	24.0	23.9	130.3	2	8	11	36.2	35.9	-62.3	3	4	7	11.0	11.0	78.7
N	5	N	20.3	20.5	187.9	2	9	11	45.6	45.3	110.9	3	5	7	11.0	11.0	18.1
N	6	N	22.0	22.0	143.1	2	0	11	27.2	27.0	43.3	3	6	7	11.0	11.0	16.3
N	7	N	24.0	24.0	160.5	2	1	11	27.9	27.9	77.4	3	7	7	11.0	11.0	11.1
N	8	N	15.0	16.0	202.2	2	2	11	31.0	30.9	-20.2	3	8	7	11.0	11.0	6.4
N	9	N	18.7	18.7	71.2	2	3	11	35.5	35.0	-57.9	3	9	7	11.0	11.0	20.7
N	0	N	16.4	16.5	189.9	2	4	11	28.7	28.3	104.5	3	0	7	11.0	11.0	13.2
N	1	N	33.7	32.9	267.3	2	5	11	19.6	18.5	-250.3	3	1	7	11.0	11.0	16.7
N	2	N	17.3	16.6	222.6	2	6	11	11.0	10.9	85.1	3	2	7	11.0	11.0	25.9
N	3	N	22.4	21.5	145.8	2	7	11	2.2	2.2	-71.7	3	3	7	11.0	11.0	8.7
N	4	N	21.6	22.0	70.0	2	8	11	3.0	3.0	-221.5	3	4	7	11.0	11.0	8.7
N	5	N	14.5	13.7	150.7	2	9	11	15.9	15.8	133.7	3	5	7	11.0	11.0	5.7
N	6	N	21.0	21.0	31.6	2	0	11	38.4	38.0	-133.0	3	6	7	11.0	11.0	8.3
N	7	N	19.8	20.0	139.5	2	1	11	24.7	24.1	265.4	3	7	7	11.0	11.0	6.7
N	8	N	21.0	22.0	95.3	2	2	11	12.0	12.0	-113.8	3	8	7	11.0	11.0	5.4
N	9	N	15.0	15.0	227.6	2	3	11	34.8	34.8	97.3	3	9	7	11.0	11.0	2.3
N	0	N	14.4	14.4	137.0	2	4	11	20.4	20.4	-58.5	3	0	7	11.0	11.0	3.3
N	1	N	21.0	21.0	187.0	2	5	11	11.0	11.0	-78.7	3	1	7	11.0	11.0	1.6
N	2	N	21.1	22.0	35.9	2	6	11	6.9	6.9	-4.3	3	2	7	11.0	11.0	4.8
N	3	N	27.0	29.0	-39.1	2	7	11	10.9	10.7	-62.6	3	3	7	11.0	11.0	6.8
N	4	N	26.2	26.0	107.1	2	8	11	13.7	13.5	-6.8	3	4	7	11.0	11.0	3.0
N	5	N	15.4	15.7	38.3	2	9	11	16.7	16.1	222.3	3	5	7	11.0	11.0	3.5
N	6	N	27.1	27.0	170.6	2	0	11	11.0	11.0	-4.3	3	6	7	11.0	11.0	15.0
N	7	N	26.0	26.0	177.0	2	1	11	13.0	13.0	242.8	3	7	7	11.0	11.0	14.5
N	8	N	19.0	19.0	-17.0	2	2	11	11.0	11.0	59.8	3	8	7	11.0	11.0	15.0
N	9	N	28.5	28.5	148.0	2	3	11	11.0	11.0	-73.5	3	9	7	11.0	11.0	15.0

2	9	14.0	135.4	203.2	33	10	14.0	14.0	117.1	4	120.4	47.2
2	0	15.0	200.9	499.1	33	11	7.0	7.0	149.8	4	10.4	-35.1
2	1	17.0	177.7	450.9	33	12	6.0	6.0	51.8	4	17.8	247.9
2	2	18.0	120.1	-16.3	33	13	48.0	48.0	89.6	4	26.9	185.4
2	3	19.0	8.4	-9.5	33	14	6.0	6.0	97.7	4	25.7	41.2
2	4	20.0	7.4	20.6	33	15	7.0	7.0	140.0	4	24.0	230.5
2	5	21.0	13.0	4.2	33	16	6.0	6.0	157.3	4	21.3	-20.7
2	6	22.0	15.2	91.6	33	17	12.0	12.0	-48.8	4	25.0	132.8
2	7	23.0	3.0		33	18	40.0	40.0	120.8	4	46.4	11.2
2	8	24.0			33	19	1.0	1.0		4		
2	9	25.0			33	20	1.0	1.0		4		
2	0	26.0			33	21	1.0	1.0		4		
2	1	27.0			33	22	1.0	1.0		4		
2	2	28.0			33	23	1.0	1.0		4		
2	3	29.0			33	24	1.0	1.0		4		
2	4	30.0			33	25	1.0	1.0		4		
2	5	31.0			33	26	1.0	1.0		4		
2	6	32.0			33	27	1.0	1.0		4		
2	7	33.0			33	28	1.0	1.0		4		
2	8	34.0			33	29	1.0	1.0		4		
2	9	35.0			33	30	1.0	1.0		4		

555555555	041345	222222222	18901	1702	-40.5	5555555	02234	1111111	451	499	136.9	77777	12012345678	011111111	22140	21922	21922	1702	103.0
555555555	041345	222222222	18901	1702	-40.5	5555555	02234	1111111	451	499	136.9	77777	12012345678	011111111	22140	21922	21922	1702	103.0
555555555	041345	222222222	18901	1702	-40.5	5555555	02234	1111111	451	499	136.9	77777	12012345678	011111111	22140	21922	21922	1702	103.0
555555555	041345	222222222	18901	1702	-40.5	5555555	02234	1111111	451	499	136.9	77777	12012345678	011111111	22140	21922	21922	1702	103.0
555555555	041345	222222222	18901	1702	-40.5	5555555	02234	1111111	451	499	136.9	77777	12012345678	011111111	22140	21922	21922	1702	103.0
555555555	041345	222222222	18901	1702	-40.5	5555555	02234	1111111	451	499	136.9	77777	12012345678	011111111	22140	21922	21922	1702	103.0
555555555	041345	222222222	18901	1702	-40.5	5555555	02234	1111111	451	499	136.9	77777	12012345678	011111111	22140	21922	21922	1702	103.0
555555555	041345	222222222	18901	1702	-40.5	5555555	02234	1111111	451	499	136.9	77777	12012345678	011111111	22140	21922	21922	1702	103.0
555555555	041345	222222222	18901	1702	-40.5	5555555	02234	1111111	451	499	136.9	77777	12012345678	011111111	22140	21922	21922	1702	103.0
555555555	041345	222222222	18901	1702	-40.5	5555555	02234	1111111	451	499	136.9	77777	12012345678	011111111	22140	21922	21922	1702	103.0

C	ALPH	FC	FD	L	K	H	ALPH	FC	FD	L	K	H	ALPH	FC	FD	L	K	H
77	070	01	130	4	7	9	-153	5.8	9.9	2	5	9	-30.2	5.8	9.9	2	5	9
79	70	04	150	4	9	9	266.8	10.1	10.0	2	7	9	266.8	10.1	10.0	2	7	9
80	70	04	150	4	9	9	222.5	21.0	20.9	2	9	9	222.5	21.0	20.9	2	9	9
81	70	04	150	4	9	9	79.8	27.0	28.0	2	1	9	79.8	27.0	28.0	2	1	9
82	70	04	150	4	9	9	203.7	4.7	4.4	2	1	9	203.7	4.7	4.4	2	1	9
83	70	04	150	4	9	9	230.8	1.1	1.0	2	1	9	230.8	1.1	1.0	2	1	9
84	70	04	150	4	9	9	215.5	1.9	1.9	2	1	9	215.5	1.9	1.9	2	1	9
85	70	04	150	4	9	9	189.9	2.7	2.4	2	1	9	189.9	2.7	2.4	2	1	9
86	70	04	150	4	9	9	150.5	1.6	1.6	2	1	9	150.5	1.6	1.6	2	1	9
87	70	04	150	4	9	9	267.9	2.5	2.5	2	1	9	267.9	2.5	2.5	2	1	9
88	70	04	150	4	9	9	150.5	2.7	2.7	2	1	9	150.5	2.7	2.7	2	1	9
89	70	04	150	4	9	9	150.5	2.7	2.7	2	1	9	150.5	2.7	2.7	2	1	9
90	70	04	150	4	9	9	150.5	2.7	2.7	2	1	9	150.5	2.7	2.7	2	1	9
91	70	04	150	4	9	9	150.5	2.7	2.7	2	1	9	150.5	2.7	2.7	2	1	9
92	70	04	150	4	9	9	150.5	2.7	2.7	2	1	9	150.5	2.7	2.7	2	1	9
93	70	04	150	4	9	9	150.5	2.7	2.7	2	1	9	150.5	2.7	2.7	2	1	9
94	70	04	150	4	9	9	150.5	2.7	2.7	2	1	9	150.5	2.7	2.7	2	1	9
95	70	04	150	4	9	9	150.5	2.7	2.7	2	1	9	150.5	2.7	2.7	2	1	9
96	70	04	150	4	9	9	150.5	2.7	2.7	2	1	9	150.5	2.7	2.7	2	1	9
97	70	04	150	4	9	9	150.5	2.7	2.7	2	1	9	150.5	2.7	2.7	2	1	9
98	70	04	150	4	9	9	150.5	2.7	2.7	2	1	9	150.5	2.7	2.7	2	1	9
99	70	04	150	4	9	9	150.5	2.7	2.7	2	1	9	150.5	2.7	2.7	2	1	9
100	70	04	150	4	9	9	150.5	2.7	2.7	2	1	9	150.5	2.7	2.7	2	1	9

8888888888888888	789	111111111111	18.1	17.9	54.1	9999999999	789	3333333333	8.2	8.1	-17.1	1111111111	451234012	334444555	8.2	8.2	2.8
	10		18.2	14.7	205.2		9	37	7.4	7.4	-74.7			34	5.7	5.7	26.3
	11		18.8	8.1	158.8		9	4	8.0	8.2	-26.4			44	9.4	9.4	6.7
	12		25.2	11.5	157.6		9	4	8.3	7.7	-13.8			44	3.3	3.3	7.1
	13		15.4	18.7	219.1		9	4	21.5	8.9	-170.8			44	5.5	5.5	4.0
	14		3.1	16.6	202.6		9	4	18.7	9.4	-55.9			44	7.0	7.0	1.8
	15		9.9	17.6	101.9		9	4	19.3	4.4	-204.2			44	10.1	10.1	8.8
	16			13.4	-172.0		9	4	10.1	2.2	-61.2			44	14.0	14.0	1.8
	17			10.1			9	4		10.2	247.7			55	16.3	16.3	2.7
	18						9	4						55	19.9	19.9	-79.1
	19						9	4						55	5.6	5.6	164.4
	20						9	4						55	14.2	14.2	1.8
	21						9	4						55	6.7	6.7	225.1
	22						9	4						55	10.3	10.3	-52.7