DOYLEITE, A NEW POLYMORPH OF AI(OH)₃, AND ITS RELATIONSHIP TO BAYERITE, GIBBSITE AND NORDSTRANDITE*

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ABSTRACT

Doyleite, a new polymorph of Al(OH)₃, occurs with calcite and pyrite in albitite veins in nepheline syenite at Mont St. Hilaire, Quebec and in silicocarbonatite sills with weloganite, cryolite, calcite, quartz and other minerals at the Francon quarry, Montreal, Quebec. A wet-chemical analysis gave: Al₂O₃ 65.2, CaO 0.48, H₂O (TGA to 1100°C) 35.76, sum 101.44 wt.%, corresponding to $Al_{0.99}Ca_{0.01}(OH)_{3.00}$. The mineral is not attacked by 1:1 HCl, H₂SO₄ or HNO₃ at room temperature. A singlecrystal X-ray study showed the mineral from Mont St. Hilaire to be triclinic, space group $P\overline{1}$ from morphology, a = 5.002(1), b = 5.175(1), c = 4.980(2) Å, $\alpha = 97.50(1)$, $\beta = 118.60(1)$, γ 104.74(1)°, Z = 2. The strongest five X-ray powderdiffraction lines [d in A(I)(hkl)] are: 4.794(100)(010), 2.360(40)(101), $1.972(30)(\overline{2}21)$, 1.857(30)(111) and $1.842(30)(\overline{1}22)$. Crystals are tabular on (010), showing forms $\{010\}, \{101\}, \{10\overline{1}\}\$ and, occasionally, $\{100\}$ and $\{001\}$. They are white, creamy white or bluish white, transparent or translucent to opaque with a white streak. Their lustre is vitreous, pearly or dull. Mohs hardness 2½ - 3, D(meas.) 2.48(1), D(calc.) 2.482 g/cm³. Cleavage is perfect on {010}, fair on {100}. Optically, the mineral is biaxial positive, α 1.545(1), β 1.553(1), γ 1.566(1), $2V = 77^{\circ}$ in Na light. Orientation of indicatrix in spherical co-ordinates (ϕ, ρ) : $X(90^{\circ}, 41^{\circ})$, $Y(240^{\circ}, 53^{\circ})$, $Z(343^{\circ}, 74^{\circ})$, with c(0,0) and b^{*} (0,90°). TGA showed a weight loss of 25.63% between 280 and 410°C, and a further gradual loss to 1000°C, giving a total weight loss of 35.76%. The infrared absorption spectrum of doyleite is similar to but simpler than those of gibbsite and nordstrandite. Its structure is predicted from the known structures of nordstrandite and gibbsite on the basis of similarities in X-ray precession photographs in two zones. Polymorphism in Al(OH)₃ results from different ways of stacking the layers of Al(OH)6 octahedra. The mineral is named after E.T. Doyle of Ottawa, Ontario.

Keywords: doyleite, aluminum hydroxide, new mineral, Mont St. Hilaire, Francon quarry, Quebec, structural relationship, bayerite, gibbsite, nordstrandite.

SOMMAIRE

La doyleïte, nouveau polymorphe de Al(OH)3, se trouve

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associée à calcite et pyrite dans des filonnets d'albitite dans la syénite néphélinique du mont St-Hilaire (Québec) et à weloganite, cryolite, calcite et quartz dans des sills de silicocarbonatite à la carrière Francon à Montréal (Québec). Une analyse par voie humide donne: Al₂O₃ 65.2% (en poids), CaO 0.48, H₂O (par TGA jusqu'à 1100°C) 35.76, total 101.44, soit $Al_{0.99}Ca_{0.01}(OH)_{3.00}$. La doyleïte est inerte dans les acides HCl 1:1, H2SO4 et HNO3 à température ambiante. Une étude radiocristallographique sur monocristal du mont St-Hilaire révèle la symétrie triclinique; son groupe spatial PI est déterminé par sa morphologie, a 5.002(1), b 5.175(1), c 4.980(2) Å, α 97.50(1)°, β 118.60(1)°, γ 104.74(1)°, pour Z = 2. Les cinq raies les plus intenses du cliché de diffraction (méthode des poudres) [d en $\tilde{A}(I)(hkl)$ sont: 4.794(100)(010), 2.360(40)(101), $1.972(30)(\overline{2}21)$, 1.857(30)(111) et $1.842(30)(\overline{1}22)$. Les cristaux, aplatis sur (010), présentent les formes {010}, $\{101\}$, $\{10\overline{1}\}$ et, dans certains cas, $\{100\}$ et $\{001\}$. Ils sont blancs, d'un blanc crémeux ou bleuâtre, allant de transparents ou translucides à opaques, à rayure blanche, d'éclat vitreux, nacré ou terne. Dureté 21/2 à 3, densité, 2.48 (mesurée), 2.482 (calculée). Le clivage est parfait sur {010}, distinct sur {100}. Biaxe positif, α 1.545(1), β 1.553(1), γ 1.566(1), $2V = 77^{\circ}$ (Na). Orientation de l'indicatrice en coordonnées sphériques (ϕ , ϱ): $X(90^{\circ}, 41^{\circ})$, $\bar{Y}(240^{\circ},53^{\circ})$, $Z(343^{\circ},74^{\circ})$, avec c(0,0) et $b^{*}(0,90^{\circ})$. L'analyse thermogravimétrique révèle une perte de poids de 25.63% entre 280 et 410°C, et une autre perte, graduelle, jusqu'à 1000°C (total 35.76%). Le spectre d'absorption infrarouge ressemble à ceux de la gibbsite et de la nordstrandite, quoique plus simple. On prédit la structure de la doyleïte à partir de celles de la gibbsite et de la nordstrandite, en se fondant sur des ressemblances notées dans deux zones sur les clichés de précession. Le polymorphisme résulte de différences d'empilement des feuillets d'octaèdres Al(OH)₆. Le nom rapelle E.T. Doyle, d'Ottawa.

(Traduit par la Rédaction)

Mots-clés: doyleïte, hydroxyde d'aluminium, mont St-Hilaire, carrière Francon, Québec, relations structurales, bayerite, gibbsite, nordstrandite.

INTRODUCTION

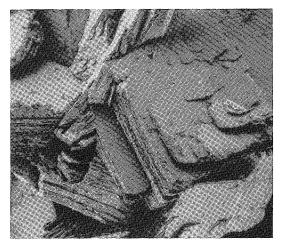
The formerly unidentified mineral UK45 from Mont St. Hilaire, Quebec (Chao & Baker 1979) has been established as a new polymorph of aluminum hydroxide on the basis of X-ray diffraction, chemical and electron-microprobe analyses and optical

studies. The unknown no. 11 from the Francon quarry in Montreal, Quebec, reported by Sabina (1979), has also been shown to be the same mineral as UK45 according to results of X-ray powderdiffraction and electron-microprobe analyses. The mineral is named doyleite after Mr. E.J. Doyle of Ottawa, Ontario who found the Mont St. Hilaire material. The mineral and its name have been approved by the Commission on New Minerals and Mineral Names, I.M.A. Type specimens from Mont St. Hilaire are deposited in the collections at the National Museum of Natural Sciences, Ottawa, Ontario (NMNS 48932) and at the Royal Ontario Museum, Toronto, Ontario (M41025). Specimens from the Francon quarry are preserved at the Geological Survey of Canada, Ottawa, Ontario.

OCCURRENCE

The mineral occurs at Mont St. Hilaire as rosettes of platy crystals (Fig. 1) lining a vug in a vein in nepheline syenite. The matrix rock, albitite, is almost wholly composed of albite with less than 5% siderite and minor amounts of pyrite, molybdenite, zircon and fluorite. Within the vug, the only associated minerals are calcite and a small amount of pyrite. The doyleite crystals are in places coated with a thin film of dark brown amorphous material, probably iron oxide. Some doyleite rosettes have a core of albite. Underlying the doyleite rosettes there is a narrow (1–5 mm) but distinct reaction-zone, suggesting that doyleite was deposited from a later generation of fluids after the emplacement of the vein.

At the Francon quarry doyleite occurs sparingly in vugs in silicocarbonatite sills intruding Ordovician limestones. The mineral is finely granular, forming



 $F_{\rm IG.}$ 1. Doyleite crystals (0.8 \times 0.8 mm) from Mont St. Hilaire, Quebec.

pulverulent to compact globules, botryoidal and smooth porcelain-like crusts and sheets commonly on weloganite, calcite, quartz and less commonly on cryolite and strontianite crystals. In some cases, the original calcite or cryolite crystals have been partly or completely leached out, leaving shells of doyleite. The mineral is generally admixed with unknown No. 3 (Sabina 1979), believed to be an aluminum hydroxide with an X-ray powder pattern similar to that of gibbsite. Other associated minerals are albite, dresserite, dawsonite, fluorite and analcime.

CRYSTALLOGRAPHY

Eight crystals and crystal fragments from Mont St. Hilaire were studied by single-crystal X-ray diffraction using a precession camera with various zone-axes of the crystals as the precession axis. The photographs show doyleite to be triclinic, space group P1 or $P\overline{1}$. The centrosymmetric space-group is suggested by the morphology of crystals. The reduced cell was established in a computer search of the shortest translation vectors in direct space. The cell parameters obtained were then refined by a leastsquares method using Gandolfi X-ray-diffraction data. The refined cell-parameters and X-ray powder data of doyleite from Mont St. Hilaire and Francon are compared with those of other polymorphs of Al(OH), in Tables 1 and 2. The reduced cells of doyleite and nordstrandite are used in Table 1 to accentuate the differences in cell geometry of the polymorphs.

Because of the presence of a perfect {010} cleavage the conventional Debye-Scherrer X-ray powder-diffraction pattern shows a strong preferred-orientation effect that causes variations in relative intensities of the 0k0 lines. The 020 reflection, which has a low to medium intensity on the single-crystal

TABLE 1. CELL PARAMETERS AND OPTICAL PROPERTIES OF ALUMINUM HYDROXIDE MINERALS

	(1)	(2)	(3)	(4)	(5)	(6)
	Doylelte	Doyleite	Nordstrandite	Gibbsite	"Triclinic	Bayerite
	,			1	an .	
a (R)	5,002(1)	5,028(8)	6,148(2)	8,684(1)	17,338	5,062(1)
b	5,175(1)	5,177(7)	6,936(2)	5,078(1)	10,086	8,671(2)
с	4.980(2)	5,026(7)	5,074(1)	9,736(1)	9,730	4,713(1)
α (°)	97,50(1)	97.50(7)	95,76(2)		94.17	
В	118,60(1)	119,36(12)	99,06(2)	94,54 (1)	92,13	90,27 (3)
Υ	104,74(1)	104,00(9)	83,30(2)		90,00	
v (8 ³)	104,52(5)	105,7(1)	211,47(7)	428.0	1694.0	205,86
z	2	2	4	8	32	4
space group D(g/cm ³)	P1		ΡΊ	P2 ₁ /n		P2 ₁ /a
meas.	2,48(1)		2,42	2,40		2,53
calc.	2,482	2,436		2.44		2.54
R.I.						
α	(,545(1)(Na)		1.580(1)(Na)	1,568		
β	1,553(1)		1,583(1)	1.568		
Ÿ	(,566(1)		1,602(1)	1.587		
2Ý	(+)77°		(+)24°	(+) 0°	24°~40°	

⁽¹⁾ Mont St. Hilaire, Quebec, this study. (2) Francon quarry, Montreal, Quebec, this study. (3) Mont St. Hilaire, Quebec, Chos & Baker (1982). (4) Sanifeld & Wedde (1974). Optical properties from Palache et al. (1947). (5) Sanifeld (1950). (6) Rothbauer et al. (1947).

TABLE 2. X-RAY POMDER-DIFFRACTION DATA FOR DOYLETTE, NORDSTRANDITE, GIBBSITE AND BAYERITE

1 Douboles		2 3		_	4				5					
Doylelte Mont St. Hilaire		Doylette Francon			Nordstrandite Mont St. Hilaire		G1bbs1te			Bayer I te				
	MORT S	T. HI IBIT	0	Franc	con	Mon	f St. Hila	Ire	P	DF 7-324		PDF	20-11	
hki	d _{calc} R	d _{odo} ₽	1	d _{obs} Ř		hkl	d _{obs} Ř	ı	hk ($h_{\rm ado}b$	1	hkl	d _{obs} &	1
01 <u>0</u> 101	4.779	4.794	100	4.802	10	110	4.779	100	002	4.85	320	001	4.71	90
001	4.279	4.296 4.182	20 20	4.322 4.186	5 2	t10 011	4-317	30	110	4.37	50	110	4.35	70
100	4.090	4.087	20	4.105	2	101	4-223 4-168	20 5	200 112	4.32 3.306	25 16	020		
110	3.883	3.889	15	3.867	2	011	3+890	10	112	3-187	12	120	4.14 3.29	2
01 T	3.743	3.746	15	3.742	2	101	3.603	10	103	3.112	8	111	3-20	30
111	3-316	3.322	15	3.326	2	020	3.428	5	021	2.454	25	021+	3+20	30
111	3.074	3.075	10	3.087	1	200	3.019	5	004	2.420	20	121 -	2.699	4
011 111	2.764	2.772	5	2.774	ŧ	121	2.852	5	311	2.388	25	200	2.531	2
211	2.422	2.422	20	2.510	4	121	2.708	3	312	2 - 285	6	130	2.510	2
020	2.389	2.462	20	2.398	ï	211	2.484	10	213	2.244	10	031 210	2.454	2
1 01	2.359	2.360	40	2.362	6	220	2.392	40	312	2.168	8	902	2.430	4
112	2-321	2.325	20	2.327	5	112	2.392	40	114	2.085	2	012	2.274	2
221	1.972	1.972	30	1.969	5	211	2.323	t	313	2.043	18	201	2.222	100
111	1 -855	1.857	30	1.863	4	211	2.263	40	023	1.993	12	131+		100
122	1.842	1.842	30	1.848	3	130	2.219	1	123	1.960	2	220	2.186	2
012 210	1.733			1.737	1	031	2.147	5	411	1.921	12	040	2+168	2
211	1.664			1.680	*	122	2.112	1	314	1.799	14	211	2.164	2
112	1.664	1 -663	5	1.661	ł	112	2.073	3	024 314	1.750	16 14	211 112	2-156	2
122	1.614	1.615	10	1.623	2b	031	2.017	30	224	1.654	4	022+	2.073	2
512	1.614	14015		1.023	20	310	1.983	1	421	1.638	2	140	1.993	2
213	1.563	1.561	5	1.572	ŧ	022	1.944	3	224	1.593	4	221	1.983	4
230	1.562			1.552	1	222	1.899	30	511		•	041	1.969	2
201	1.540	1.540	5	1.543	ł	132	1.779	15	422	1.584	2	122	1.917	2
231	1.523	1.518	10	1.524	1ъ	301			512			230	1.904	2
23	1.475			1+488	1	04 <u>0</u> 31 <u>2</u>	1.716	1	230 503	1.573	4	141	1.835	2
510	1.459	1.458	10	1.456	4	311	1+698	2	404	1.555	2	032 231	1.826	2
513	1.457	1.496	10	1.470	4	141	1.670	7	231	1.551	2	202		
520	1 - 429	1.428	15	1 - 436	t	222	1.594	7		1.486	2	132+	1.723	40
503	1.426			11100	•	222	14234	,		1.477	2	212	1.695	2
113	1.396	1.397	10	1.398	2b	132	1.571	2		1 - 457	10	212	1.688	2
223	1.396	4 430				123				1.441	6	310	1.656	2
32	1.265	1.278	10	1.270	lb åb	1 4 <u>1</u> 41 1	1.550	5		1.409	6	246	1.646	2
102	1.208			1.240	10	141	1.513	10		1.398	6	150 051	1.641	2
iti	1.205	1.207	5			213	1.478	10		1.361	4	222		
231	1.196	1-196	5	1.202	2ь	332	1+464	1		1.340	2	042+	1.600	10
				1.182	÷	312				1.330	2	320	1.572	2
				1.162	ŧ	330	1 - 438	15		1.320	4	003		-
						123				1.246	2	311	1.554	8
						123				1.214	4	241+		_
						033	1 - 403	2				142	1.523	2
						303	1,386	1				142	1,520	2
						15 <u>0</u> 523	1,370	t				321 252	1,492	2
						213		_				252	1,484	2
						223	1.353	3				023+	1.478	2
						422						330	1,457	12
						251	1,305	5				060	1,445	8
						332						250	1,431	2
						043	1,248	5				123 123	1.420	2
						014 014						052	1,416	2
						323	1,227	3				331	1,392	6
						422	1.44.1	,				160+	14392	۰
						114	1,217	1				06 t	1,381	2
						341						033		
						44 <u>0</u> 521	1,195	5				251 251	1,370	2
						350		2				312	1,358	2
						152	1.183	2					23 Ines	
												1,1256		

^{1.} CuK are disting, λ = 1.5418K, 114.6 mm Gandoiff commore, NBS SI as internal standard, visual intensifies.

photographs, is either absent or too weak to be measured on the Gandolfi photographs but is always present on the Debye-Scherrer photographs; its relative intensity varies from 5 to 20.

The crystals of doyleite from Mont St. Hilaire (Fig. 1) are tabular on (010) and bounded by {101} and $\{10\overline{1}\}$ pinacoids, giving rise to a nearly square outline. On some crystals the {100} and {001} pinacoids are also present, modifying the shape of the plates to different degrees depending on the prominence of these forms. A centre of symmetry is apparent.

The material from the Francon quarry is very fine grained. The scanning-electron microscope shows the

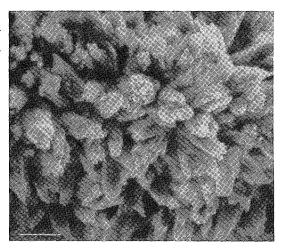


Fig. 2. Doyleite from the Francon quarry, Montreal Island, Quebec. Scale bar 10 μ m.

crystals to be platy with pointed terminations (Fig. 2), resembling the common habit of nordstrandite (Chao & Baker 1982).

PHYSICAL AND OPTICAL PROPERTIES

Doyleite from Mont St. Hilaire is colorless and transparent to translucent, with a vitreous to pearly lustre and a white streak. The mineral from the Francon quarry is white, creamy white or bluish white, translucent to opaque with a dull lustre. The Mohs hardness is about 2½ to 3. The density of doyleite from Mont St. Hilaire, determined by flotation in a heavy liquid, is 2.48(1) g/cm³, in good agreement with the calculated density of 2.482 g/cm³. The crystal plates are slightly flexible but not elastic. The mineral is not fluorescent in long- or short-wave ultraviolet light. It is not soluble in 1:1 HCl, H₂SO₄ or HNO₃ at room temperature. In addition to a perfect {010} cleavage, a much less distinct {100} cleavage has been observed on some crystals.

Optically, doyleite is biaxial with α 1.545(1), β 1.553(1), γ 1.566(1), $2V = 77^{\circ}$ (meas.), 76.8° (calc.) in Na light. The orientation of the indicatrix, with respect to [001] and (010), is shown in Figure 3 and is defined by the spherical co-ordinates (ϕ, ρ) $X(90^{\circ},41^{\circ}), \ \overline{Y}(240^{\circ},53^{\circ}), \ Z(343^{\circ},74^{\circ}) \ \text{with } \mathbf{c}(0,0)$ and b*(0,90°). In white light the mineral shows moderately strong dispersion, r > v.

CHEMICAL COMPOSITION

A hand-picked sample of doyleite from Mont St. Hilaire was leached with weak HCl to remove the iron-oxide coating on some grains and analyzed by conventional wet-chemical methods for major ele-

 $CNK_{\rm C}$ redistion, λ = 1.5418R, 114.6 mm Debye-Scherrer came intensity less than 1 (3.615, 2.565 and 2.470R) are press oyleite cell. neo & Baker (1982).

Indices based on the P2₁/n cell, a = 8.659, b = 5.077, c = 9.7038, β = 94*12*. Synthetic, d values calculated from cell dimensions (Table 1), averaged for lines with multiple

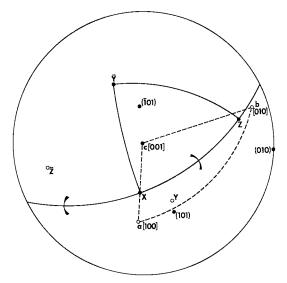


Fig. 3. Optical orientation of doyleite.

ments. The water content was determined by thermal gravimetric analysis to 1100°C. The results (Table 3, no. 4) correspond to $Al_{0.99}Ca_{0.01}(OH)_{3.00}$. The Mont St. Hilaire material was also analyzed by electron microprobe using a series of ten-second counts, a defocused beam, and natural gibbsite (Al), anorthite (Ca), albite (Na, Si) and olivine (Fe, Mg) as standards. K and Ti were looked for but were not detected. The Francon material was analyzed by electron microprobe using a broad beam and a movingsample technique with synthetic corundum (Al) and kaersutite (Si, Ca, Mg, Fe, and Na) as standards. Results of four analyses, corrected against that of a natural gibbsite internal standard, were averaged. No other elements with Z > 11 were found. The water content of the Francon mineral was not determined owing to the small amount of pure material available. The electron-microprobe data are compared with the results of the wet-chemical analysis in Table 3.

The Gladstone-Dale calculations (Mandarino 1979), using the results of the wet-chemical analysis normalized to 100%, gave $K_{\rm P}/K_{\rm C}=0.223/0.253=0.881$. The large discrepancy between $K_{\rm P}$ and $K_{\rm C}$ could not be accounted for by experimental errors in the chemical analysis or measurements of indices of refraction and density. It is possible that structural configurations such as packing and hydrogen bonding may play an important role in this case.

THERMAL ANALYSES AND INFRARED ABSORPTION SPECTRUM

The TGA and DTG analyses of doyleite from

IADLE 3.	COMPUSTITUR	UF	DOILETTE
2	3	4	5

	1	2	3	4	5	ь
Al203 Si02	64.8	63.7 0.03	63.1 0.12	65.2	59.6 3.22	65.36
Ca0 Mg0	0.01			0.48	0.23 0.96	
FeO Na ₂ O	0.16 0.08	0.14	0.21 0.06		0.08 0.35	
H ₂ 0	35.76	35.76	35.76	35.76	35.56	34.64
Total	100.81	99.72	99.25	101.44	100.00	100.00

- 1, 2, 3. Mont St. Hilaire, Quebec. Electron microprobe analyses by P. Jones. H₂O by TGA.
- Mont St. Hilaire, Quebec. Wet-chemical analysis by Bondar-Clegg & Co. Ltd. H₂O by TGA.
 Francon quarry, Montreal, Quebec. Average of four
- Francon quarry, Montreal, Quebec. Average of four electron-microprobe analyses by M. Bonardi, GSC. Corrected against gibbsite internal standard. H₂0 by difference.
- Calculated for theoretical Al(OH)3.

Mont St. Hilaire show that the dehydration begins at about 200°C; the maximum rate of dehydration occurs between 280° and 410°C, with a weight loss of 25.63% at 425°C. Thereafter, the dehydration continues at a much slower rate, leveling off at 1000°C. The total weight-loss at 1100°C is 35.76%. On cooling from 425°C to room temperature the partly dehydrated mineral regains some of the lost water, giving a net weight-loss of 18\%, approximately one half of the water in the mineral. X-ray diffraction shows the partly dehydrated material to be essentially amorphous, with faint diffuse lines of γ-Al₂O₃, indicating a complete destruction of the doyleite structure and commencement of the formation of γ -Al₂O₃. The final product of dehydration quenched from 1100°C is γ -Al₂O₃ in three cases but it is corundum with a trace of an unidentified phase in another. The sample used in the latter analysis may have been slightly impure.

The infrared absorption spectrum of doyleite from Mont St. Hilaire is compared with that of nordstrandite and gibbsite in Figure 4. The spectrum of doyleite is characterized by its simplicity in the OH-stretching (3300–3700 cm⁻¹), OH-bending (700–1100 cm⁻¹) and AlO-stretching (200–600 cm⁻¹) regions. The difference is attributable to the fact that there is only one crystallographically independent Al(OH)₆ octahedron in the doyleite structure, whereas there are two in the nordstrandite and gibbsite structures.

STRUCTURAL RELATIONSHIP TO OTHER Al(OH)₃ MINERALS

Doyleite possesses a perfect cleavage, which is common to the other Al(OH)₃ minerals, for instance, {001} in gibbsite and {110} in nordstrandite (Chao & Baker 1982). Although cleavage in natural bayerite from Hartrurim, Israel (Gross & Heller 1964) was not reported, Debye-Scherrer pho-

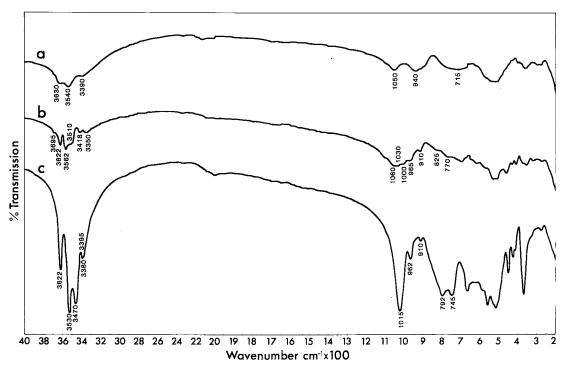


Fig. 4. Infrared absorption spectra of doyleite (a), nordstrandite (b) and gibbsite (c).

tographs of synthetic bayerite show a strong preferred-orientation effect for 001 reflections, suggesting that a perfect {001} cleavage is also present. Furthermore, the 0-level b-precession photograph of doyleite is nearly identical to the 0-level [110]precession photograph of nordstrandite, and both are very similar to the c-precession photograph of gibbsite. Therefore, there is little doubt that doyleite also has a layered structure with the layers of Al(OH)₆ octahedra essentially similar to those in gibbsite (Saalfeld & Wedde 1974), nordstrandite (Saalfeld & Jarchow 1968) and bayerite (Yamaguchi & Sakamoto 1958, Rothbauer et al. 1967). Hence, the structural relationship of doyleite to other Al(OH)₃ minerals can be deduced from the geometry of its unit cell in relation to the cells of other polymorphs. This is shown in terms of the structural cell of gibbsite in Figure 5, where the pseudotrigonal cell of bayerite (Montoro 1942, Yamaguchi & Sakamoto 1958) is shown by dashed lines and the true monoclinic cell (Rothbauer et al. 1967) is approximated by the gibbsite cell with a and b interchanged. The doyleite cell is shown by dotted lines. The nordstrandite cell is approximated by that of gibbsite with a and b of gibbsite corresponding to [110] and -c, respectively. Based on the near-identity of the bprecession photograph of doyleite and the [110]precession photograph of nordstrandite, the x and z atomic co-ordinates of doyleite can be predicted from the atomic co-ordinates of nordstrandite (Rothbauer *et al.* 1967) to two decimal places with confidence.

Similarly, the 0-level [101]-precession photograph of doyleite is nearly identical to the 0-level c-precession photograph of nordstrandite and the 0-level b-precession photograph of gibbsite. Thus the projection of the doyleite structure along [101] must be almost identical to that of nordstrandite along c and that of gibbsite along b. Therefore, the y atomic co-ordinates of doyleite can be determined. The structure of doyleite so derived is shown in Figure 6, where it is compared with that of bayerite, gibbsite and nordstrandite. To facilitate comparison, all structures are shown with respect to a gibbsite-like cell, with the projections made along the axes corresponding to a of gibbsite.

The polymorphism in $Al(OH)_3$ is a result of different ways of stacking octahedral layers, as shown in Figure 6. In bayerite, each layer is stacked directly above the layer below. In gibbsite, the stacking is similar to that in bayerite, but every second layer is turned upside down, creating n-glide planes and 2_1 axes between the layers. In nordstrandite, the successive layers are displaced by 1.70 Å along -b of gibbsite, whereas in doyleite the successive layers are shifted by 1.95 Å along b of gibbsite. The

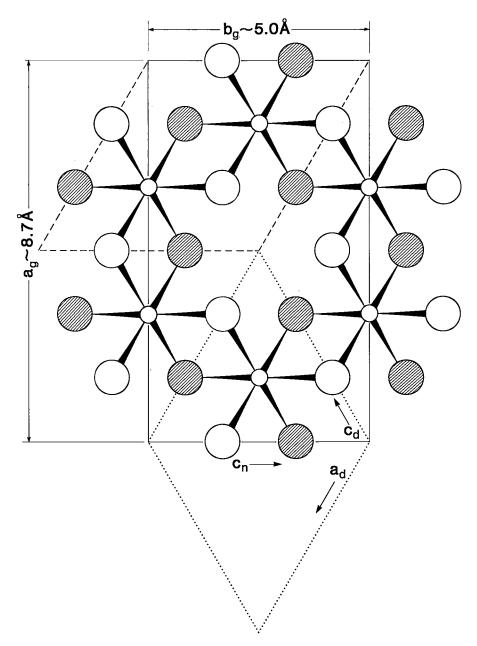


Fig. 5. Idealized structure of gibbsite projected on (001), showing geometric relations of the cells of gibbsite (solid lines), bayerite (dashed lines), doyleite (dotted lines) and nordstrandite. Subscripts: g for gibbsite, d for doyleite and n for nordstrandite. The oxygen atoms are at heights of 0.11 (shaded large circles) and -0.11 (unshaded).

shifts of the layers in the directions corresponding to a of gibbsite are relatively small, 0.53 Å in nord-strandite and 0.32 Å in doyleite.

Theoretically, other schemes of stacking the octa-

hedral layers are possible; for example, displacement of successive layers along a or -a of gibbsite or mixed doyleite-nordstrandite, doyleite-bayerite and nordstrandite-bayerite layers are possible.

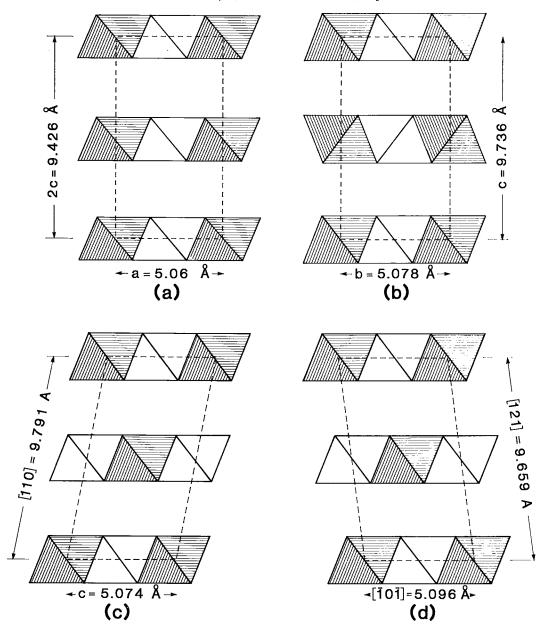


Fig. 6. Idealized structures of (a) bayerite, (b) gibbsite, (c) nordstrandite and (d) doyleite viewed along a' of the gibbsite-like cells which are related to the respective adopted cells (Table 1) by 010/100/002, 100/010/001, 110/001/110 and 101/101/121. Shaded octahedra are approximately at heights of 2/6 and 4/6, unshaded, 1/6 and 5/6.

"Triclinic hydrargillite" (Saalfeld 1960), which has large values of *a* and *b*, could perhaps be explained by such mixed layers in an ordered arrangement.

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