

DOYLEITE, A NEW POLYMORPH OF $\text{Al}(\text{OH})_3$, AND ITS RELATIONSHIP TO BAYERITE, GIBBSITE AND NORDSTRANDITE*

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ABSTRACT

Doyleite, a new polymorph of $\text{Al}(\text{OH})_3$, 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: Al_2O_3 65.2, CaO 0.48, H_2O (TGA to 1100°C) 35.76, sum 101.44 wt.%, corresponding to $\text{Al}_{0.99}\text{Ca}_{0.01}(\text{OH})_{3.00}$. The mineral is not attacked by 1:1 HCl , H_2SO_4 or HNO_3 at room temperature. A single-crystal X-ray study showed the mineral from Mont St. Hilaire to be triclinic, space group $P\bar{1}$ from morphology, 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)°, $Z = 2$. The strongest five X-ray powder-diffraction lines [d in Å(hkl)] are: 4.794(100)(010), 2.360(40)(101), 1.972(30)(221), 1.857(30)(111) and 1.842(30)(122). Crystals are tabular on (010), showing forms {010}, {101}, {101} 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 $2\frac{1}{2}$ - 3, $D(\text{meas.})$ 2.48(1), $D(\text{calc.})$ 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): $X(90^\circ, 41^\circ)$, $\bar{Y}(240^\circ, 53^\circ)$, $Z(343^\circ, 74^\circ)$, 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 $\text{Al}(\text{OH})_3$ results from different ways of stacking the layers of $\text{Al}(\text{OH})_6$ 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 $\text{Al}(\text{OH})_3$, se trouve

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: Al_2O_3 65.2% (en poids), CaO 0.48, H_2O (par TGA jusqu'à 1100°C) 35.76, total 101.44, soit $\text{Al}_{0.99}\text{Ca}_{0.01}(\text{OH})_{3.00}$. La doyleïte est inerte dans les acides HCl 1:1, H_2SO_4 et HNO_3 à température ambiante. Une étude radiocristallographique sur monocristal du mont St-Hilaire révèle la symétrie triclinique; son groupe spatial $P\bar{1}$ 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 Å(hkl)] sont: 4.794(100)(010), 2.360(40)(101), 1.972(30)(221), 1.857(30)(111) et 1.842(30)(122). Les cristaux, aplatis sur (010), présentent les formes {010}, {101}, {101} 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 $2\frac{1}{2}$ 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°). 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 feuillettes d'octaèdres $\text{Al}(\text{OH})_6$. Le nom rappelle 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

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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 powder-diffraction 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

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 $P\bar{1}$. 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 least-squares 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 $Al(OH)_3$ 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

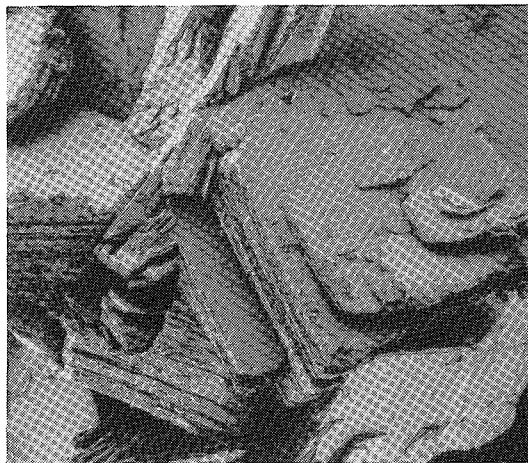


FIG. 1. Doyleite crystals (0.8×0.8 mm) from Mont St. Hilaire, Quebec.

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

	(1) Doyleite	(2) Doyleite	(3) Nordstrandite	(4) Gibbsite	(5) "Triclinic hydrargillite"	(6) Bayerite
a (Å)	5.002(1)	5.028(6)	6.148(2)	6.684(1)	17.338	5.062(1)
b	5.175(1)	5.177(7)	6.936(2)	5.078(1)	10.086	6.671(2)
c	4.980(2)	5.026(7)	5.074(1)	9.736(1)	9.730	4.713(1)
α (°)	97.90(1)	97.50(7)	95.76(2)		94.17	
β	118.60(1)	119.36(12)	99.06(2)	94.54 (1)	92.13	90.27 (5)
γ	104.74(1)	104.00(9)	85.30(2)		90.00	
V (Å ³)	104.52(5)	105.71(1)	211.47(7)	428.0	1694.0	205.86
Z	2	2	4	8	32	4
space group	$P\bar{1}$		$P\bar{1}$	$P2_1/n$		$P2_1/a$
D (g/cm ³)						
meas.	2.48(1)		2.42	2.40		2.55
calc.	2.482	2.436		2.44		2.54
R _i						
α	1.545(1)(Na)		1.580(1)(Na)	1.568		
β	1.935(1)		1.583(1)	1.968		
γ	1.966(1)		1.602(1)	1.967		
2V	(+177°)		(+124°)	(+)	0°	24°–40°

(1) Mont St. Hilaire, Quebec, this study. (2) Francon quarry, Montreal, Quebec, this study. (3) Mont St. Hilaire, Quebec, Chao & Baker (1982). (4) Szaifeld & Wedde (1974). Optical properties from Palache et al. (1944). (5) Szaifeld (1960). (6) Rothbauer et al. (1967).

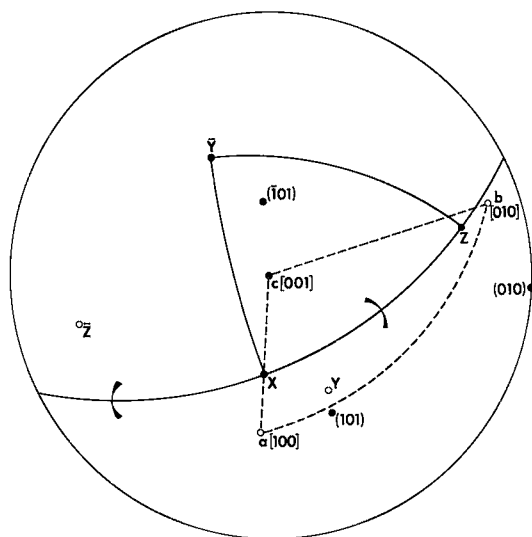


FIG. 3. Optical orientation of doyleite.

ments. The water content was determined by thermal gravimetric analysis to 1100°C. The results (Table 3, no. 4) correspond to $\text{Al}_{0.99}\text{Ca}_{0.01}(\text{OH})_{3.00}$. 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 moving-sample 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 $K_p/K_c = 0.223/0.253 = 0.881$. The large discrepancy between K_p and K_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

TABLE 3. COMPOSITION OF DOYLEITE

	1	2	3	4	5	6
Al_2O_3	64.8	63.7	63.1	65.2	59.6	65.36
SiO_2		0.03	0.12		3.22	
CaO	0.01			0.48	0.23	
MgO					0.96	
FeO	0.16	0.14	0.21		0.08	
Na ₂ O	0.08	0.09	0.06		0.35	
H ₂ O	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.
 4. Mont St. Hilaire, Quebec. Wet-chemical analysis by Bondar-Clegg & Co. Ltd. H₂O by TGA.
 5. Francon quarry, Montreal, Quebec. Average of four electron-microprobe analyses by M. Bonardi, GSC. Corrected against gibbsite internal standard. H₂O by difference.
 6. Calculated for theoretical $\text{Al}(\text{OH})_3$.

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 $\gamma\text{-Al}_2\text{O}_3$, indicating a complete destruction of the doyleite structure and commencement of the formation of $\gamma\text{-Al}_2\text{O}_3$. The final product of dehydration quenched from 1100°C is $\gamma\text{-Al}_2\text{O}_3$ 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 $\text{Al}(\text{OH})_6$ octahedron in the doyleite structure, whereas there are two in the nordstrandite and gibbsite structures.

STRUCTURAL RELATIONSHIP TO OTHER $\text{Al}(\text{OH})_3$ MINERALS

Doyleite possesses a perfect cleavage, which is common to the other $\text{Al}(\text{OH})_3$ 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-

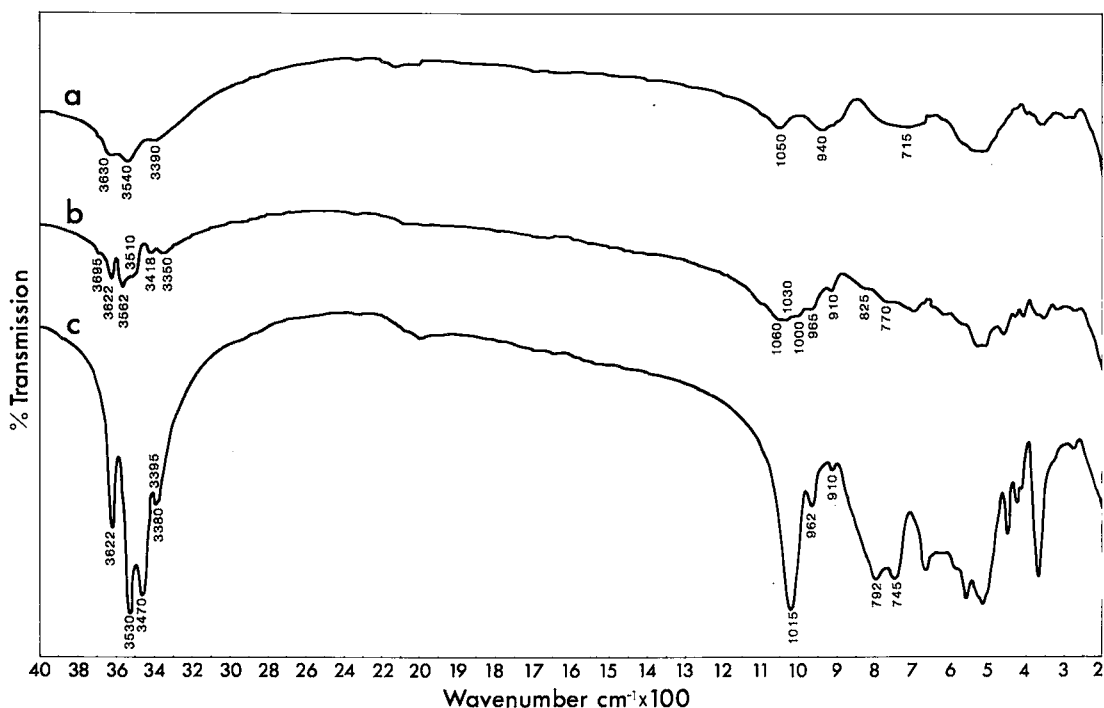


FIG. 4. Infrared absorption spectra of doyleite (a), nordstrandite (b) and gibbsite (c).

tographs of synthetic bayerite show a strong preferred-orientation effect for $00l$ 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 $\text{Al}(\text{OH})_6$ 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 $\text{Al}(\text{OH})_3$ 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 $[1\bar{1}0]$ and $-c$, respectively. Based on the near-identity of the b -precession 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 $\text{Al}(\text{OH})_3$ 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 \AA along $-b$ of gibbsite, whereas in doyleite the successive layers are shifted by 1.95 \AA along b of gibbsite. The

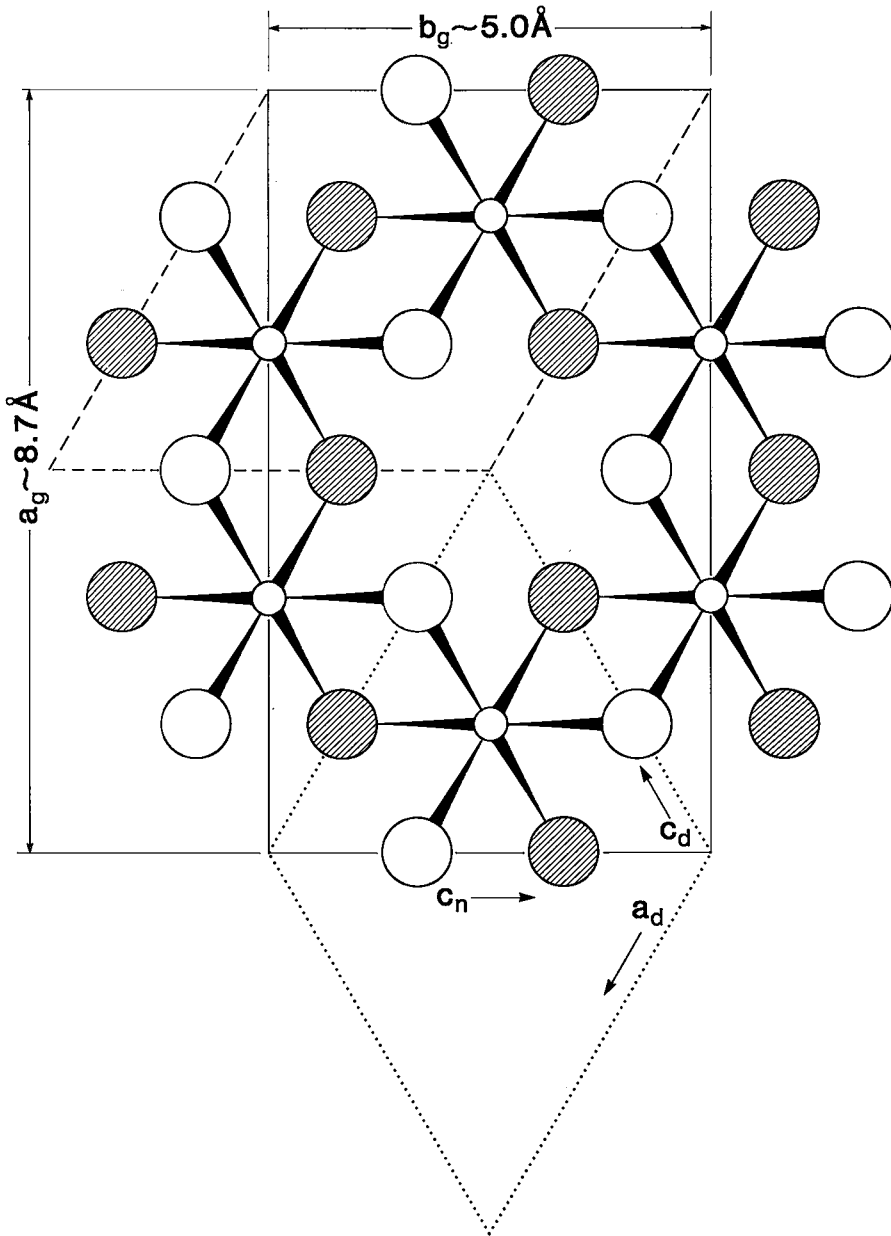


FIG. 5. Idealized structure of gibbsite projected on (001), showing geometric relations of the cells of gibbsite (solid lines), bayerite (dashed lines) and nordstrandite. Subscripts: g for gibbsite, d for doyleite and n for nordstrandite. The oxygen atoms are at heights of 0.11 (shaded large circles)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

shifts of the layers in the directions corresponding to a of gibbsite are relatively small, 0.53 \AA in nordstrandite and 0.32 \AA 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.

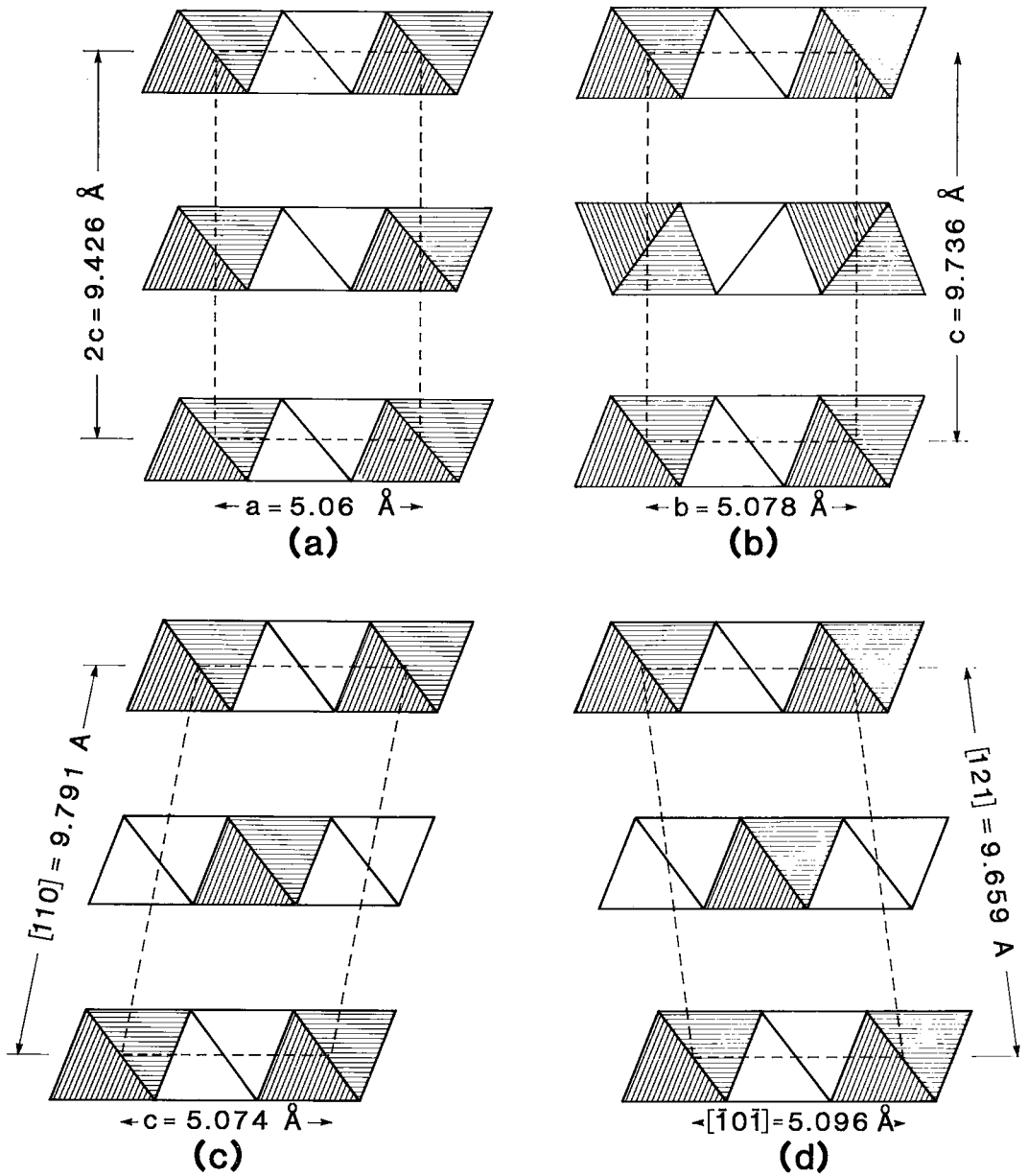


FIG. 6. Idealized structures of (a) bayerite, (b) gibbsite, (c) nordstrandite and (d) doyleite viewed along a' of the gibbsite-like cells which are related to the respective adopted cells (Table 1) by $010/100/002$, $100/010/001$, $1\bar{1}0/00\bar{1}/110$ and $10\bar{1}/10\bar{1}/121$. Shaded octahedra 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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