Canadian Mineralogist
Vol. 28, pp. 147-153 (1990)

A FLUORINE-BEARING GIBBSITE-LIKE MINERAL FROM THE FRANCON QUARRY, MONTREAL, QUEBEC

JOHN L. JAMBOR
CANMET, 555 Booth Street, Ottawa, Ontario K1A 0G1

ANN P. SABINA
Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario K1A 0E8

ROBERT A. RAMIK AND B. DARKO STURMAN
Department of Mineralogy, Royal Ontario Museum, 100 Queen's Park, Toronto, Ontario M5S 2C6

ABSTRACT

A hydrous aluminum oxide containing about 7 wt.% F is widely distributed in small amounts at the Francon quarry, Montreal, Quebec. Chemical analyses have given variable results, but the formula of the mineral is interpreted to be $Al(OH,F)_3$. The F is concluded to be incorporated structurally, whereas excess water and persistently present Si, in amounts up to several wt.%, are attributed to absorption and admixture with amorphous silica. The fluorine-bearing mineral occurs mainly as white powdery coatings and coalesced globules. The globules are typically 0.1 to 0.2 mm in diameter and consist of fine-grained aggregates in a radial pattern. Individual grains are colorless and have a parallel or almost parallel extinction, with Z' parallel to the elongation and nx′ 1.535(5), nz′ 1.550(5). The X-ray powder pattern, indexed by analogy to gibbsite, has its strongest five lines [d in Å(I)(hkl)] at 4.83(100)(002), 4.340(60)(200,110), 2.420(30)(004,021), 2.006(20)($\bar{3}13,\bar{4}02$) and 1.446(30)(133,600,423). TGA curves are similar to those of gibbsite, but the IR spectrum is simpler than that of other $Al(OH)_3$ minerals.

Keywords: $Al(OH)_3$ polymorphs, F-bearing gibbsite-like mineral, physical and chemical properties, X-ray powder data, IR spectrum, Francon quarry, Montreal, Quebec.

SOMMAIRE

Un oxyde d'aluminium hydraté contenant environ 7% en poids de F se retrouve couramment en petites quantités dans la carrière Francon, à Montréal, Québec. Des analyses chimiques ont donné des résultats variables, mais la formule chimique du minéral serait $Al(OH,F)_3$. Le F serait incorporé dans la structure, mais l'excès d'eau et la présence persistente de Si en quantités pouvant atteindre quelques % en poids, sont attribuables à l'absorption et à un mélange avec de la silice amorphe. Le minéral, qui contient donc du fluor, se présente surtout sous forme d'enduit pulvérulent et de globules enchevêtrées. Les globules sont typiquement de l'ordre de 0.1 à 0.2 mm de diamètre et consistent d'agrégats de grains fibroradiés. Les cristaux individuels sont incolores et montrent une extinction parallèle ou presque parallèle, avec Z' parallèle à l'allongement et nx′ 1.535(5), nz′ 1.550(5). Le cliché de poudre aux rayons X, indexé par analogie à la gibbsite, montre, comme raies principales [d en Å(I)(hkl)], 4.83(100)(002), 4.340(60) (200,110), 2.420(30)(004,021), 2.006(20)($\bar{3}13,\bar{4}02$) et 1.446(30)(133,600,423). Les courbes ATG sont similaires à celles de la gibbsite, mais le spectre IR est plus simple que ceux d'autres minéraux $Al(OH)_3$.

Mots-clés: polymorphes $Al(OH)_3$, minéral fluoré semblable à la gibbsite, propriétés physiques et chimiques, cliché de diffraction X (méthode des poudres), spectre IR, carrière Francon, Montréal, Québec.

INTRODUCTION

Among the several rare minerals that have been described from the dawsonite-bearing sills in the Francon quarry at Montreal, Quebec (Roberts *al.* 1986), one of the most common and earliest noted is an aluminum hydroxide that gives an X-ray powder-diffraction pattern resembling that of gibbsite (Sabina *et al.* 1968). The Francon mineral was reported as unidentified No. 3 in Sabina (1976, 1979). Despite its widespread distribution and abundance relative to some of the compositionally more exotic Francon species, no detailed description of the gibbsite-like mineral has been published. This omission has not been accidental, for despite the common presence of the mineral on Francon specimens, milligram quantities of hand-picked pure material are extremely difficult to obtain.

Seven polymorphs of $Al(OH)_3$ have been reported to occur as minerals or probable minerals (gibbsite, bayerite, nordstrandite, doyleite, "triclinic hydrargillite", UK 45, and UK 51), and four additional polymorphs are known only as synthetic phases (Table 1). All eleven are interpreted to differ in important respects from the Francon mineral, which probably has the composition $Al(OH_{1-x}F_x)_3$. The X-ray powder pattern of the Francon mineral resembles that of gibbsite and has no similarity to that of zharchikhite, $AlF(OH)_2$ (Bolokhontseva *et al.* 1988).

TABLE 1. CELL PARAMETERS (Å) OF THE POLYMORPHS OF $Al(OH)_3$

Phase	System	a	b	c	α	β	γ	Reference
gibbsite	monocl.	8.684	5.078	9.736	-	94.54	-	Saalfeld & Wedde (1974)
bayerite	monocl.	5.062	8.671	4.713	-	90.27	-	Rothbauer et al. (1967)
nordstrandite	tricl.	6.148	6.936	5.074	95.76	99.06	83.30	Chao & Baker (1982)
doyleite	tricl.	5.002	5.175	4.980	97.50	118.60	104.74	Chao et al. (1985)
triclinic hydrargillite	tricl.	17.338	10.086	9.730	94.17	92.13	90.00	Saalfeld (1960)
UK 45	tricl.	5.002	5.175	4.980	97.50	118.60	104.74	Chao et al. (1985)
UK 51	nordstrandite-like							Chao et al. (1985)
synthetic, bayerite-like	monocl.	5.062	8.671	9.462	-	90.27	-	Gigl & Dachille (1972)
synthetic	orthorh.	5.141	5.063	7.259				Gigl (1972)
synthetic	tetrag.	7.26	-	14.43				Gigl & Dachille (1969)
synthetic	cubic	7.20	-	-				Baneeva & Bendeliani (1973)

OCCURRENCE AND PROPERTIES

The occurrence of the gibbsite-like mineral in the Francon quarry sills has been outlined by Sabina (1979), who described the mineral as "Chalk-white powdery coatings; also porcelain-like and waxy granular; white translucent globules and botryoidal crusts; white shells. Fluorescent and phosphorescent upon irradiation with ultraviolet light: bluish white ("short" rays) and cream-white ("long" rays)".

The globules are typically 0.1 to 0.2 mm in diameter and consist of radial aggregates. Some globules have coalesced into botryoidal crusts; surface areas of the crusts are generally no more than 1 to 2 mm^2, and contamination by dawsonite, fluorite, calcite and halloysite is common. An exceptional specimen (Fig.1) consists of divergent fibers that form stepped columns (Fig. 1b) having a flat termination of pseudohexagonal outline.

Globules provide the best source of pure material for determinative purposes, and optical examination shows that the coarsest individual grains in these are only about 2 × 1 × 1 micrometers. The grains are colorless and have parallel or almost parallel extinction, with Z' parallel to the elongation and nx' 1.535(5), nz' 1.550(5). A measured density of 2.43 g/cm^3 was obtained by suspension of globules in heavy liquids. The calculated density obtained for $8[Al(OH_{2.5}F_{0.5})_{\Sigma 3.0}]$ and the cell derived from the X-ray powder pattern is 2.51 g/cm^3. The measured density is similar to that of gibbsite (2.3–2.4 g/cm^3), but the optical properties of gibbsite are much different, *e.g.*, $n_x \sim n_y$ 1.565–1.577, n_z 1.58–1.595, $Z{:}c \sim 21°$ (Winchell & Winchell 1951).

CHEMICAL COMPOSITION

In 1968 a wet-chemical analysis of hand-picked concentrate of the Francon mineral gave Al_2O_3 53.7 wt.%, and indications were obtained that the remaining component is water. A decade later, a neutron-activation analysis, using a new hand-picked sample and the SLOWPOKE facility at the University of Toronto, gave 54.8 wt.% Al_2O_3 and <4 wt.% SiO_2. Subsequently, evolution of fluorine accompanying H_2O was detected in another sample during thermal decomposition using a Mettler Thermoanalyzer with an integrated mass spectrometer. Two additional samples were used for fluorine determinations; one of these, weighing 5 mg, was analyzed by wet-chemical methods at the Geological Survey of Canada and gave a F value of 7±1 wt.%. The other, weighing 9.6 mg, was run on the Mettler Thermoanalyzer and gave an SiF_4 upper limit of 6.3 wt.% and H_2O 25.0 wt.%.

Quantitative electron-microprobe analyses are difficult to carry out on the Francon mineral because it, like gibbsite, is highly susceptible to decomposition under the electron beam. Surface damage, which presumably reflects partial dehydration of the mineral, can be minimized by using a defocused beam. Microprobe compositions (Table 2) were obtained with three different instruments using a variety of standards. Most analyses were obtained at 15 kV and were done on spheres and spherical aggregates from several samples. The microprobe results are interpreted to represent variations of a gibbsite-type formula, $Al(OH)_3$. The analyses performed with the MAC probe show the highest apparent H_2O contents, and the accompanying Al_2O_3 values are in good agreement with results of older analyses obtained by other methods. The more recent CAMECA and JEOL data show higher Al and more closely approach the 65.36 wt.% Al_2O_3 of gibbsite.

Also notable is the much higher SiO_2 contents in these analyses, but the X-ray powder patterns of these spheres and the ones analyzed with the MAC probe do not differ. The various analytical results lead to substantial differences in inferred H_2O calculated by subtraction from 100 wt.%, but the lack of variation in the X-ray patterns suggests that either a loss of absorbed water or partial decomposition occurred under the electron beam.

The formulas shown in Table 2 are calculated on the assumption that F and the minor cations are incorporated structurally. Substitution of F for OH is reasonable because of their similar radii and valences, and the interchange of these ions has been demonstrated by Cowley & Scott (1948) to have little effect on the cell dimensions of synthetic simple aluminum hydroxide compounds. The possible substitution of substantial amounts of tetravalent silicon for trivalent aluminum is, however, more difficult to accept. Where the silica values are comparable to those in Table 2, back-scattered electron photographs show that the element is not present as inclusions or concentrated in specific areas, but instead is uniformly distributed. Halloysite has been detected in some globules as colloform-type intergrowths that are recognizable readily because of their much higher levels of Si. The halloysite-bearing zones are clearly demarcated rather than either uniformly or complexly intergrown with the gibbsite-like phase.

Adsorption of ligand-exchanged anions (Hingston *et al.* 1974) and cations (Alvarez *et al.* 1976, Eremin *et al.* 1980, McBride *et al.* 1984) on gibbsite has been experimentally demonstrated, but it has also been reported that silica and fluoride anions inhibit $Al(OH)_3$ crystallization (Huang & Jackson 1966, Hsu 1979). Farrah *et al.* (1987) reported that $Al(OH)_3$ can scavenge F from aqueous phases in the pH 4–7 region, but product yields in these experimental studies are small, and the solids have not been characterized by X-ray methods. Evidently fluorine contents of the magnitude that occur in the Francon mineral have not been confirmed in experimentally derived crystalline precipitates, and the high contents of silicon also are anomalous. With respect to silicon, it is interesting that in the initial description of the $Al(OH)_3$ polymorph named *doyleite*, Chao *et al.* (1985) reported 0.03 and 0.12 wt.% SiO_2 in samples from Mont St. Hilaire, but up to 3.22 wt.% SiO_2 for material from the Francon quarry. The apparent abundance and variability of the silicon in the fluorine-bearing Francon mineral are substantial and should result in changes in the X-ray pattern, but in the absence of such effects it seems reasonable to conclude that Si is not structurally bound and perhaps is present as disseminated amorphous silica. The true composition of the Francon mineral is therefore thought to be $Al(OH_{1-x}F_x)_3$.

FIG. 1. SEM photographs of the Francon mineral showing partly divergent clusters (a) that on enlargement are seen as stepped columns having a pseudohexagonal outline (b). Bar scale represents 10 μm in (a), and 1 μm in (b).

X-RAY DATA

The fine grain-size of the Francon mineral

TABLE 2. REPRESENTATIVE MICROPROBE COMPOSITIONS OF THE FRANCON MINERAL

		MAC probe, CANMET					CAMECA probe, GSC (av. and range of 4)		JEOL probe, CANMET* (av. and range of 4)	
		sphere A-1	sphere A-2	sphere B-4	sphere 454	av.	av.	range	av.	range
wt%	MgO	0.4	0.4	0.5	n.d.	0.3	n.a.		0.6	0.5–0.7
	CaO	0.6	0.5	0.6	0.5	0.6	n.a.		0.6	0.6–0.7
	Al_2O_3	56.9	58.8	55.2	52.5	55.9	61.3	60.5–62.7	64.9	62.9–66.1
	SiO_2	4.0	1.5	3.7	1.6	2.7	9.5	8.6–10.5	8.7	8.1–10.1
	**F	n.a.	n.a.	n.a.	n.a.	6.3	5.5	4.8–5.8	7.4	6.4–8.3
	Total					65.8	78.3		82.2	
	O=F					2.7	2.3		3.1	
						63.1	76.0		79.1	
	(H_2O)					36.9	24.0		20.9	
						100.0	100.0		100.0	

average compositions

MAC: $(Al_{0.90}Si_{0.07}Ca_{0.02}Mg_{0.01})_{\Sigma 1.00}(OH_{2.41}F_{0.54}O_{0.05})_{\Sigma 3.00}\cdot 2.1H_2O$

CAMECA: $(Al_{0.79}Si_{0.21})_{\Sigma 1.00}(OH_{2.41}F_{0.38}O_{0.21})_{\Sigma 3.00}\cdot 0.5H_2O$

JEOL: $(Al_{0.79}Si_{0.18}Mg_{0.02}Ca_{0.01})_{\Sigma 1.00}(OH_{2.38}F_{0.48}O_{0.14})_{\Sigma 3.00}\cdot 0.2H_2O$

*some decomposition evident, thus accounting for the high Al_2O_3 values, and low H_2O by difference

**inferred F; Cl at or below the detection limit of 0.03 wt%.

n.d. not detected; n.a. not analyzed

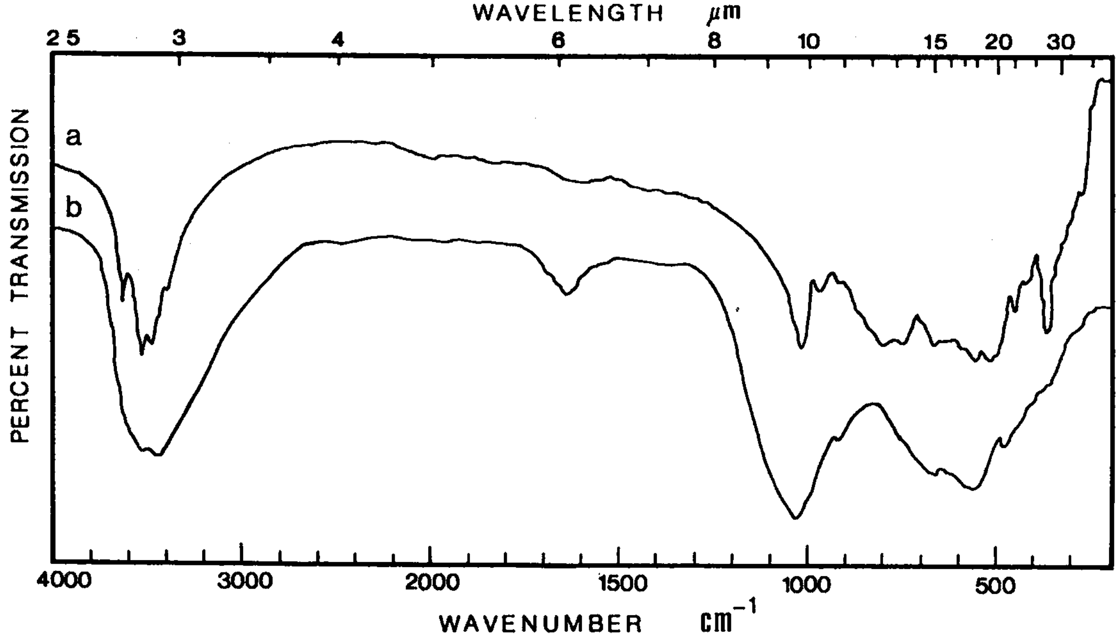

FIG. 2. Infrared absorption spectrum of (a) gibbsite from Wingellina, West Australia (NMC 12878), and (b) the mineral from the Francon quarry.

precluded single-crystal X-ray studies. Transmission electron microscopy showed that the grains have an elongate, rectangular shape similar to that of nordstrandite (Schoen & Roberson 1970) and gibbsite. The Francon mineral is unstable under the electron beam, and electron-diffraction investigations at three different laboratories have revealed only that the elongation axis has a periodicity of about 2.35 Å; a whole multiple of this value approximates the axial length of several $Al(OH)_3$ phases, especially that of *c* for bayerite (Table 1). Nevertheless, the cell parameters of gibbsite were used for the initial indexing because the first few lines of its powder pattern most closely approximate those of the Francon mineral.

X-ray powder data for the Francon mineral are given in Table 3. Variations from sample to sample are negligible. With a 114-mm Debye–Scherrer camera, the diffraction line at 2.42 Å typically is unresolved for copper radiation. With cobalt radiation, however, the line appears as a doublet; further apparent resolution into a triplet is present on all Guinier - de Wolff films (Table 3), but all of the Guinier patterns contain lines due to contaminant minerals. The calculated cell-dimensions of the Francon mineral are *a* 8.66, *b* 4.99, c 9.67 Å, *β* 92.12°; those of gibbsite (PDF 29–41) are *a* 8.684, *b* 5.078, *c* 9.736 Å, *β* 94.54°. The respective cell-volumes are 417.6 and 428.0 Å^3; the smaller cell of the Francon mineral is in accord with the smaller ionic radius of fluorine relative to oxygen (Whittaker & Muntus 1970).

THERMOGRAVIMETRIC DATA

A 9.6-mg sample initially stored at a relative humidity of 40% was analyzed by TG–EGA. Of the total loss of 31.3 wt.% up to 1500°C, 2.1% was lost under vacuum at 20°C. At a heating rate of 10°C/min., about 16 wt.% was lost between 50 and 315°C; an additional 7 wt.% was lost between 315 and 615°C, with H_2O pressure maxima at 240 and 405°C, respectively. The cumulative loss to 615°C amounted to 25.0 wt.%, and is attributable to evolution of H_2O and a minor loss of SiF_4.

Another sample was first desiccated for several days. It then lost 1.7 wt.% in vacuum, and a further 29.4 wt.% H_2O between 50 and 615°C, for a total of 31.1 wt.%. The peak due to H_2O partial pressure, and corresponding to the second lesser weight-loss, lies at 490°C, almost 100° higher than for the first sample. A further 9.5 wt.% was lost between 615 and 1400°C. It is uncertain whether the loss was due to SiF_4 or AlF_3.

The TG, DTA and H_2O partial pressure curves of vacuum-dried gibbsite from Richmond, Massachusetts (ROM M4704) were compared to those of the Francon mineral. Decomposition temperatures and the two-step evolution of water were found to be similar. For gibbsite, 33.6–34.2 wt.% was lost between 25 and 400°C, followed by an additional 2.4–2.5 wt.% loss between 400 and 800°C. Two corresponding maxima attributed to H_2O partial pressure were noted near 220°C and 510°C, respectively. These losses are 97–99% and 7%, respectively, of the theoretical 34.64 wt.% H_2O for ideal $Al(OH)_3$. It is interesting to note that most of the second loss is in excess of this theoretical amount. The gibbsite DTA curves showed an exothermic event at 850°C, which may be attributed to the γ–θ transition of Al_2O_3 (Mackenzie & Berggren 1970). (Decomposition in vacuum may explain why the expected χ–κ transition was not seen near 950°C.) In comparison, DTA curves for the second Francon sample lack high-temperature exotherms, probably because recrystallization was too sluggish to be detected. The 9.6-mg sample, heated to 1505°C, gave an X-ray pattern of well-crystallized mullite and corundum. The second Francon sample, heated to 1000°C, gave a weak diffuse pattern with lines at 2.18 (1), 2.09 (2) and 1.38 Å (10); the material is probably a polymorph of alumina.

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR THE FRANCON GIBBSITE-LIKE MINERAL

(a) Guinier 1620B			(b) 78-324			
I_{est}	d_{meas}Å	d_{calc}Å	I_{est}	d_{meas}Å	d_{calc}Å	hkl
100	4.85	4.832	100	4.83	4.834	002*
		4.326			4.325	200
80	4.34		60	4.34		
		4.323			4.317	110
20	3.281	3.284	10	3.276	3.284	$\bar{2}02$*
		3.193			3.191	112*
10	3.181		5	3.177		
		3.165			3.166	202
2	2.557	2.561			2.560	113
30	2.438	2.437			2.435	$\bar{3}11$
		2.416			2.417	004
50	2.418		30	2.420		
		2.416			2.412	021*
20	2.400	2.399			2.398	311
5	2.254	2.248	5	2.247	2.247	$\bar{3}12$*
		2.190			2.189	312*
5	2.194		5	2.190		
		2.189			2.189	$\bar{3}03$
		2.005			2.004	$\bar{3}13$*
10	2.010		20	2.006		
		2.002			2.002	$\bar{4}02$
		1.948			1.948	402
5	1.945		10	1.944		
		1.944			1.944	313
		1.772			1.770	$\bar{3}22$*
1	1.772		10	1.767		
		1.765			1.764	$\bar{3}14$
		1.714			1.714	$\bar{5}01$
4	1.709	1.711	10	1.709	1.709	$\bar{1}24$
		1.709			1.709	314*
		1.693			1.692	501
1	1.691					
		1.693			1.692	124
		1.646			1.644	$\bar{3}23$
		1.644			1.644	215
3	1.642		5	1.641		
		1.642			1.642	$\bar{4}04$
		1.640			1.636	031
		1.626			1.625	$\bar{2}24$
1	1.624					
		1.621			1.621	$\bar{5}11$
		1.565			1.565	$\bar{5}12$
2	1.568		2	1.565		
		1.562			1.560	$\bar{4}22$
					1.451	133
			30	1.446	1.442	600
					1.441	423
					1.400	521
			5	1.396		
					1.396	$\bar{6}02$*
					1.374	$\bar{3}16$+
			2	1.374		
					1.372	332+
			1	1.353	1.353	026*+
			1	1.335		
			2	1.206		

* indices used to obtain the cell dimensions; (a) Guinier-de Wolff pattern, Co*K*α_1 radiation (λ = 1.78896 Å), after purging of extra lines of impurities; indexed with *a* 8.658, *b* 4.991, *c* 9.671 Å, β 92.12°. (b) Debye-Scherrer 114.6-mm camera, *a* 8.656, *b* 4.981, *c* 9.675 Å, β 92.10° for Cu*K*α_1 radiation.

INFRARED ABSORPTION SPECTRUM

The infrared absorption spectra of the $Al(OH)_3$ polymorphs are discussed by Elderfield & Hem (1973), Vivien *et al.* (1973), and Chao *et al.* (1985). The spectra of gibbsite and the Francon mineral are shown in Figure 2. In the high-frequency region of OH stretching, the Francon mineral is characterized by having only two strong absorption bands, at 3445 and 3520 cm^{-1}, whereas all other $Al(OH)_3$ minerals have multiple bands in this region. In the OH-bending region from 1100 to 900 cm^{-1} the spectrum of the Francon mineral is similar to that of gibbsite, but the main absorption band has a slightly higher frequency. The weak but distinct absorption band at about 1625 cm^{-1} is a bending mode for water, and probably represents absorbed water. In the Al–O stretching region below 900 cm^{-1} the Francon spectrum is even less complex than that of doyleite; the simplicity of the doyleite spectrum was attributed by Chao *et al.* (1985) to the presence of only one crystallographically independent $Al(OH)_6$ octahedron in its structure, whereas two are present in gibbsite. Thus, despite the fact that the X-ray pattern of the Francon mineral has been indexed with a gibbsite cell, the two minerals apparently differ in structure.

ACKNOWLEDGEMENTS

D.R. Owens of CANMET, and S. Courville, J.-L. Bouvier and D.C. Harris of the Geological Survey of Canada kindly provided various chemical data over a number of years. E.E. Lauffer, formerly with CANMET, G.C. Weatherly of the University of Toronto, and M.J. Carr of Sandia National Laboratories examined the Francon mineral by TEM, and D.A. Walker of the Geological Survey of Canada obtained the photographs for Figure 1. Other technical assistance at CANMET was provided by V. Rolko, J.E. Dutrizac, E.J. Murray and J.H.G. Laflamme. D.L. Bish, S. Guggenheim and an unidentified referee are thanked for reviewing the initial version of the manuscript.

REFERENCES

ALVAREZ, R., FADLEY, C., SILVA, J. & UEHARA, G. (1976): A study of silicate adsorption on gibbsite ($Al(OH)_3$) by X-ray photoelectron spectroscopy (XPS). *J. Soil Sci. Am.* **40**, 615-617.

BANEYEVA, M.I. & BENDELIANI, N.A. (1973): New modification of aluminum hydroxide II obtained at high pressures and temperatures. *Dokl. Akad. Nauk SSSR* **212(2)**, 361-362 (in Russ.).

BOLOKHONTSEVA, S.V., BATURIN, S.V., ILMEYEV, E.S., PAPOVA, M.A. & PURUSOVA, S.P. (1988): Zharchikhite $AlF(OH)_2$ — a new mineral. *Zap. Vses. Mineral. Obshchestva* **117**, 79-83 (in Russ.).

CHAO, G.Y. & BAKER, J. (1982): Nordstrandite from Mont St-Hilaire, Quebec. *Can. Mineral.* **20**, 77-85.

______, ______, SABINA, A.P. & ROBERTS, A.C. (1985): Doyleite, a new polymorph of $Al(OH)_3$, and its relationship to bayerite, gibbsite and nordstrandite. *Can. Mineral.* **23**, 21-28.

COWLEY, J.M. & SCOTT, T.R. (1948): Basic fluorides of aluminum. *J. Am. Chem. Soc.* **70**, 105-109.

ELDERFIELD, H. & HEM, J.D. (1973): The development of crystalline structure in aluminium hydroxide polymorphs on ageing. *Mineral. Mag.* **39**, 89-96.

EREMIN, N.I., CHEREPANOVA, M.I., SHMORGUNENKO, N.S. & MAKSAKOVA, M.A. (1980): The nature of the inclusion of alkali impurity in the structure of aluminum hydroxide. *Sov. J. Non-Ferrous Metals* **21**, 132-135.

FARRAH, H., SLAVEK, J. & PICKERING, W.F. (1987): Fluoride interactions with hydrous aluminum oxides and alumina. *Austral. J. Soil Res.* **25**, 55-69.

GIGL, P.D. (1972): *Pressure-Temperature Studies of the Alumina-Water and the Aluminum-Water Systems.* Ph.D. thesis, Pennsylvania State Univ., University Park, Pennsylvania. (Dissertation Abstr. Internat., 1973, Sect.B, **33(8)**, 4029-B).

______ & DACHILLE, F. (1969): P–T studies in the alumina–water system. *Geol. Soc. Am., Program Abstr.* **7**, 77.

______ & ______ (1972): Contributions to the alumina–water P–T system. *Am. Ceram. Soc. Bull.* **51**, 653 (abstr.).

HINGSTON, F.J., POSNER, A.M. & QUIRK, J.P. (1974): Anion adsorption by goethite and gibbsite. II. Desorption of anions from hydrous oxide surfaces. *J. Soil Sci.* **25**, 16-26.

HSU, P.H. (1979): Effect of phosphate and silicate on the crystallization of gibbsite from OH–Al solutions. *Soil Sci.* **127**, 219-226.

HUANG, P.M. & JACKSON, M.L. (1966): Fluoride interaction with clays in relation to third buffer range. *Nature* **211**, 779-780.

MACKENZIE, R.C. & BERGGREN, G. (1970): Oxides and hydroxides of higher-valency elements. *In* Differential Thermal Analysis 1 (R.C. Mackenzie, ed.). Academic Press, New York (271-302).

MCBRIDE, M.B., FRASER, A.R. & MCHARDY, W.J. (1984): Cu^{2+} interaction with microcrystalline gibbsite. Evidence for oriented chemisorbed copper ions. *Clays Clay Minerals* **32**, 12-18.

ROBERTS, A.C., SABINA, A.P., BONARDI, M., JAMBOR, J.L., RAMIK, R.A., STURMAN, B.D. & CARR, M.J. (1986): Montroyalite, a new hydrated Sr–Al hydroxycarbonate from the Francon quarry, Montreal, Quebec. *Can. Mineral.* **24**, 455-459.

ROTHBAUER, R., ZIGAN, F. & O'DANIEL, H. (1967): Verfeinerung der Struktur des Bayerits, $Al(OH)_3$. Einschliesslich eines Vorschlags für die H-Positionen. *Z. Kristallogr.* **125**, 317-331.

SAALFELD, H. (1960): Structuren von Hydrargillite, Entwasserungsmechanismus und Struktur der Zwischenprodukte. *Neues Jahrb. Mineral., Abh.* **95**, 1-87.

______ & WEDDE, M. (1974): Refinement of the crystal structure of gibbsite, $Al(OH)_3$. *Z. Kristallogr.* **139**, 129-135.

SABINA, A.P. (1976): The Francon quarry, a mineral locality. *Geol. Surv. Can. Pap.* **76-1B**, 15-19.

______ (1979): Minerals of the Francon quarry (Montreal Island): a progress report. *Geol. Surv. Can. Pap.* **79-1A**, 115-120.

______, JAMBOR, J.L. & PLANT, A.G. (1968): Weloganite, a new strontium zirconium carbonate from Montreal Island, Canada. *Can. Mineral.* **9**, 468-477.

SCHOEN, R. & ROBERSON, C.E. (1970): Structures of aluminum hydroxide and geochemical implications. *Am. Mineral.* **55**, 43-77.

VIVIEN, D., STEGMANN, M.-C. & MAZIÈRES, C. (1973): Contribution à l'étude par spectroscopie infrarouge et RMN large bande des hydroxydes d'aluminium: gibbsite, bayerite, nordstrandite. *J. Chimie Phys.* **70**, 1502-1508.

WHITTAKER, E.J.W. & MUNTUS, R. (1970): Ionic radii for use in geochemistry. *Geochim. Cosmochim. Acta* **34**, 945-956.

WINCHELL, A.N. & WINCHELL, H. (1951): *Elements of Optical Mineralogy* II (4th ed.). John Wiley & Sons, New York.

Received January 26, 1987, revised manuscript accepted September 25, 1989.