Nordstrandite, Al(OH)₃, from the Green River Formation in Rio Blanco County, Colorado¹

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Abstract

Nordstrandite, $Al(OH)_8$, occurs as thin fissure fillings in dolomitic marlstones and oil shale of the Green River Formation in northwestern Colorado. Here, and in New South Wales, Australia, it is found with dawsonite, $NaAlCO_8(OH)_2$, but in the seven other known occurrences it is found with gibbsite in bauxitized igneous rock or karst limestone residues. The occurrence may explain the "surplus Al_2O_8 " observed in chemical analyses of dawsonite-bearing oil shale in Colorado; thermal study suggests that this is present as an aluminum hydroxide.

Reported Occurrences

Van Nordstrand, Hettinger, and Keith (1956) synthesized a new form of Al(OH)₃ which they termed "bayerite II"; Papee, Tertian, and Biais (1958) established its difference from bayerite and gibbsite—two other polymorphs of Al(OH)₃—and named it nordstrandite. A few years later, nordstrandite was discovered in Guam (Hathaway and Schlanger, 1962, 1965), in Sarawak (Wall, Wolfenden, Beard, and Deans, 1962), in Montenegro (Tertian, 1966), in Hungary (Naray-Szabo and Peter, 1967), in Croatia (Maric, 1967–68), in New South Wales, Australia (Goldberry and Loughnan, 1970), in Jamaica (Davis and Hill, 1973), and now in Colorado.

In Colorado and New South Wales nordstrandite is associated with dawsonite, $NaAlCO_3(OH)_2$. In all other known occurrences, the association is with gibbsite in bauxite, or in residual terra rossa soils.

Nordstrandite has been found in two core samples (Fig. 1, a and b) of dolomitic marlstone ("oil shale") from the Green River Formation, in the Sinclair Cross V No. 1 well, Sec. 21, T. 1 S., R. 98 W., Rio Blanco County, in the Piceance Basin of northwestern Colorado, at depths of 1087 feet and 1154.4 feet. This is the first discovery of the mineral in the United States.

Hathaway and Schlanger (1965) described the Guam nordstrandite as deposits in voids in basal limestone overlying fossil soils formed in basaltic rocks and tuffs. Ground water, leaching these soils, deposited nordstrandite in the limestone, at pH 8.5 or 9. Similarly, in Sarawak (Wall et al, 1962), nordstrandite occurs in limestone near bauxitized intermediate-to-basic igneous rocks. Maric (1967-68) described and gave powder data for nordstrandite associated with gibbsite and bayerite from Jurassic karst limestone terra rossa in the Dinaric Alps of Croatia. He also referred to a similar occurrence in Montenegro (Tertian, 1966). In Hungary, Naray-Szabo and Peter (1967) examined six occurrences of nordstrandite, all but one containing gibbsite (or bayerite) as well. In New South Wales, Australia (Goldberry and Loughnan, 1970), nordstrandite rims dawsonite nodules. In Jamaica, Davis and Hill (1973) observed nordstrandite with gibbsite in ferruginous limestone soils (terra rossa).

Therefore, three distinct types of nordstrandite occurrence have been reported: (1) most commonly, as a weathering product in bauxitic soils derived from limestone, in Europe, Guam, Sarawak, and Jamaica; (2) as a vein or fissure-filling mineral in dolomitic oil shale in the Green River Formation, northwestern Colorado; (3) as alteration products of dawsonite which may have replaced glauberite in New South Wales, Australia.

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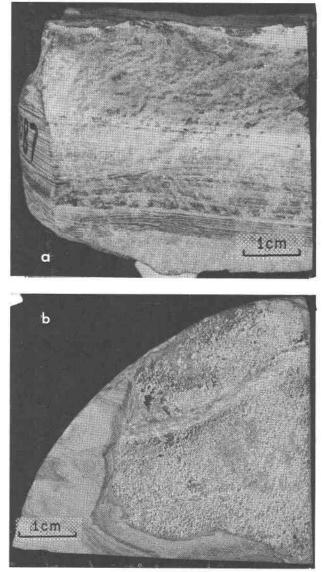


FIG. 1. Core samples from the Sinclair Cross V No. 1 well, Rio Blanco County, Colorado, showing nordstrandite as a whitish coating. **a.** Core from a depth of 1087 ft; **b.** from 1154.4 ft.

Because many of its properties, in particular the Xray diffraction pattern, are similar to those of gibbsite, nordstrandite is probably an unrecognized constituent in many other similar bauxite-terra rossa occurrences.

Nordstrandite in Colorado

Appearance and Optical Properties

The Colorado nordstrandite occurs as very thin layers of white platy or fibrous aggregates in fractures at high angles to bedding in fine-grained dolomitic siltstones and oil shale (Fig. 1). Under high magnification (Fig. 2), these deposits resemble those from Guam shown by Hathaway and Schlanger (1965, their Fig. 2).

The aggregates have a silky luster, and in the core specimen from 1087 feet they grade into extremely thin bluish films, individual crystals only being discernible under the scanning electron microscope (Fig. 2). Individual crystals are too small for optical measurements, but aggregates have a mean index of refraction near 1.570. This is lower than the indices reported for nordstrandite from Guam ($\alpha, \beta = 1.580$, $\gamma = 1.596$) and from Sarawak ($\alpha = 1.580, \beta = 1.581$, $\gamma = 1.613$), but is closer to those from Croatia ($\alpha, \beta =$ $1.565-1.570, \gamma = 1.585-1.590$) (all ± 0.005).

X-Ray Diffraction Data

Table 1 gives X-ray powder data for various nordstrandites and comparative data for gibbsite and bayerite, the other two Al(OH)₃ polymorphs. The most complete nordstrandite pattern is that of the synthetic (Bosmans, 1970), but his indexing and unit cell constants are here omitted. Bosmans' definitive work on the crystallography of nordstrandite supersedes the earlier studies by Van Nordstrand *et al* (1956), Papee *et al* (1958), and Lippens (1961), which were cited by Hathaway and Schlanger (1962, 1965) in verification of their discovery of the mineral in Guam. Similarly, Bosmans' study reviews and ex-



FIG. 2. Scanning electron photomicrograph of a radiating cluster of nordstrandite. Sample from the Sinclair Cross V No. 1 well, Rio Blanco County, Colorado (1154.4 ft depth). (× 560).

tends that of Saalfeld and Mehrotra (1966, XRPD 18-31).

Table 2 gives three patterns of Colorado nordstrandite to indicate the range of variability observed. Patterns 2a and 2b, from relatively large and therefore probably impure samples, are nevertheless in fair agreement. The third, 2c (considered the best and previously shown in Table 1), was obtained by long exposure (20 hours) of a very small, carefully selected, probably quite pure sample.

The powder patterns of the three $Al(OH)_8$ polymorphs—nordstrandite, gibbsite, and bayerite all show a general similarity, so that in some cases confusion is possible, more so between nordstrandite and gibbsite. Bosmans (1966) shows this graphically, and others have commented to the same effect. The strongest line of (synthetic) gibbsite is 4.82 Å (XRPD 12-460); and the strongest lines of Guam, Sarawak, and Jamaica nordstrandites (Table 1) are respectively 4.789, 4.790, and 4.80, as compared to 4.775, 4.80, and 4.791—mean 4.789—for Colorado nordstrandite. A second "standard" gibbsite pattern is given in XRPD 7-324, where the strongest line is 4.85 (gibbsite from Massachusetts).

M. C. Van Oosterwyck (written communication, 1974) noted that four small peaks appear to be diagnostic of nordstrandite vs gibbsite and bayerite, citing those described by Van Nordstrand et al (1956)—that is, d = 4.20, I = 15; 4.15, 13; 3.89, 7; 3.60, 7—and by Papee et al (1958)—that is, 4.205, m; 4.153, m; 3.880, m; 3.600, m. This is confirmed graphically by Schoen and Roberson (1970), whose Figure 1 clearly shows these four peaks for nordstrandite, but not for gibbsite and bayerite.

As Table 2 shows, these four peaks are well represented in the three patterns of the Colorado nordstrandite except, possibly, the first (d = 4.20), which appears in about half of a dozen patterns of the Colorado nordstrandite. In some patterns, a dark band in this region may obscure weak reflections; however, in others, such as the one cited in Table 1, it is absent.

Chemical Analyses

Because of the extreme thinness of the films of nordstrandite in the fractured rock, wet-chemical analysis of the nordstrandite was not possible. However, two samples from 1087 feet were examined by emission spectrography, and one from 1154.4 feet was examined by the electron probe. (Three X-ray powder patterns of the last sample are given in Table 2). Three such semiquantitative analyses, each indicating a composition essentially $Al(OH)_3$, are given in Table 3. The Si and Ca in analyses 378 and 386 are undoubtedly due to admixed matrix. Sample 895, the smallest and purest sample, shows Al as virtually the only constituent.

With respect to the 3 percent Ca in one sample, detrital calcic plagioclase is abundant in these cores as well as authigenic albite (and K-feldspar).

The nordstrandite from New South Wales, Australia, also contained 7.9 percent SiO_2 , mostly as quartz, and was intergrown with calcite and dawsonite; in the published powder pattern, quartz lines were omitted. The agreement with other published nordstrandite patterns, although not perfect, is acceptable.

Thermal Behavior

The thermal behavior of nordstrandite is of particular interest since this was the first intimation that Al(OH)_a might be present with dawsonite in the Colorado Green River Formation. Thus, from thermal analysis of the dawsonite-bearing Colorado Green River oil shale, Smith and Johnson (1967) reported indications of an unknown mineral with endotherms at 330°-350° and at about 500°C. It was rapidly soluble in 10 percent HCl or strong base, contained aluminum but no sodium, and is "not detectable in oil shale by X-ray diffraction," because it is "amorphous, X-ray amorphous, or has very weak reflections." They found that the unknown mineral "seems to occur ubiquitously with dawsonite," and suggested gibbsite or bayerite, both Al(OH)₃, as the unknown mineral. Smith and Young (1969) also cited Schmidt-Collerus and Hollingshead as having "selectively enriched this mineral in a dawsonitic oil shale by density gradient centrifugation, detecting this enrichment by thermal analysis." They, too, were unable to identify it. Although not specifically identifying the mineral, Smith and Johnson (1967) showed its properties to be those of an amorphous or X-ray amorphous form of Al(OH)₃. As a matter of convenience, the material is termed "gibbsite" in their report. Ordinary diffractometer analysis of bulk samples of complex composition, such as oil shale, may not reveal some minor constituents, particularly if they occur in crystallites of extremely small dimensions. The possibility may therefore be considered that occult nordstrandite, whose existence in these sediments has been shown, is the aluminum hydroxide postulated by Smith and Johnson (1967) and Smith and Young (1969). Neither gibbsite nor bayerite has been observed in the Green River Formation, despite many years of intensive mineralogical

TABLE 1. X-Ray Powder Diffraction Data for Nordstrandite, Gibbsite, and Bayerite

				Nordstran	dite					Gibb	site	Bayer	
Guan		Sar	awak	Jama	ica	Color	ado	Synth	netic	Synt	hetic	Synth	
Hathaway and Schlanger (1962, 1965)		Wall and others (1962)		Davis and Hill (1973)		This paper (pattern C)		Bosmans (1970)		XRPD 12-460		XRPD 20-11 Rothbauer and others (1967)	
d (Å)	1/11	d (Å)	I/I ₁	d (Å)	1/1 ₁	d(Å)	1/1_1	d (Å)	1/1 ₁ (obs.)	d (Å)	I/I ₁	d (Å)	1/1 ₁
				<u>222</u>		7.155	ms						
4.789	100	4.78	vs	4.80	100	4.791	vvs	4.791	100.0	4.82	100	4.71	90
				4.51	7								
4.322 4.207	12 10	4.33 4.206	9 8	4.34 4.23	25 22	4.331	ms	4.320	27.0	4.34	40	4.35	70
+.207	10	4.200	8	4.23	22								
4.156	7	4.153	8	4.18	17	4.152	ms	4.205 4.160	18.0 12.0			4.14	< ;
-			ä.	3.92	12								
3.887	4	3.886	m			3.879	W	3.888	11.0				
3.600	4	3.600	m	3.62	10	3.581	w	3.609	8.0				
			1111	3.55	7								
3.429	4	3.425	m	3.46	7	1.11		3.427	5.0	1000		1111	
					100	3.379	vw		(<u>1911)</u> (<u>1914)</u>	3.35 3.31	10 6	3.29	< 2
			22	3.24	2	0.000	100			3.31		3.29	< Z
		2 140		3.19	2					3.17	8	3.20	30
3.022	2	3.140 3.023	VW W	3.04	2	3.031	vvw	3.028	3.3	3.08	4		
2.850	2	2.849	w	2.86	2	3.031		2.848	3.0		4		
2.704	1	2.704	bw	2.71	2	-		2.710	2.5		-	2.699	4
.663	< 1	2.637	w		-		10000						
-					0.2222	2,562	VVW	2.22		0202	1000	2.531	< 2
.497	< 1	222		2.49	10			(2.501)	1.0		222	2.510	< 2
.480	3	2.479	bm	2.46				2.480	12.0				
2,450	1			2.46	7	2.461	VVW	2,455	8.0	1		2.464	2
- 1675		2.445	w			-	-			2.44	16 4	2.430	< 2
2.392	9	2.392	s	2.40	25	2.382	ms	2.393	27.0	2.37	20	2.356	4
2.349	< 1	2.330	vw	(<u>1995)</u>	-	2,335	vw	2.333	5.0			44	
.263	15	2.261	8	2.27	31	2.281	ms	2.271	29.0	2.28	4		
		2.225	w					2.217	3.0	2.23	6	2.222	100
								1000				2.186 2.168	< 2 < 2
										-		2.164	< 2
2,148	1	2.148	vw	13 434				2.146	2.5	2.15	8	2.156	2
		2.097	vw		-	-		2.113	1.6	-			
2.074	1			0. 1114				2.074	3.0			2.073	2
2.033 2.016	< 1	2.016	8	2.02	22			2.016	24.0	2.03	12		
-						2.003	ms	(1.991)	2.0			1.993	< 2
-		1.982	vw				-			1.98	10	1.983	< 4
-					-			1.975	1.0			1.969	2
-	***	1.959	VW			-				1.95	2		
.9434	< 1	1.939	ww			in the second	5 414 5	1.945	5.0			1.917	2
												1.71/	2
. 9008	8	1.899	9	1.90	19	1.887	ms	1.902	19.0	1.90	8	1.904	< 2
.8797	< 1		and and a second se					(1.877)	2.0			1.835	2
		1.1110-111	(1.821	2.0			1.826	2
.8017	< 1		(million	1.78	11	1.802	W	1.804	3.0				
								1.784	13.0	1.79	10	1.765	< 2
								1.715	1.0	1.74	10	1.723	40
								1.704	2.0			1.695	2
								1.668	4.0	1.67	10	1.688	2
								1.653	3.0	1.65	4	1.656	2
								1,632	1.5	1.63	2	1.646	2
								1.616	1.0			1.641	2
								1.598	5.0	1.58	4	(plus 3	lines
								1.572	4.0	1.57	2	to 1.12	

		Nordstrandite								Gibbsite Bayerit			
Guam Hathaway and Schlanger (1962, 1965)		Sarawak Wall and others (1962)		Jamaica Davis and Hill (1973)		Colorado This paper (pattern C)		Synthetic Bosmans (1970)		Synthetic XRPD 12-460		Synthetic XRPD 20-11 Rothbauer and others (1967)	
								1.547	6.0	1.55	2		
1.513	4							1.517	7.0				्तन्तः ।
						1,486	VVW						
1.477	4					1.477	VVW	1.479	6.0				
								1.465	2.0				
1.4395	4							1.441	14.0				
						1.435	VVW	1.430	5.0				
								1.404	3.0				
								1.388	1.5				
								1.370	1.0				
								1.365	0.6				

TABLE 1. Continued

study. Bayerite is reported only from a single locality in Israel (Gross and Heller, 1963).

Maric (1967-68), describing the Croatian nordstrandite, found a strong exotherm peak at 310°-340°, indicating nordstrandite or gibbsite, which cannot be distinguished by their thermal behavior. A peak at 500° was attributed to boehmite formed (by loss of hydroxyl) from nordstrandite or gibbsite. Similarly, Hathaway and Schlanger (1965, p. 1032) noted that "The D.T.A. of nordstrandite is very similar to that of gibbsite and is of limited diagnostic value." Lodding (1969) has shown that gibbsite dehydroxylates when heated at a constant rate, part becoming boehmite (AlOOH) at about 250°C, the remainder becoming Al₂O₃ between 250°C and 330°C. Smith (personal communication, 1970) has found that synthetic nordstrandite behaves similarly.

Synthesis

Nordstrandite was synthesized (Van Nordstrand *et al*, 1956) prior to its discovery in 1962, and since then by others who have also published X-ray powder data. Frisch (1965) found that grinding α -Al₂O₃ in water produced a surface film of nordstrandite.

Schoen and Roberson (1970, p. 43), reviewing prior syntheses, concluded that nordstrandite forms "from bayerite during aging at intermediate to high pH values," bayerite being metastable. Gibbsite is formed at a pH less than 5.8, bayerite at a pH greater than 5.8. The alkalic environment of the Colorado nordstrandite (in a dolomitic marlstone series containing dawsonite, analcite, nahcolite, and other sodic minerals) supports Schoen and Roberson's conclusion that nordstrandite in nature forms from prior-formed bayerite under alkalic rather than acidic conditions.

Chesworth (1971) reported that aluminum-mercury amalgam reacts with 2M NaOH at atmospheric pressure and 30°C to give boehmite with nordstrandite in a 408 hour run, and with concentrated NH₄OH, same temperature and pressure, to give nordstrandite in a 48 hour run.

Geochemistry of Nordstrandite and Accompanying Minerals

Goldberry and Loughnan (1970, p. 489), when discussing the origin of the New South Wales, Australia, dawsonite and nordstrandite, admitted that the formation of the dawsonite is "far from understood"; but account for the nordstrandite thus: "nordstrandite. . . as rims around the margins of dawsonite nodules suggests that it is a secondary product formed through loss of soda from the latter mineral. . .

 $NaAlCO_{3}(OH)_{2} + H_{2}O \rightleftharpoons Al(OH)_{3} + NaHCO_{3}."$

The same equilibrium equation is proposed by Smith (personal communication, 1974) to explain the excess of acid-extractable alumina consistently appearing in analyses of Colorado dawsonite rocks (Smith and Young, 1969; Young and Smith, 1970). He suggests that Al(OH)₃ was precipitated (as nordstrandite) from strongly basic lake waters charged with Na⁺, CO₃²⁻, and aluminate ion. In the water trapped in the sediment, the increasing con-

 TABLE 2.
 Three X-ray Diffraction Patterns of Nordstrandite from Colorado*

(a) Cu/Ni		(ъ) С	r/V	(c) Cu/Ni		
ī	<u>d</u>	Ī	d	Ī	₫	
				ms	7.155	
S	4.775	vvs	4.80	VVS	4.791	
	(4.36	w	4.32	ms	4.331	
₩b	{	W	4.186		00	
D	14.10	w	4.156	ms	4.152	
vw	3.829	WWW	3.892	w	3.879	
VW	3.576	VVW	3.588	W	3.581	
vw	3.335	VVV	3.356	VVV	3.379	
VVS	3.014		5-57-	WWW	3.031	
WWW	2.961				5:452	
vvv	2.694					
8	2.477			vvv	2.562	
8	2.4//			1001	2.461	
W	2.374		2.386	~ ~ ~	2.382	
w	2.314	W	2.300	ms	2.302	
	0.0(7		0.000	A.M.	2.335	
VS	2.267	AM	2.278	ms	2.281	
8	2.077					
ms	1.996	VVW	2.007	ms	2.003	
ms	1.901			ms	1.887	
vwb	1.789			W	1.802	
VW	1.721					
ms	1.592					
W	1.511			VVV	1.486	
VW	1.468			VVW	1.477	
ms	1.432			VVW	1.435	
VVV	1.411					
VVW	1.332					
VWb	1.289					
VVW	1.1925					
AAA	1.182					
vw	1.146					
VW	1.040					

centration of CO_2 arising from organic matter caused the reaction

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2 NaHCO_3$$

with an accompanying shift in pH from near 11 to about 9 (Smith, 1974). Under these conditions, the aluminate ion precipitates as $Al(OH)_3$. As represented in the following equilibrium equation (Smith, 1974),

$$NaHCO_3 + Al(OH)_3 \subseteq NaAl(OH)_2CO_3 + H_2O$$

the bicarbonate combines with the aluminum trihydroxide to produce dawsonite. This is the (reversed) Goldberry-Loughnan equation. Smith suggests that since nordstrandite is the phase of $Al(OH)_3$ that is thus formed, this mineral, rather than the commoner gibbsite as previously assumed, is

responsible for "excess alumina" in the Green River analyses.

Hay (1970) derived the Green River dawsonite by a different mechanism from that which he proposed for the Olduvai Gorge (Tanzania, Africa) dawsonite. For the Green River, he proposes an origin by reaction of analcite (or another zeolite) under high $P_{\rm CO_2}$ determined by equilibrium with nahcolite

$$\underset{\text{analeite}}{\text{NaAlSi}_2O_6} \cdot \underset{\text{H}_2O}{\text{H}_2O} + \underset{\text{Quartz}}{\text{CO}_2} \rightarrow \underset{\text{guartz}}{2\text{SiO}_2} + \underset{\text{daweonite}}{\text{NaAl(OH)}_2\text{CO}_3}$$

In Olduvai Gorge, dawsonite (and analcite) forms from alteration of halloysite in mudflow deposits thus:

$$Al_{2}Si_{2}O_{5}(OH)_{4} + 2Na^{+} + CO_{3}^{2-}$$

$$\rightarrow NaAlSi_{2}O_{6} \cdot H_{2}O + NaAl(OH)_{2}CO_{3}$$

Elsewhere in Olduvai Gorge, in an "alkali carbonate ash bed" Hay (1970, p. 251) suggested that dawsonite and natrolite form from chabazite and analcite; in a similar bed, nepheline is given as the source of dawsonite and natrolite. Hay does not consider $Al(OH)_3$ (gibbsite specifically) as having any role in the formation of dawsonite.

It may be concluded from the foregoing citations that the geochemistry of these substances is to a considerable degree a matter of conjecture.

Goldberry and Loughnan discussed in some detail many sulfate minerals, which they termed secondary, from the Bary Formation of New South Wales, Australia. However, they suggested that the glauberite $(Na_2Ca(SO_4)_2)$ was formed by reaction of precipitated mirabilite $(Na_2SO_4 \cdot 10H_2O)$ with gypsum $(CaSO_4 \cdot 2H_2O)$, and that dawsonite has replaced

TABLE 3. Analyses of Nordstrandite, Rio Blanco County, Colorado

	Spectrogra	aphic*	Electron Probe**
2	Samples from	n 1087 ft	Samples from 1054.4 ft
	X-ray film		
	378	386	895
Al	>10†	>10	30
Si	3	3	~3
Ca	3	0.1	<1
Fe	1	0.003	<1
K	0.1		<1
Na	0.03	0.01	<1
Mg	0.03	0.01	<1
Ba	and and the	0.01	2 20 2 20
Cr,Ti,Cu	0.01		

*Claude Waring, U.S. Geological Survey.

**Robert Finkelman, U.S. Geological Survey; semi-quantitative energy dispersive analysis. tin percent. this glauberite, and in turn has been replaced, wholly or in part, by nordstrandite. Nothing in the Green River dawsonite-nordstrandite occurrence suggests such a mechanism. Sulfate minerals in the Green River Formation, other than weathering products of iron sulfides, are extremely sparse.

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