

Nordstrandite, $\text{Al}(\text{OH})_3$, from the Green River Formation in Rio Blanco County, Colorado¹

CHARLES MILTON

*The George Washington University, Washington, D.C.,
and U.S. Geological Survey, Washington, D.C.*

EDWARD J. DWORNIK, AND ROBERT B. FINKELMAN

U.S. Geological Survey, Washington, D.C.

Abstract

Nordstrandite, $\text{Al}(\text{OH})_3$, 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, $\text{NaAlCO}_3(\text{OH})_2$, 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_3 " 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 $\text{Al}(\text{OH})_3$ which they termed "bayerite II"; Papee, Tertian, and Bias (1958) established its difference from bayerite and gibbsite—two other polymorphs of $\text{Al}(\text{OH})_3$ —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, $\text{NaAlCO}_3(\text{OH})_2$. 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 feruginous 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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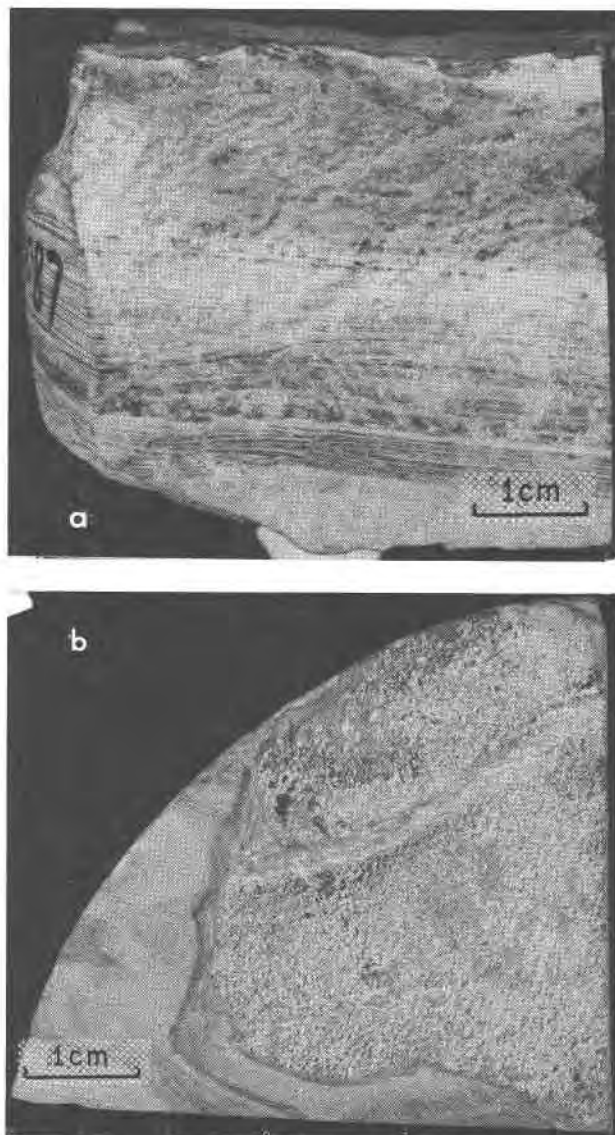


FIG. 1. Core samples from the Sinclair Cross V No. 1 well, Rio Blanco County, Colorado, showing nordstrandite as a whitish coating. **a.** Core from a depth of 1087 ft; **b.** from 1154.4 ft.

Because many of its properties, in particular the X-ray 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 $\text{Al}(\text{OH})_3$ 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-

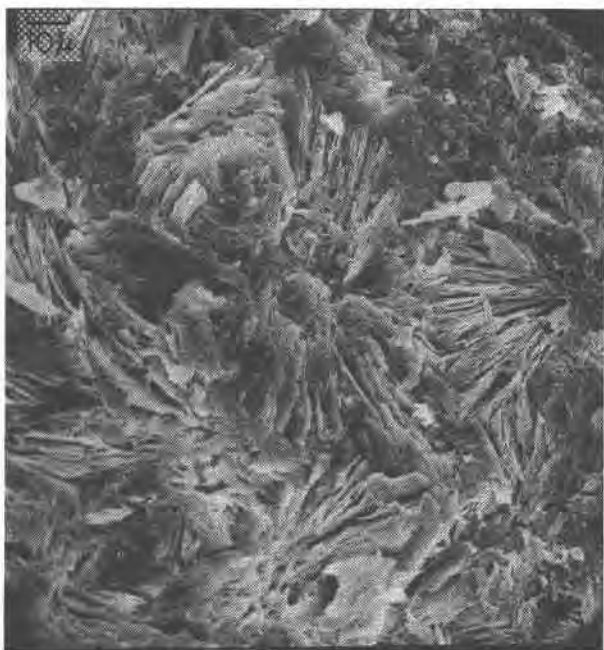


FIG. 2. Scanning electron photomicrograph of a radiating cluster of nordstrandite. Sample from the Sinclair Cross V No. 1 well, Rio Blanco County, Colorado (1154.4 ft depth). ($\times 560$).

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 $\text{Al}(\text{OH})_3$ 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 $\text{Al}(\text{OH})_3$, 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 $\text{Al}(\text{OH})_3$ 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 $\text{Al}(\text{OH})_3$, 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 $\text{Al}(\text{OH})_3$. 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

Guam		Nordstrandite				Gibbsite				Bayerite			
Hathaway and Schlanger (1962, 1965)		Sarawak		Jamaica		Colorado		Synthetic		Synthetic		Synthetic	
		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)	I/I ₁	d (Å)	I/I ₁	d (Å)	I/I ₁	d (Å)	I/I ₁	d (Å)	I/I ₁ (obs.)	d (Å)	I/I ₁	d (Å)	I/I ₁
4.789	100	4.78	vs	4.80	100	7.155	ms	--	--	--	--	4.71	90
4.322	12	4.33	s	4.51	7	4.791	vvs	4.791	100.0	4.82	100	--	--
4.207	10	4.206	s	4.34	25	4.331	ms	4.320	27.0	4.34	40	4.35	70
				4.23	22	--	--	--	--	--	--	--	--
4.156	7	4.153	s	4.18	17	4.152	ms	4.205	18.0	--	--	--	--
--	--	--	--	3.92	12	4.160	--	4.160	12.0	--	--	4.14	< 2
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	--	--	--	--
--	--	--	--	3.55	7	--	--	--	--	--	--	--	--
3.429	4	3.425	m	3.46	7	--	--	3.427	5.0	--	--	--	--
--	--	--	--	--	--	3.379	vw	--	--	3.35	10	--	--
--	--	--	--	--	--	--	--	--	--	3.31	6	3.29	< 2
--	--	--	--	3.24	2	--	--	--	--	--	--	--	--
--	--	--	--	3.19	2	--	--	--	--	3.17	8	3.20	30
3.022	2	3.023	w	3.04	2	3.031	vvw	3.028	3.3	3.08	4	--	--
2.850	2	2.849	w	2.86	2	--	--	2.848	3.0	--	--	--	--
2.704	1	2.704	bw	2.71	2	--	--	2.710	2.5	--	--	2.699	4
2.663	< 1	2.637	w	--	--	--	--	--	--	--	--	--	--
2.497	< 1	--	--	2.49	10	2.562	vvw	--	--	--	--	2.531	< 2
2.480	3	2.479	bm	--	--	--	--	(2.501)	1.0	--	--	2.510	< 2
2.450	1	--	--	2.46	7	2.461	vvw	2.480	12.0	--	--	--	--
--	--	2.445	w	--	--	--	--	2.455	8.0	--	--	2.464	2
2.392	9	2.392	s	2.40	25	2.382	ms	--	--	2.44	16	--	--
2.349	< 1	2.330	vw	--	--	2.335	vw	2.393	27.0	2.42	4	2.430	< 2
2.263	15	2.261	s	2.27	31	2.281	ms	2.333	5.0	2.37	20	2.356	4
--	--	2.225	w	--	--	--	--	2.271	29.0	--	4	--	--
--	--	--	--	--	--	--	--	2.217	3.0	2.23	6	2.222	100
--	--	--	--	--	--	--	--	--	--	--	--	2.186	< 2
--	--	--	--	--	--	--	--	--	--	--	--	2.168	< 2
2.148	1	2.148	vw	--	--	--	--	2.146	2.5	--	--	2.164	< 2
--	--	2.097	vw	--	--	--	--	--	--	2.15	8	2.156	2
2.074	1	--	--	--	--	--	--	2.113	1.6	--	--	--	--
2.033	< 1	--	--	--	--	--	--	2.074	3.0	--	--	2.073	2
2.016	8	2.016	s	2.02	22	--	--	--	--	2.03	12	--	--
--	--	--	--	--	--	2.003	ms	2.016	24.0	--	--	--	--
--	--	1.982	vw	--	--	--	--	(1.991)	2.0	--	--	1.993	< 2
--	--	1.959	vw	--	--	--	--	--	--	1.98	10	1.983	< 4
1.9434	< 1	1.939	vw	--	--	--	--	1.975	1.0	--	--	1.969	2
--	--	--	--	--	--	--	--	1.945	5.0	1.95	2	--	--
1.9008	8	1.899	s	1.90	19	1.887	ms	--	--	--	--	1.917	2
1.8797	< 1	--	--	--	--	--	--	1.902	19.0	1.90	8	1.904	< 2
--	--	--	--	--	--	--	--	(1.877)	2.0	--	--	--	--
1.8017	< 1	--	--	1.78	11	1.802	w	1.821	2.0	--	--	1.835	2
--	--	--	--	--	--	--	--	1.804	3.0	--	--	1.826	2
--	--	--	--	--	--	--	--	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 39 lines to 1.125)	
--	--	--	--	--	--	--	--	1.572	4.0	1.57	2		
--	--	--	--	--	--	--	--	1.560	1.0	--	--		

TABLE 1. Continued

Guam Hathaway and Schlanger (1962, 1965)		Nordstrandite				Colorado		Synthetic		Gibbsite		Bayerite	
		Sarawak		Jamaica		This paper (pattern C)		Bosmans (1970)		Synthetic XRPD 12-460		Synthetic XRPD 20-11 Rothbauer and others (1967)	
d (Å)	I/I ₁	d (Å)	I/I ₁	d (Å)	I/I ₁	d (Å)	I/I ₁	d (Å)	I/I ₁ (obs.)	d (Å)	I/I ₁	d (Å)	I/I ₁
--	--	--	--	--	--	--	--	1.547	6.0	1.55	2	--	--
1.513	4	--	--	--	--	--	--	1.517	7.0	--	--	--	--
--	--	--	--	--	--	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	--	--	--	--

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.

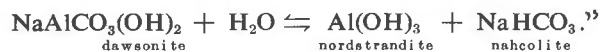
Schoen and Roberson (1970, p. 43), reviewing prior syntheses, concluded that nordstrandite forms "from bayerite during aging at intermediate to high pH values," bayerite being metastable. Gibbsite is formed at a pH less than 5.8, bayerite at a pH greater than 5.8. The alkalic environment of the Colorado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

clusion 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. . .



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-

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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