

NORDSTRANDITE ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) FROM GUAM¹

JOHN C. HATHAWAY and SEYMOUR O. SCHLANGER, *U. S. Geological Survey, Woods Hole, Massachusetts, and Dept. of Geology, University of California, Riverside, California.*

ABSTRACT

Nordstrandite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) occurs in Miocene limestone on Guam. A chemical analysis of the mineral including small amounts of quartz, goethite, halloysite and montmorillonite as impurities gives SiO_2 4.14%, Al_2O_3 63.97%, Fe_2O_3 0.25%, $\text{H}_2\text{O} + 29.05\%$, $\text{H}_2\text{O} - 1.59\%$, total 99.00%. The *x*-ray powder diffraction data differ from those of both gibbsite and bayerite. Nordstrandite gives strong reflections at 4.789, 4.322, 4.207, 2.392 and 2.263 Å. The mineral occurs principally as void fillings in the basal part of the limestone where the lime stone overlies deeply weathered basaltic rocks.

INTRODUCTION

Van Nordstrand *et al.* (1956) and Papée *et al.* (1958) have reported the synthesis of an alumina trihydrate differing from both gibbsite and bayerite. Van Nordstrand and his coworkers obtained the new form only in mixtures with gibbsite and bayerite and considered the new trihydrate to be a screw dislocation polymorph composed of alternating layers of gibbsite and bayerite-like packing. Papée *et al.* (1958) were able to synthesize the new material in essentially pure form and were able to present more precise *x*-ray powder data on the phase. Papée *et al.* (1958) and Rooksby (1961) imply that the name "nordstrandite" was given to this phase by Van Nordstrand *et al.* (1958), but the latter paper makes no mention of the name "nordstrandite." Instead Van Nordstrand proposed the name "bayerite II." Papée *et al.* (1958) point out that the new trihydrate is no closer to bayerite than to "hydrargillite" (gibbsite) and therefore the name "nordstrandite" is preferable. Rooksby (1961) states that de Boer *et al.* (1954) have distinguished between two varieties of bayerite and two of gibbsite, each respective pair being isostructural but varying in dehydration characteristics. The members of these pairs have been referred to as bayerite-1 and bayerite-2, and gibbsite-1 and gibbsite-2. Because of this previous use of the term "bayerite 2" we believe that the name "bayerite II" should not be used for the third alumina trihydrate phase described by Van Nordstrand *et al.* (1956) and Papée *et al.* (1958) but that the name "nordstrandite" should be retained for this compound. The name is after Robert A. Van Nordstrand of Sinclair Research Laboratories, Inc. of Harvey, Illinois.

One other natural occurrence of nordstrandite has recently been reported. A sample of nordstrandite from West Sarawak was exhibited by Deans (1962) at the June 1962 meeting of the Mineralogical Society of

¹ Publication authorized by Director, U. S. Geological Survey

Great Britain, and was described by Wall *et al.* (1962) concurrently with a report (Hathaway and Schlanger, 1962) of the occurrence described in this paper.

Ginsberg *et al.* (1962) reported the synthesis of a form of $\text{Al}(\text{OH})_3$ that they described as "bayerite with distorted lattice." They considered this material to be the equivalent of nordstrandite. Their *x*-ray patterns, however, indicate a mixture of gibbsite and bayerite. The patterns show strong peaks at 3.20, 2.22, and 1.72 Å which are characteristic bayerite peaks, but none of which are present in the synthetic nordstrandite of Papée *et al.* (1958) or Lippens (1961), or in the natural nordstrandite of Wall *et al.* (1962) or Hathaway and Schlanger (1962). Thus, the material that Ginsberg *et al.* (1962) described may indeed be bayerite with a distorted lattice, but the material is not nordstrandite.

OCCURRENCE ON GUAM

During the U. S. Geological Survey's studies of the mineralogy of limestones from the island of Guam, a mineral having the *x*-ray diffraction characteristics of nordstrandite was discovered. Amounts large enough for observation in thin section were found in samples from the basal part of an upper Miocene limestone on Guam. In south Guam this limestone forms a cap, several hundreds of feet thick, on the Mount Alifan-Mount Lamlam ridge and overlies upper Eocene and lower Miocene basalt flows and volcanic conglomerates. In north Guam less than 100 feet of this limestone flanks a series of Eocene basalt flows, volcanic conglomerates, and tuffaceous sandstones and shales around Mount Santa Rosa (Tracey *et al.* 1964; Schlanger, 1964). Near Mount Alifan, the basal limestone is pink to red due to included clays; it is porous, fossiliferous and crudely bedded. Molds of stick-like corals, pelecypods and gastropods are set in a matrix of sand and granule-size skeletal debris and fine-grained carbonate mud. Around the flanks of Mount Santa Rosa the basal limestone is also pink to red and made up largely of tests of foraminifera and fragments of coral. In both areas the limestones are interpreted as shallow-water deposits that were probably laid down as lagoonal or near-reef sediments in a tropical sea. The volcanic rocks below the limestone are deeply weathered.

The nordstrandite occurs in secondary solution cavities in the limestone, as illustrated in Figs. 1 and 2. The mineral fills spaces between aggregates of previously deposited calcite; it does not replace the calcite. In plain polarized light (Fig. 1), nordstrandite shows marked negative relief against the abutting calcite. The crystals are clear and barely distinguishable from one another. Some crystals show gray to first order deep-yellow colors; birefringence in thin section is estimated at .015 to

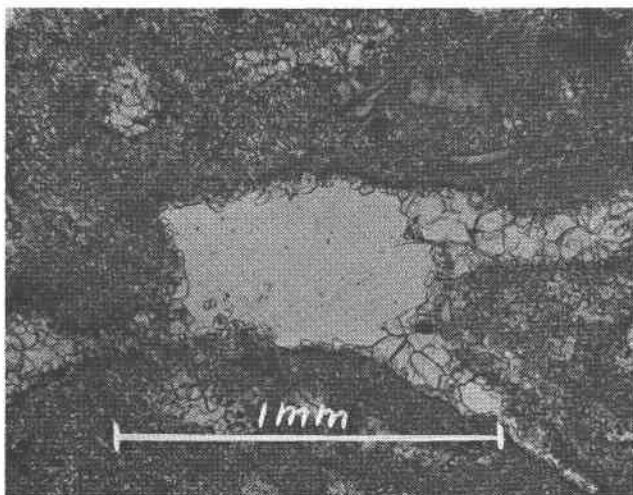


FIG. 1. Thin section showing nordstrandite in limestone from Guam, Plane polarized light, $\times 50$. The nordstrandite occupies the light area in the center of the photomicrograph.

.020. Between crossed nicols the crystals are seen to be arranged radially from discrete points or areas on the wall of the original void. The crystals, as bladed and flamboyant aggregates, fan out from these centers toward the opposite wall reaching a length of as much as 0.4 mm. In some voids the nordstrandite shows up as a mosaic of intricately intergrown, twinned

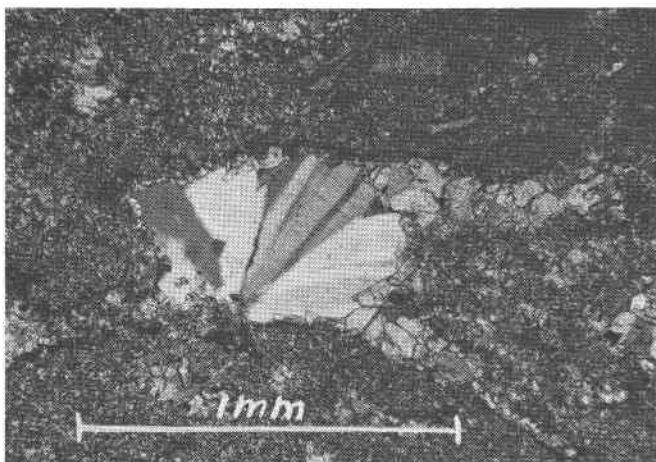


FIG. 2. Thin section showing nordstrandite in limestone from Guam. Crossed polars, $\times 50$. Same field as Fig. 1. The nordstrandite forms bladed crystals radiating from a point in the original cavity.

anhedra. Several crystals seen do not impinge on the void walls; these are tabular in form and terminate in sharp, well-defined, pyramidal (?) faces. Many of the crystals show polysynthetic twinning parallel to their length. Interference figures on many larger crystals are off-center biaxial, or pseudo-uniaxial (+); $2V$ is low; dispersion is high. The elongate twinned crystals show consistent negative elongation. The tabular crystals show inclined extinction with angles as great as 34° .

SUMMARY OF OPTICAL AND PHYSICAL PROPERTIES

$\alpha = 1.580 \pm .004$ (colorless)	optic sign = (+)
$\beta = 1.580 \pm .004$ (colorless)	$2V = \text{low}$
$\gamma = 1.596 \pm .004$ (colorless)	elongation = negative
$\gamma - \alpha = .016$	extinction = inclined

Hardness = 3

Specific gravity = 2.43. Determined by Edward J. Young using suspension-Westphal balance method.

As the DTA curve of nordstrandite is very similar to that of gibbsite and is of limited diagnostic value, it has not been reproduced in this paper.

X-RAY ANALYSIS

Samples of nordstrandite were separated from the limestone by hand-picking and by solution of the limestone in dilute acetic acid and hot 1:1 HCl. The finer clay materials were removed from the acid insoluble residues by wet sieving with distilled water. Except for the amount of impurities, the x -ray diffraction patterns of the material obtained by the three methods were identical, indicating that the nordstrandite observed is not an artificial product resulting from the method of separation but is a phase existing in the original rock.

The x -ray powder diffraction data for the separated material are given in Table 1 along with the data for synthetic nordstrandite given by Van Nordstrand *et al.* (1956), Papée *et al.* (1958), and Lippens (1961), and along with data on natural nordstrandite from Sarawak by Wall and others (1962).

An attempt at single crystal studies was abandoned after several "crystals" selected proved to be aggregates of many crystallites or to be badly bent and distorted. As a result, no attempt was made to index the x -ray data. Lippens (1961) has made a study of the structure of synthetic nordstrandite and indexed the interplaner spacings on the basis of the following monoclinic cell:

$$\begin{aligned}
 a & 8.63 \pm 0.02 \text{ \AA} \\
 b & 5.01 \pm 0.02 \text{ \AA} \\
 c & 19.12 \pm 0.03 \text{ \AA} \\
 \beta & 92^\circ 00' \pm 10'
 \end{aligned}$$

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR NORDSTRANDITE, GIBBSITE, AND BAYERITE

Synthetic Nordstrandite				Nordstrandite				Gibbsite		Bayerite				
Van Nordstrand and others (1956)		Papée and others (1958)		Lippens (1961)		Guam		Sarawak Wall and others (1962)		Rooksby (1961, p. 384-385)		Rooksby (1961, p. 384-385)		
d(Å)	I/I ₁	d(Å)	I/I ₁ ²	d(Å)	I/I ₁ ³	hkl	d(Å) ¹	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁
4.785	100	4.790 FF		4.787 vs	004		4.789	100	4.78	vs	4.85	100	4.71	100
		4.373 ft									4.37	40	4.35	55
4.33	20 ⁵	4.310 m		4.33	m	200, 110	4.322	12	4.33	s	4.31	20	3.20	20
4.20	15	4.205 m		4.205	m	201, 11 $\bar{1}$	4.207	10	4.206	s	3.35	6	2.70	3
4.15	13	4.153 m		4.156	m	111	4.156	7	4.153	s	3.31	10	2.462	3
				3.928	w	202, 11 $\bar{2}$					3.18	7	2.358	6
3.89	7	3.880 m		3.892	m	112	3.887	4	3.886	m	3.10	4	2.217	60
3.60	7	3.600 m		3.604	m	11 $\bar{3}$	3.600	4	3.600	m	2.451	15	2.157	4
				3.56	vw	203					2.422	4	2.075	3
		3.462 f		3.467	w	113	3.429	4	3.425	m	2.382	25	2.027	4
				3.270	w	11 $\bar{4}$					2.288	4	1.985	3
				3.22	w	204					2.244	6	1.839	1
3.18	11			3.184	w	006					2.165	8	1.722	20
									3.140	vw	2.082	1	1.694	1
		3.022 f					3.022	2	3.023	w	2.042	15	1.647	3
		2.845 f					2.850	2	2.849	w	2.024	1	1.602	6
		2.706 ff					2.704	1	2.704	bw	1.991	8	1.572	3
							2.663	<1	2.637	w	1.916	6	1.555	4
							2.497	<1			1.801	10	1.458	8
		2.490 ff					2.480	3	2.479	bm	1.750	9	1.446	5
		2.478 m		2.475	m	02 $\bar{1}$, 311	2.450	1	2.445	w	1.685	7	1.393	4
		2.451 f		2.451	w	021, 311	2.392	9	2.392	s	1.655	2	1.382	3
2.39	15	2.390 F		2.307	s	008	2.349	<1	2.330	vw	1.590	2	1.349	1
							2.263	15	2.261	s	1.574	1	1.334	8
2.26	15	2.261 F		2.264	s	023			2.225	w	1.555	1	1.278	1
							2.148	1	2.148	vw	1.533	1	1.256	1
									2.097	vw	1.485	1	1.213	4
		2.277 ⁶ ff					2.074	1	2.073	ww	1.477	1	1.180	1
		2.029 ff					2.033	<1			1.457	8		
2.01	11	2.013 m		2.014	s	223	2.016	8	2.016	s	1.440	4		
									1.982	vw	1.411	5		
									1.959	vw	1.402	4		
							1.9434	<1	1.939	vw	1.380	1		
				1.914	vw	00-10					1.361	2		
1.898	11	1.898 m		1.899	m	22 $\bar{5}$	1.9008	8	1.899	s	1.330	1		
							1.8797	<1			1.319	1		
							1.8017	<1			1.249	1		

¹ Rad.—Cu K α_1 λ —1.54050 Filter, Ni, cut off—2° 2 θ I/I₁—diffractometer

² FF—intense m—medium
F—strong f—faint
ff—very faint

³ vs—very strong vw—very weak
s—strong
m—medium or moderate b—broad
w—weak

⁴ This line may be the result of a trace of admixed gibbsite or bayerite unrecognized by Papée *et al.* (1958).

⁵ Van Nordstrand and others (1956) report that this intensity is uncertain because of its overlap with a line of bayerite.

⁶ Typographical error?; perhaps should be 2.077.

TABLE 1—(continued)

Synthetic Nordstrandite				Nordstrandite		Gibbsite		Bayerite						
Van Nordstrand and others (1956)		Papée and others (1958)		Lippens (1961)		Guam		Saratwak Wall and others (1962)		Rooksby (1961, p. 384-385)		Rooksby (1961, p. 384-385)		
d(Å)	I/I ₁	d(Å)	I/I ₁ ²	d(Å)	I/I ₁ ²	hkl	d(Å) ¹	I ₁ /I ²	d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁
1.777	m						1.7807	5	1.779	m/s	1.231	1		
1.717	ff						1.7152	<1	1.715	vw	1.222	1		
1.698	ff						1.7016	<1	1.704	w	1.213	2		
1.680	ff										1.193	1		
1.667	ff						1.6706	2	1.672	w				
1.647	f						1.6518	<1	1.6513	vw				
1.591	f			1.591	w	00·12	1.5948	2	1.593	w/m				
1.569	f						1.5722	<1	1.574	w				
1.545	f						1.5495	1	1.549	w/m				
1.510	m			1.510	w	135	1.5134	4	1.513	m				
1.475	m			1.475	w		1.4773	3	1.477	m				
							1.4638	<1	1.465	vw				
1.438	F			1.438	s	600	1.4395	5	1.440	m/s				
							1.4273	1	1.429	w/m				
1.400	f						1.4037	1	1.405	w				
							1.3866	<1	1.387	vw				
									1.373	vw				
							1.3534	<1	1.353	w				
							1.3051	1	1.305	m				
							1.2753	<1	1.276	vw				
							1.2499	1	1.250	w/m				
									1.242	v/w				
							1.2257	1	1.226	w/m				
									1.216	w				
							1.1969	1	1.197	} Bm				
							1.1936	1	1.192					
							1.1832	<1	1.183	w/m				
									1.175	vw				
							1.1615	<1	1.162	w/m				
							1.1146	<1	1.116	w/m				

CHEMICAL ANALYSIS

A chemical analysis of about 1 g of nordstrandite is given in Table 2.

The mineral is essentially an alumina hydrate. Recalculation of the Al_2O_3 and $\text{H}_2\text{O}+$ to 100% (anal. 2, Table 2) shows an excess of Al_2O_3 and a deficiency of water compared with the theoretical trihydrate composition. This deficiency results partly from the montmorillonite and halloysite (which occur in about equal amounts) as well as goethite and a little quartz which accompany the nordstrandite in the non-carbonate fraction of the limestone; these minerals could not be completely separated from the nordstrandite that was analyzed. Calculation of the composition of the nordstrandite after assignment of Al_2O_3 and H_2O to montmorillonite and halloysite (about 4% each) in accordance with the amount of SiO_2

TABLE 2. CHEMICAL ANALYSIS OF NORDSTRANDITE FROM GUAM

	1.	2.	3.
	Nordstrandite Guam	Al ₂ O ₃ and H ₂ O ⁺ of analysis 1 recalculated to 100%	Theoretical composition Al ₂ O ₃ ·3H ₂ O
SiO ₂	4.44	—	—
Al ₂ O ₃	63.97	68.78	65.35
Fe ₂ O ₃	.25	—	—
H ₂ O ⁺	29.05	31.22	34.65
H ₂ O ⁻	1.59	—	—
	99.00	100.00	100.00
Analyst	Alexander Sherwood	—	—
Loss on ignition (H ₂ O ⁻ , H ₂ O ⁺)	31.92		

present still leaves a deficiency of water of about 3%. At least 1% of this may be analytical error inasmuch as the ignition loss which includes both H₂O⁺ and H₂O⁻ exceeds the sum of determined H₂O⁺ and H₂O⁻ by 1.28% (Table 2). The rest of the discrepancy is unaccounted for. There is no evidence in the x-ray patterns of the presence of other aluminum minerals such as boehmite that would appreciably alter the Al₂O₃:H₂O ratio.

Semiquantitative spectrographic analyses of two different separates from the limestone are given in Table 3. These analyses confirm that the material is essentially an aluminum mineral with minor Si and other ele-

TABLE 3. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSIS OF TWO SAMPLES OF NORDSTRANDITE FROM GUAM (Analyst, Katherine V. Hazel)

	1.	2.
Over 10%	Al	Al
5-10%	—	—
1-5%	—	Si
.5-1%	Si	—
.1-.5%	Fe	Fe
.05-.1%	Ti, K, Na, Sn	—
.01-.05%	Ca, Mg, Ni	Ca, Mg, Na, Ti, Sn
.005-.01%	Cr	Cr
.001-.005%	Cu, Ga	Cu, Ni
.0005-.001%	Mn	Ba
.0001-.0005%	—	—

ments. The Fe content reflects the small quantity of goethite, and Na, K, Ca, +Mg in the 0.01 to 0.1% ranges reflect the small amount of montmorillonite. Ti, Sn, Ni, and Cr possibly occur in traces of unidentified heavy minerals were noted in the acid insoluble residues. All visible heavy minerals were removed by hand picking before analysis but undoubtedly some were missed. Ga, Mn and Ba were not duplicated in both samples but very likely are also contained in the heavy mineral contaminants.

PROBABLE ORIGIN

The original voids now filled by nordstrandite apparently were produced by structurally controlled solution, probably subaerial, of the limestone. The three converging, linear areas of clear calcite leading in to the central, clear areas shown on Fig. 1 are healed fractures that traverse the rock and connect with other nordstrandite-filled voids. The initial deposit on the walls of the solution voids was a thin film of reddish clay. Directly overlying the clay film clear calcite was deposited as subhedral crystals that fill the smaller fractures and line the larger voids. The final deposit was nordstrandite. The nordstrandite growth centers from which the crystals radiate are commonly the areas of the original void wall that lack a deposit of clear calcite. At these points the nordstrandite crystals are in contact with the clay film and the crystals contain scattered, possibly residual, blebs of the clay. Nordstrandite does not occur in those voids that are thickly and completely lined with calcite even though some void space may remain. Emergence of the limestone above sea level, lithification, and fracturing must have occurred before subaerial solution produced the voids preferentially along fissures. Precipitation of calcite from solution produced the first void linings. The precipitation of the nordstrandite was, then, a late-stage event in the history of the limestone.

Papée *et al.* (1958) noted that mixtures rich in nordstrandite were obtained when alumina gels were aged at pH 13. Van Nordstand *et al.* (1956) obtained nordstrandite mixed with the other trihydrates at lower pH (7.5–9) but noted that the relative proportions varied according to pH, ionic concentrations, seeding, and temperature. The pH of the limestone environment in which the natural nordstrandite was deposited was probably no higher than 8.5 or 9 judging from the limestone environment field given by Krumbein and Garrels (1952). Temperature and ionic concentration are unknown, but as the precipitation of the nordstrandite was a subaerial late stage, the temperature was probably moderate. The aluminous solutions which deposited the nordstrandite could have been ground waters that leached residual soils on basaltic rocks and tuffaceous

material and that migrated along the contact between the basalt and the limestone. This source would account for the concentration of nordstrandite in the basal part of the limestone near its contact with the basalt. The relation of nordstrandite to clay in the limestone voids suggests that the growth of clear nordstrandite may have been initiated by nucleation on the clay surfaces. Further precipitation of alumina from solution must then have taken place around these nucleation centers to produce radiating groups of crystals such as those shown in Figs. 1 and 2.

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Manuscript received, July 23, 1962; accepted for publication, January 20, 1965.