HYDRODRESSERITE, A NEW Ba-Al CARBONATE FROM A SILICOCARBONATITE SILL, MONTREAL ISLAND, QUEBEC

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ABSTRACT

Hydrodresserite occurs in an alkalic sill at Montreal Island, Quebec, as white spheres and hemispheres which average about 2 mm in diameter and consist of radiating, fibrous, colorless crystals with a white streak, hardness of 3 to 4, and perfect cleavages $\{010\}$ and $\{2\bar{1}0\}$. Crystals are triclinic, elongate [001], terminated (102), with prominent $\{010\}$ and narrower $\{2\bar{1}0\}$, a 9.79, b 10.42, c 5.62Å, α 96.05, β 92.20, γ 115.71°. The mineral is biaxial negative, $2V=17°$, $n\alpha$ 1.520, $n\beta$ 1.594, $n\gamma$ 1.595, Z' parallel to elongation and X' normal to it. Strongest lines of the powder X-ray pattern are 8.52–10 ($\bar{1}$10); 3.42–7 (210); 3.10–6 (030,21$\bar{1}$); 8.75–4 (100); 4.26–5 ($\bar{2}$20). Chemical analysis gave BaO 35.0, Al_2O_3 23.7, CO_2 21.8, H_2O 20.3, sum 100.8 wt. %, corresponding to $Ba_{0.97}Al_{1.99}(CO_3)_{2.12}(OH)_{3.68} \cdot 2.97H_2O$, theoretically $BaAl_2(CO_3)_2(OH)_4 \cdot 3H_2O$; D(meas.) 2.80, D(calc.) 2.81 g/cm³ for the theoretical formula with $Z=2$. Hydrodresserite is unstable and gradually dehydrates to $BaAl_2(CO_3)_2(OH)_4 \cdot H_2O$ (dresserite) after passing through an intermediate phase (with $2H_2O$?). DTA, TGA, and static heating experiments indicate that several compounds form during the breakdown to $BaAl_2O_4$.

SOMMAIRE

L'hydrodressérite se rencontre dans un filon-couche alcalin de l'Ile de Montréal, Québec, sous forme de sphères et d'hémisphères blanches dont le diamètre moyen est d'environ 1 mm. Le minéral se présente en cristaux radiés, fibreux et incolores; le trait est blanc, la dureté de 3 à 4, les clivages $\{010\}$ et $\{2\bar{1}0\}$ sont parfaits. Les cristaux sont tricliniques, allongés [001], terminés (102), avec $\{010\}$ proéminent et $\{2\bar{1}0\}$ plus étroit; a 9.79, b 10.42, c 5.62Å, α 96.05, β 92.00, γ 115.71°. Le cristal est biaxe négatif, $2V$ 17°, $n\alpha$ 1.520, $n\beta$ 1.591, $n\gamma$ 1.594, Z' parallèle à l'allongement. Les raies les plus intenses du diagramme de poudre sont: 8.52–10 ($\bar{1}$10), 3.42–7 (210), 3.10–6 (030,21$\bar{1}$), 8.75–5 (100), 4.26–5 ($\bar{2}$20). L'analyse chimique donne: BaO 35.0, Al_2O_3 23.7, CO_2 21.8, H_2O 20.3, total 100.8%, ce qui correspond à $Ba_{0.97}Al_{1.99}(CO_3)_{2.12}(OH)_{3.68} \cdot 2.97H_2O$, théoriquement $BaAl_2CO_3)_2(OH)_4 \cdot 3H_2O$. La densité est de 2.80 (mes.) et de 2.814 (calc.) pour la formule théorique avec $Z=2$. L'hydrodressérite est instable et se déshydrate progressivement en passant par une phase intermédiaire (avec $2H_2O$?) pour donner $BaAl_2(CO_3)_2(OH)_4 \cdot H_2O$ (dressérite). Les analyses A.T.D. et A.T.G. et les expériences de chauffage statique démontrent que plusieurs composés se forment durant le processus de décomposition qui aboutit à la formatiton de $BaAl_2O_4$.

INTRODUCTION

The new mineral hydrodresserite, $BaAl_2(CO_3)_2(OH)_4 \cdot 3H_2O$, occurs in a silicocarbonatite sill, two metres thick, which is exposed in a limestone quarry at St-Michel, Montreal Island, Quebec. The host rock is part of the Ordovician Montreal Formation and the sill, which is in the Monteregian alkalic petrological province, is probably genetically related to the plutonic intrusions which form the core of Mount Royal, about 7 km south of the quarry. Quarry development and drillhole data indicate that the silicocarbonatite sheet extends over an area of 1100 by 450 m, with the continuation open in all directions. The silicocarbonatite is unique in that much or most of it contains dawsonite, $NaAl(CO_3)(OH)_2$, rather than calcite or dolomite as the principal carbonate mineral (Jambor et al. 1976). Other significant features of the intrusion are its above-average zirconium and niobium contents (Steacy & Jambor 1969), and a varied mineralogy comprising more than 40 species, several of which are known only from this locality (Sabina 1976; Sabina et al. 1968).

The presence of the mineral now named hydrodresserite was reported some years ago (Jambor et al. 1969) as possibly being the new barium analogue of alumohydrocalcite. X-ray data given by Lazarenko et al. (1963), Kautz (1968, 1969), and Aikawa et al. (1972) indicate that the two minerals are unrelated.

Hydrodresserite is unstable at most atmospheric conditions and dehydrates to dresserite. The new mineral and its name, hydrodresserite, which alludes to the composition and this reaction, have been approved by the Commission on New Minerals and Mineral Names, IMA.

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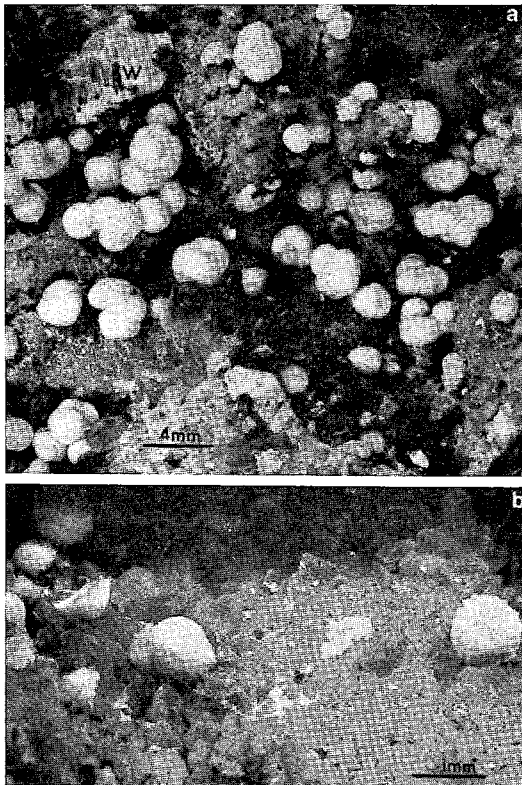
FIG. 1. (a) Typical smooth-surface form of dresserite and some hydrodresserite. These spheres are pseudomorphs of dresserite after hydrodresserite. The groundmass and large, clear crystals are quartz; weloganite (w) is at upper left. (b) Rough, well-crystallized surface of right-side sphere is characteristic of a minor amount of hydrodresserite. Matrix is quartz.

Type material is stored at the Royal Ontario Museum (specimen M34547), and in the National Mineral Collection, Geological Survey of Canada (No. 13936).

PHYSICAL PROPERTIES

Hydrodresserite occurs in cavities in the sill as white to partly translucent spheres and hemispheres which average about 2 mm in diameter. Most of these are indistinguishable from associated dresserite which is much more abundant. Both consist of compact groups of fibrous crystals that radiate outward from the centres of the spheres. Features that characterize a minor amount of hydrodresserite under a hand lens or binocular microscope are that its microcrystals are slightly coarser and some spheres are more translucent than those of dresserite; protruding ends of hydrodresserite crystals are transparent

and are terminated by an inclined face (Figs. 1, 2). Thus some hydrodresserite spheres have a rougher, better crystallized, more translucent surface than those of dresserite.

Individual grains of hydrodresserite are colorless, have a white streak, vitreous lustre, and a hardness of 3 to 4. Crystals are elongate [001], terminated (102), with prominent {010} and narrow {2$\bar{1}$0}. Cleavages, {010} and {2$\bar{1}$0}, are perfect. A specific gravity of 2.80(2) was obtained by the suspension method and an appropriately calibrated Westphal balance. The mineral is readily soluble in dilute HCl.

OPTICAL AND X-RAY CRYSTALLOGRAPHY

The optical orientation of five crystals of hydrodresserite was determined on a universal stage, and refractive indices were measured in sodium light. Hydrodresserite is biaxial negative, $2V 17(1)°$, $n\alpha$ 1.502(2), $n\beta$ 1.594(1), $n\gamma$ 1.595(1). Crystals lying on {010} have nearly parallel extinction and positive elongation; Z' is parallel to the elongation and X' normal to it. The orientations of the optical and crystallographic axes are given in Figure 2 and Table 1.

Weissenberg and precession photographs of hydrodresserite gave a 9.77, b 10.45, c 5.66Å, α 95°42', β 92°22', γ 115°47'. For indexing of the powder X-ray pattern (Table 2), the least-squares refinement involved the use of 17 diffraction lines between 4.38 and 2.540Å; only 10 of these lines could be indexed unambiguously. The resultant cell dimensions (a 9.79, b 10.42, c 4.62Å, α 96.05, β 92.20, γ 115.71°) yield a cell volume of 511.4Å^3. With $Z=2$ the calculated density is 2.79 g/cm^3 for the analytical formula and 2.81 g/cm^3 for the theoretical formula, in good agreement with the measured value of 2.80.

CHEMICAL COMPOSITION

Table 3 gives the results of a chemical analysis of a hydrodresserite sample hand-picked under a 50× binocular microscope. With O=13, the analytical formula is Ba$_{0.97}$Al$_{1.99}$(CO$_3$)$_{2.12}$(OH)$_{3.68}$ • 2.97H$_2$O, theoretically BaAl$_2$(CO$_3$)$_2$(OH)$_4$ • 3H$_2$O. X-ray spectrography indicated that only traces of Ca and Sr were present; simi-

TABLE 1. ORIENTATION OF THE OPTICAL AND CRYSTALLOGRAPHIC AXES OF HYDRODRESSERITE

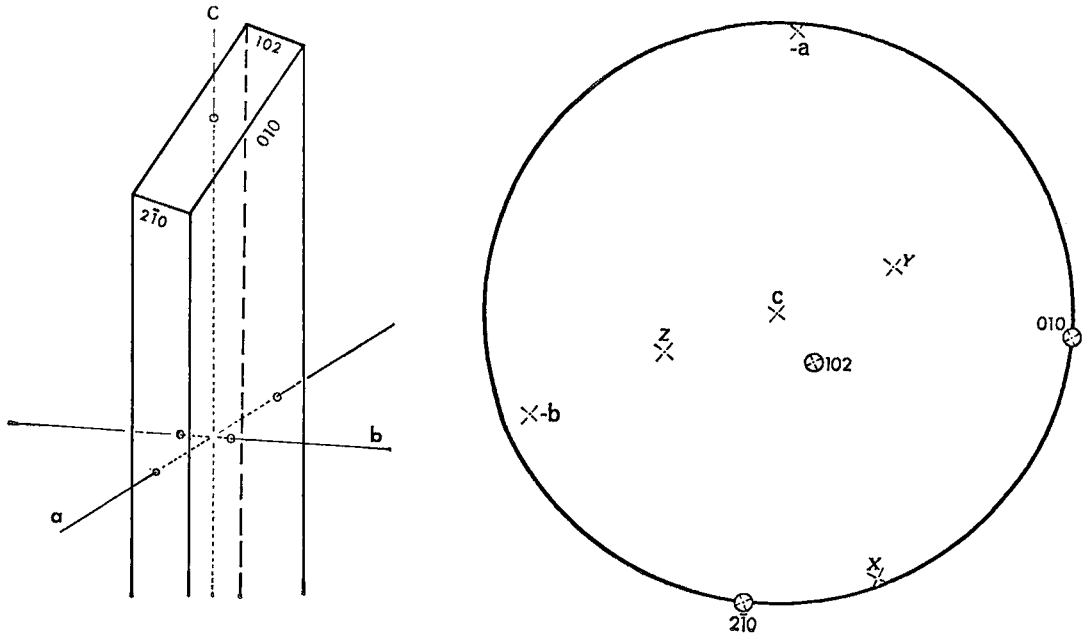|	φ	ρ		φ	ρ
−α	−90°	88°15'	X	65°	88°
−b	153°	84°30'	Y	−27°	46°
a	0	0	Z	158½°	44½°
(102)	50°	23½°			
(2$\bar{1}$0)	92°	90°			
(010)	0°	90°			

FIG. 2. Morphology of hydrodresserite and stereographic projection of the optical and crystallographic axes.

TABLE 2. POWDER X-RAY DATA FOR HYDRODRESSERITE

I_{est}	d_{meas}	d_{calc}	hkl	I_{est}	d_{meas}	d_{calc}	hkl
3	9.30	9.30	010			2.544	02$\bar{2}$
4	8.75	8.78	100	2	2.540	2.542	$\bar{1}$40
10	8.52	8.53	$\bar{1}$10			2.537	22$\bar{1}$
3	5.32	5.32	110	1	2.493	2.495	310
1	5.09	5.09	01$\bar{1}$	½	2.459	2.457	$\bar{2}$02
1	4.92	4.91	$\bar{1}$01	<½	2.420	2.426	$\bar{1}$4$\bar{1}$
<½	4.70	--				2.385	$\bar{4}$10
<½	4.67	4.65	020	2	2.385	2.384	21$\bar{2}$
<½	4.53	4.51	011			2.383	31$\bar{1}$
1	4.38	4.39	200	1	2.339	2.344	$\bar{4}$30
5	4.26	4.27	$\bar{2}$20			2.340	112
½	4.13	4.13	11$\bar{1}$	½	2.296	2.296	2$\bar{2}$2
2	3.96	3.98	12$\bar{1}$			2.294	$\bar{1}$32
<½	3.83	3.83	02$\bar{1}$	½	2.255	2.257	04$\bar{1}$
1	3.73	3.73	$\bar{2}$11	<½	2.223	2.226	032
3	3.62	several	poss.	½	2.188	2.184	311
2	3.52	3.52	$\bar{1}$20	<½	2.125	2.129	230
7	3.42	3.44	$\bar{1}$30	<½	2.109	2.107	322
		3.43	210	2	2.068	2.072	$\bar{2}$50
1	3.30	3.30	201			2.057	23$\bar{2}$
<½	3.21	3.23	310	½	2.055	2.052	$\bar{1}$32
		3.19	320			2.025	$\bar{3}$50
<½	3.18	3.18	12$\bar{1}$	½	2.022	2.023	33$\bar{2}$
		3.10	030	<½	2.010	several	poss.
6	3.10	3.10	21$\bar{1}$	<½	1.954	several	poss.
2	2.929	2.927	300			1.911	41$\bar{1}$
<½	2.861	2.864	311	<½	1.908	1.902	231
		2.787	$\bar{1}$31			1.883	several	poss.
<½	2.785	2.782	002	½	1.883	1.840	540
		2.758	231	1	1.812	1.846	
2	2.761	2.757	32$\bar{1}$	<½	1.795		
		2.727	31$\bar{1}$	½	1.761		
2	2.725	2.727	102	½	1.718		
1	2.660	2.661	220	<½	1.685		
		2.583	102	<½	1.655		
1	2.582	2.578	240	<½	1.595		
				<½	1.550		

Camera diameter 114.6 mm, Cu/Ni radiation. Indexed with a 9.79, b 10.42, c 5.62Å, $\bar{a}$ 96.05, β 92.20, γ 115.71°. Intensities estimated visually.

TABLE 3. CHEMICAL ANALYSIS OF HYDRODRESSERITE

wt.%		recalc. to 100%	theoretical wt.%	wt.%/M.W.	BaO as unity	O = 13	
BaO	35.0	34.7	35.38	0.2264	1.000	Ba	0.975
Al_2O_3	23.7	23.5	23.53	0.2306	1.019	Al	1.987
CO_2	21.8	21.6	20.31	0.4915	2.171	CO_3	2.116
H_2O	20.3	20.2	20.78	1.1179	4.938	OH	3.667
	100.8	100.0	100.00			H_2O	2.974

Analysis by Analytical Chemistry Section, Geological Survey of Canada

the instability of hydrodresserite had not been recognized. A TGA curve of a 168 mg sample was obtained two weeks after the chemical analysis, and the result was a 37.8% weight loss to 1050°C. The product was $BaAl_2O_4$, and thus the theoretical weight loss should have been 41.1%. The discrepancy could not be resolved because no more hydrodresserite could be found on the specimens available. In subsequent years additional specimens were collected at the quarry, and it was established that, under most natural conditions, hydrodresserite gradually transforms to dresserite, $BaAl_2(CO_3)_2(OH)_4 \cdot H_2O$.

lar results were obtained by a microprobe check of another hydrodresserite sample collected some years later.

At the time of the chemical analysis in 1967,

HYDRODRESSERITE STABILITY

Stability near room temperature

The stability of hydrodresserite near room

temperature has not been investigated with specific controlled conditions, but some observations indicate that the mineral is particularly susceptible to humidity variations. All material kept indoors in Ottawa, including in air-conditioned laboratories, undergoes at least partial breakdown to dresserite in less than a month, and in some cases after only a few days. On the other hand, hydrodresserite has been successfully stored outdoors for a period extending from April to October, and material kept in water for six months did not alter.

Experiments with powder X-ray diffraction spindles showed that the breakdown of hydrodresserite to dresserite can be arrested and partly reversed. Reversal was achieved by placing the spindle above the water line in cork-stoppered glass vials and warming them to 35 to 45°C. After 2 weeks in this environment, a spindle of hydrodresserite, which previously had decomposed totally to disordered dresserite, was regenerated to a mixture of approximately equal parts of hydrodresserite, and dresserite with improved crystallinity. After 7 weeks, hydrodresserite predominated and although it increased subsequently, total conversion was never attained. Powder X-ray patterns obtained after 10 weeks of warming at 35-45°C differed little from those obtained after 22 weeks. The final product consisted of hydrodresserite, dresserite, and a few unassigned X-ray diffraction lines. Similar results were obtained from this X-ray mount after it had been stored at room temper-

ature in the water-bearing vial for an additional 16 weeks.

A single crystal of hydrodresserite was monitored for 9 months with an X-ray precession camera. A progressive increase in dresserite at the expense of hydrodresserite was recognized easily because the initial, partial conversion is an oriented transformation: the a^*b^* net of dresserite (orthorhombic) gradually appears on the a^*b^* net of hydrodresserite (triclinic). Moreover, the $0k0$ diffraction row of dresserite is superimposed on that of hydrodresserite. Thus, although the cell dimensions and symmetry of the two minerals are radically different, a structural relation is indicated both from the X-ray and infrared studies (Farrell 1977).

The final precession photograph in the monitoring process was blank, but a Debye-Scherrer film confirmed that the material was still crystalline and had converted completely to dresserite.

Intermediate phase. Although most hydrodresserite seems to break down directly to dresserite, in a few cases it was observed that dresserite formation was preceded by that of an evanescent intermediate compound which gives well-defined X-ray patterns (Table 5). The reproducibility of the patterns obtained from different samples, and the absence of dresserite and hydrodresserite contamination, suggest that this compound is single-phase. Since it forms from hydrodresserite (3H$_2$O), but precedes dresserite (1H$_2$O), this "intermediate phase" may be BaAl$_2$-
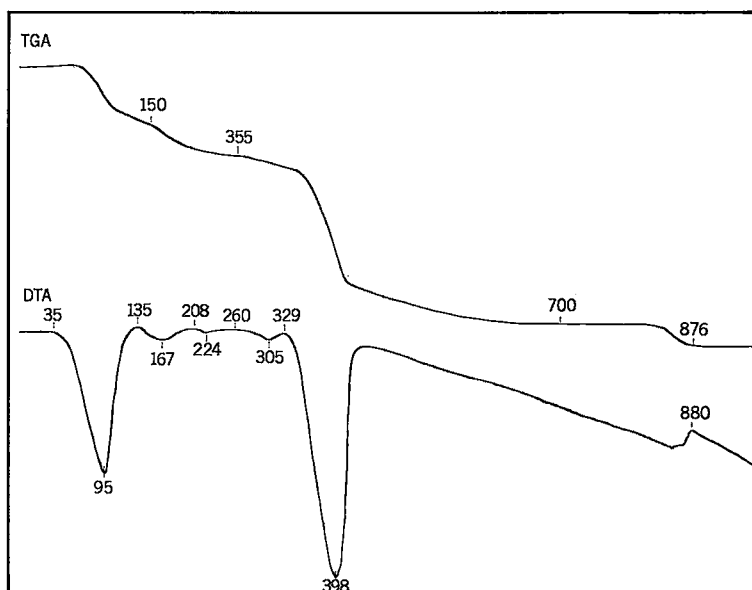

FIG. 3. TGA and DTA curves of hydrodresserite. Temperatures are in °C.
Results are summarized in Table 4.

TABLE 4. SUMMARY OF RESULTS OF TGA AND DTA OF HYDRODRESSERITE

compound	theoretical loss	product	theoretical loss wt. %		measured loss wt. %		endothermic reactions (°C)	
			for reaction	cumulative	cumulative	temp °C	start	peak temp
Initial: $BaAl_2(CO_3)_2(OH)_4 \cdot 3H_2O$ (hydrodresserite)	$1H_2O$	intermediate phase*	4.16	4.16			35	95
$BaAl_2(CO_3)_2(OH)_4 \cdot 2H_2O(?)$ (intermediate phase)	$1H_2O$	dresserite	4.34	8.31	8.81	to 150	{135 208	167 224
$BaAl_2(CO_3)_2(OH)_4 \cdot H_2O$ (dresserite)	$1H_2O$	$BaAl_2(CO_3)_2(OH)_4$ (phase X)	4.53	12.47	13.28	to 355	260	305
$BaAl_2(CO_3)_2(OH)_4$ (phase X)	$1\frac{1}{2}H_2O + 2CO_2$	$BaAl_2O_4 \cdot \frac{1}{2}H_2O$	30.33	39.02	38.73	to 700	329	398
$BaAl_2O_4 \cdot \frac{1}{2}H_2O$	$\frac{1}{2}H_2O$	$BaAl_2O_4$	3.41	41.09	41.96	to 1000	849†	876

*Powder X-ray data given in Table 5; patterns for dresserite and $BaAl_2O_4$ are in XRPDF; in this study the $\frac{1}{2}H_2O$ product only has not been detected in the X-ray patterns.

†From 849° to 876°C there may be almost simultaneous endothermic and exothermic reactions; the curve wavers, reaches an endothermic peak at 876°C, and then becomes slightly exothermic.

TABLE 5. POWDER X-RAY DATA FOR DECOMPOSITION PRODUCTS OF HYDRODRESSERITE

breakdown at room temp. $BaAl_2(CO_3)_2(OH)_4 \cdot 2H_2O(?)$†				thermal decomposition product* $BaAl_2(CO_3)_2(OH)_4(?)$			
I_{est}	d_{meas}(Å)	I_{est}	d_{meas}(Å)	I_{est}	d_{meas}(Å)	I_{est}	d_{meas}(Å)
4	8.84	5	2.792	8	7.64	4	2.05
10	7.82	3	2.679	<½	6.54	3	1.986
½	6.18	5	2.634	10	5.92	2	1.924
3	5.03	½	2.580	4	4.65	2	1.858
5	4.77	½	2.524	6	4.29	1	1.751
½	4.67	½	2.470	1	4.14	4	1.691
1	4.39	2	2.413	1	3.68	1	1.630
½	4.23	3	2.370	4	3.54	1	1.602
1	4.12	2	2.281	9	3.34	1	1.521
1	3.85	<½	2.216	3	3.08	1	1.439
1	3.72	½	2.145	3	2.97	2	1.404
6	3.64	3	2.108	4	2.80	1	1.374
½	3.52	½	2.079	2	2.69	1	1.366
3	3.39	1	2.039	5	2.63	2	1.247
½	3.30	½	1.948	3	2.54		
3	3.22	1	1.863	2	2.43		
<½	3.08	3	1.820	4	2.34		
3	3.02	1	1.746	3	2.25		

Nickel-filtered Cu radiation, camera diameter 114.6 mm.

†Designated the "intermediate" compound.

*Product from step at 300°C, 2½ hrs., in the sequences in Table 6.

$(CO_3)_2(OH)_4 \cdot 2H_2O$.

DTA and TGA

In 1976 a new suite of hydrodresserite samples was collected and 22.4 mg of the mineral were hand-picked under a 50× binocular microscope.

The material was checked by powder X-ray patterns and the next day, through prior arrangement with Dr. F. J. Wicks of the Royal Ontario Museum, Toronto, DTA and TGA curves were obtained with a Mettler Thermalanalyser (Pt crucible, N_2 atmosphere, heating rate 8°C/min., Al_2O_3 reference). The results, summarized in Figure 3 and Table 4, show that three minor weight losses precede the major breakdown, at 398°C, which signals the loss of CO_2 and some hydroxyl. The measured cumulative minor weight losses total 13.3 wt. %. In comparison, the original TGA curve obtained in 1967 was run in air at a heating rate of 6°C/min., and although the lowest temperature part of the curve is not clear, two weight-loss steps to 130°C and 320°C are well-defined. The cumulative loss to 320°C is 9.3%, and thus it may be interpreted that part of this thermogravimetric sample had dehydrated to dresserite.

The breakdown of hydrodresserite seems to proceed along the following path before CO_2 is lost: $3H_2O$ (hydrodresserite) → nH_2O where $n \sim 2$ (the "intermediate phase") → H_2O (dresserite) → $0H_2O$ (phase X). All except phase X form at room temperature.

TABLE 6. RESULTS OF STATIC HEATING OF DRESSERITE AND HYDRODRESSERITE

hydrodresserite (open tube)			dresserite (open tube)			dresserite (open tube)			dresserite (closed tube)**		
temp (°C)	heating time (hrs.)	identification	temp (°C)	heating time (hrs.)	identification	temp (°C)	heating time (hrs.)	identification	temp (°C)	heating time (hrs)	identification
~22	–	hydrodresserite	~22	–	dresserite	~22	–	dresserite	~22	–	dresserite
50	6	dresserite + hydrodresserite	50	6	dresserite	350	21.5	amorphous	350	20	$BaCO_3$
100	65	phase X*	100	65	dresserite + phase X	400	6	amorphous	400	18	$BaCO_3$
200	20	phase X	150	2.5	dresserite + phase X	450	7	amorphous	550	23	$BaCO_3$
250	2.5	phase X	200	20	phase X	500	4	amorphous	650	8	$BaAl_2O_4$
300	2.5	phase X	250	2.5	phase X						
350	16	amorphous	300	2.5	phase X						
			400	6.5	amorphous						

* Powder X-ray data for phase X are given in Table 5.   **Evacuated silica-glass tubes.

Static heating experiments

Hydrodresserite and dresserite were heated in horizontal furnaces to detect decomposition phases. Most runs were made with dresserite because of the small amount of hydrodresserite available, and because the TGA high-temperature products of both dresserite and hydrodresserite were known to be $BaAl_2O_4$. The results are summarized in Table 6.

After heating to 50°C, both the presence of remnant hydrodresserite and the absence of the "intermediate phase" were unexpected. Dresserite, both pristine and that derived from hydrodresserite, breaks down at about 100°C to phase X, which persists to 300-500C°. Beyond this temperature the product is amorphous, but tests with dilute HCl indicate that part of the CO_2 is retained to at least 600°C.

DISCUSSION

Hydrodresserite is chemically the barium analogue of alumohydrocalcite, but the two minerals otherwise seem to be unrelated. Srebrodol'skiy (1974) noted in his review of alumohydrocalcites that their published analyses fall into two groups which correspond generally to $CaAl_2(CO_3)_2(OH)_4 \cdot 3H_2O$ and $CaAl_2(CO_3)_2(OH)_4 \cdot 6H_2O$. The optical properties, densities, and other properties for these two groups differ, and the disparities in their powder X-ray patterns are considered by the present writers to be significant. It seems most likely that Srebrodol'skiy's "alumohydrocalcites" consist of at least two distinct mineral species, neither of which is structurally related to hydrodresserite.

ACKNOWLEDGMENTS

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