

HYDROBASALUMINITE AND BASALUMINITE IN CABANISS
FORMATION (MIDDLE PENNSYLVANIAN),
SOUTHEASTERN KANSAS¹

PEI-LIN TIEN, *Kansas Geological Survey,*
Lawrence, Kansas 66044.

ABSTRACT

Hydrobasaluminite and basaluminite are found in sedimentary rocks in southeastern Kansas. Hydrobasaluminite is closely associated with gypsum and iron oxides and occurs locally above a Middle Pennsylvanian coal. Basaluminite, a dehydrated form of hydrobasaluminite, is found only as debris on dry slopes. X-ray studies indicate no intermediate stages between hydrobasaluminite and basaluminite.

Basaluminite changes to metabasaluminite between 75°C and 330°C, but samples heated below 200°C partly or completely rehydrated upon cooling. Part of the material becomes amorphous if heated above 280°C. Two intermediate stages of poorly crystalline material are developed at temperatures between 340°C and 850°C. Above 850°C, samples gradually change to α -alumina.

Single crystallites of basaluminite have well-defined rhombic plates. Sides of the plates are about one micron in length with thicknesses of 0.05 micron. The chemical composition of basaluminite is approximately $2\text{Al}_2\text{O}_3 \cdot \text{SO}_3 \cdot 10\text{H}_2\text{O}$; composition of hydrobasaluminite is questionable.

Differential thermal analyses of hydrobasaluminite show endothermic peaks at 155°C, 220°C, 355°C, 890°C, and 940°C. Basaluminite has endothermic peaks at 125°C, 170°C, 220°C, 355°C, and 940°C. Infrared spectra of basaluminite in the range 400 to 4000 cm^{-1} show typical sulfate absorption bands from 580 to 690 cm^{-1} and 1050 to 1200 cm^{-1} . X-ray diffraction data indicate basaluminite samples from Kansas, England, and Tennessee are identical.

Field evidence suggests that the formation of hydrobasaluminite is related to weathering, local structure, topography, and mineral composition of associated rocks. Local accumulations of alkalic and acidic solutions caused precipitation of hydrobasaluminite and associated gypsum and iron oxides.

INTRODUCTION

A light yellowish brown, claylike material was found above the Fleming coal (Cabaniss Formation, Cherokee Group, Middle Pennsylvanian) in Crawford County, Kansas at a locality described by Howe (1956, p. 115, locality 63). Basaluminite, a dehydrated form of hydrobasaluminite, is found only as debris on dry slopes. X-ray powder diffraction data of these two minerals are similar to those of the type minerals from Jurassic Ironstone deposits of England reported by Hollingworth and Bannister (1950). Hydrobasaluminite also has been reported at the Mississippian-Pennsylvanian unconformity in southwestern Indiana (Sunderman and Beck, 1964). Basaluminite has been reported at the lower contact of the Chattanooga Shale in Tennessee (Milton and others, 1955), in a core

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from Russia by Fominykh (Fleischer and Friedman, 1966), and from Temple Mountain, Utah, by Frondel (1968).

Specimens of basaluminite were obtained from the type locality in England and from Marshall County, Tennessee for comparison with Kansas samples. Because data are sparse for these two minerals, a detailed study was made in their physical and chemical properties.

OCCURRENCE

Hydrobasaluminite was collected on the north side of an east-draining gully leading to an abandoned strip pit in SW SW sec. 24, T. 30 S., R. 24 E., Crawford County, Kansas. Occurring in a damp, weathered zone under colluvium as irregular-shaped aggregates, hydrobasaluminite ranges from 0.1 mm to 10 mm (Fig. 1). Aggregates are concentrated

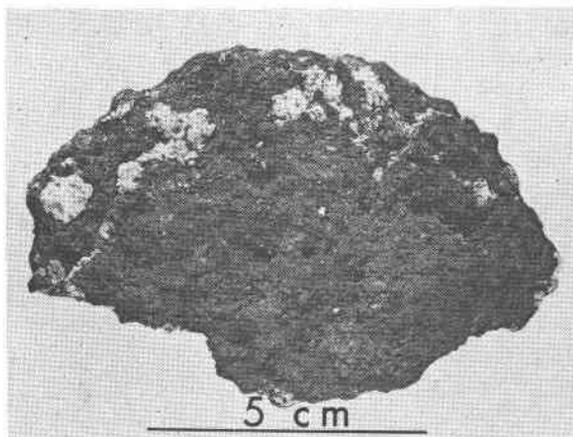


FIG. 1. Photograph of hydrobasaluminite aggregates.

locally in a 2-inch layer associated with gypsum and iron oxides above the Fleming coal and below a marine shale of the Cabaniss Formation. Irregular lenses of pyritized coquinoidal limestone were found near the lower contact of the shale unit which dips gently to the southeast. Quartz, feldspar, illite, and kaolinite are major constituents of the shale.

Field relations suggest that formation of hydrobasaluminite and associated minerals is controlled by weathering, local structure, topography and mineral composition of country rocks. During weathering, aluminosilicates, carbonates and iron sulfides are decomposed by hydrolysis. Acidic and alkalic solutions migrated along bedding planes and probably accumulated due to the sealing by the colluvium and the coal seam. Gypsum, iron oxides, and hydrobasaluminite were deposited from these

solutions. Basaluminite occurs as debris on the dry slopes below the hydrobasaluminite deposits, suggesting it is the dehydration product of hydrobasaluminite.

PHYSICAL AND CHEMICAL PROPERTIES

Hydrobasaluminite is light yellowish brown, dense, and compact. If exposed to air, it changes rapidly to basaluminite, which is white with chalky texture.

Specific gravity of basaluminite was obtained by pycnometer. Air bubbles in water and sample were removed by placing sample and pycnometer under vacuum before weighing. Five determinations gave a mean specific gravity of 2.10.

DEHYDRATION OF HYROBASALUMINITE

X-ray examination. A one-milligram sample of hydrobasaluminite was dispersed in distilled water with an ultrasonic probe, and filtered onto a 1.2μ Millipore filter. The filter was mounted on a glass slide and X-rayed immediately. The first and strongest reflection of hydrobasaluminite occurs at $7^\circ 2\theta$, and that of basaluminite occurs at $9.5^\circ 2\theta$. The time required to transform hydrobasaluminite into basaluminite by dehydration is short. In order to study this transformation, the range between 4° and $12^\circ 2\theta$ was repeatedly scanned at a speed of $1^\circ 2\theta$ per minute and a chart speed of 0.5 inch per minute.

During the first 30 minutes, X-ray patterns showed only the hydrobasaluminite reflection with a peak intensity of 170 cps (counts per second). After 85 minutes, the intensity of the hydrobasaluminite peak decreased to 160 cps. Shortly thereafter (at 87.3 minutes), a basaluminite peak of intensity 8 cps appeared. From this time peak intensities of hydrobasaluminite continually decreased while those of basaluminite increased. The hydrobasaluminite peak completely disappeared after 134 minutes and the basaluminite peak reached its maximum intensity of 96 cps at 135.3 minutes. No intermediate stage or rehydration could be detected. Figure 2 shows curves of intensity versus time for first reflections of hydrobasaluminite and basaluminite. These results can be reproduced only if the same amounts of sample are used under same laboratory conditions. Repeated experiments indicate that smaller samples require shorter transformation time. Slope of the intensity-time curves, however, is not changed.

Weight loss. A sample of hydrobasaluminite was weighed and loss in weight by dehydration was recorded at different time intervals until no further weight loss was observed. Repeated experiments using varying

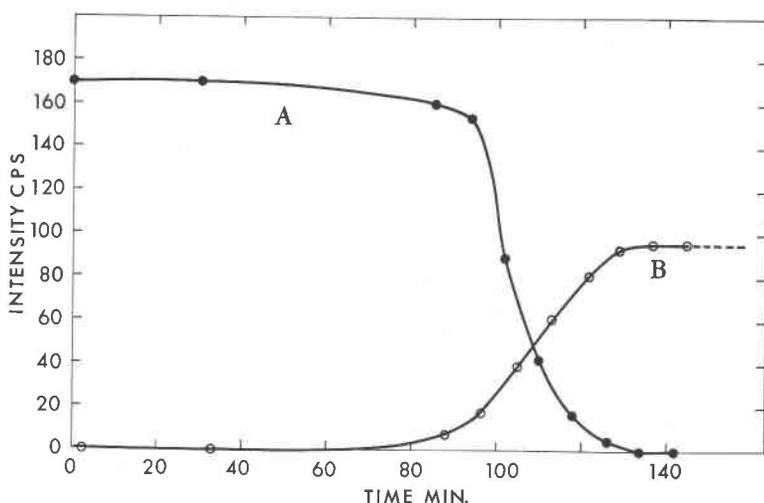


FIG. 2. Diagram showing changes of first diffraction peak-intensity of hydrobasaluminite (A) and basaluminite (B) against length of time of dehydration. Tests run in atmosphere having 50% relative humidity and temperature of 20°C.

initial amounts of sample showed that the rate of dehydration varies with sample size. Average total weight loss was 47 percent. Maximum difference among five separate measurements was less than one percent. It is believed that the total weight loss represents both loss of molecular water in the hydrobasaluminite and loss of adsorbed water.

EFFECT OF HEAT TREATMENT ON BASALUMINITE

Temperatures below 500°C. A basaluminite sample was dispersed in distilled water with an ultrasonic probe. The basaluminite-water suspension was evaporated to dryness under room conditions on preweighed glass slides. Weight of the dried sample was checked periodically until no further weight loss was noted. The prepared slides were then heated to predetermined temperatures and removed from the furnace without cooling. The samples were cooled in a desiccator, weight losses recorded, and the samples X rayed.

Temperatures above 500°C. Preweighed fine powder samples of basaluminite were heated in porcelain crucibles to predetermined temperatures, cooled in a desiccator, weighed and recorded (Fig. 3). The cooled samples were packed in aluminum sample holders and X rayed.

The basaluminite X-ray diffraction peaks were replaced by a new series of peaks in those samples heated to temperatures between 75°C and 335°C. Samples heated between 340°C and 850°C developed two inter-

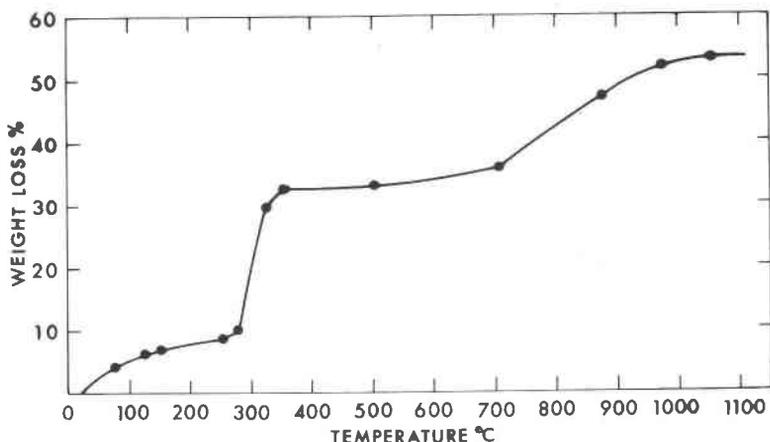


FIG. 3. Weight losses of basaluminite upon heating.

mediate stages of poorly crystallized material which have not been identified. Above 850°C, samples changed to α -alumina. Differences were noted in X-ray patterns of samples heated between 75°C and 150°C, but patterns of samples heated between 200°C and 280°C are identical. Above 280°C, peak intensities gradually decreased, suggesting that part of the sample was amorphous.

Heat-treated samples were rerun after being exposed to room conditions for different periods in order to check for rehydration. X-ray patterns of samples treated between 75°C and 185°C and allowed to remain at room conditions for two months showed that the material partly or completely rehydrated to basaluminite. Samples heated to between 200°C and 1050°C did not rehydrate within two months. Hollingworth and Bannister (1950, p. 10) postulated that a metastable phase, metabasaluminite, existed at 150°C. The new data suggest that a metastable phase might exist within a narrow stability range in the neighborhood of 250°C.

MICROSCOPIC EXAMINATION

Because hydrobasaluminite is not stable under normal laboratory conditions, only basaluminite could be examined under petrographic and electron microscopes. In thin section, basaluminite occurs as irregularly shaped, fine crystalline aggregates. In some areas, small gypsum clusters are present as inclusions in basaluminite aggregates. Basaluminite is colorless and transparent, and shows weak polarization and dark-gray interference color under crossed nicols (Fig. 4). Individual crystallites are so small that optical properties cannot be determined, but a mean re-

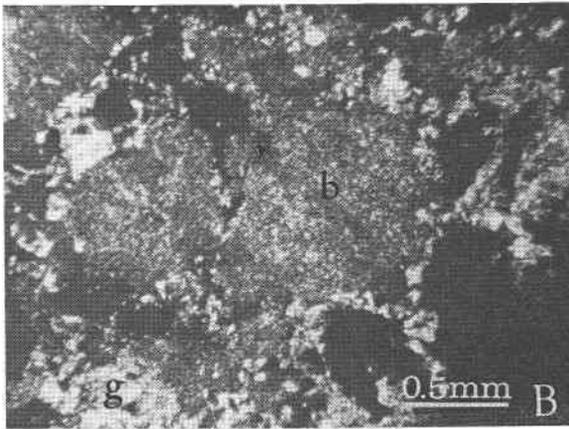
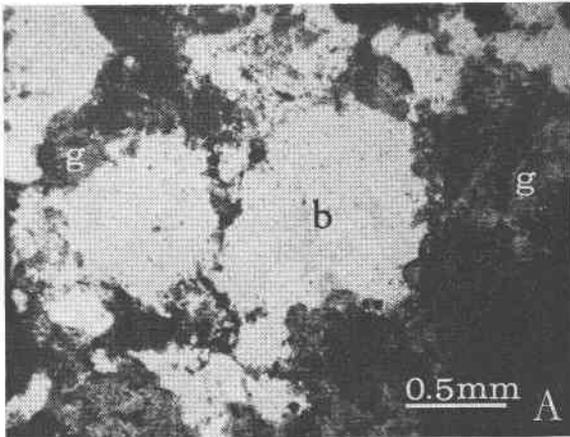


FIG. 4. Photomicrographs of basaluminite aggregates (b) and associated gypsum (g); A, plane polarized light; B, crossed nicols.

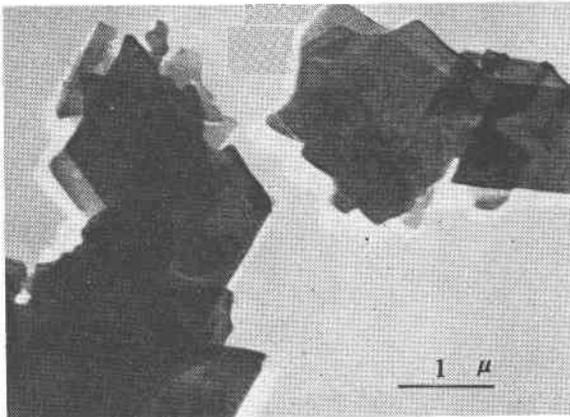


FIG. 5. Electron photomicrograph of basaluminite crystallites.

fractive index of 1.520 ± 0.002 was obtained. Mean index of refraction calculated by the Gladstone-Dale Law (Jaffe, 1956) is 1.539.

Crystallites of basaluminite are thin plates which show well-defined rhombic outlines and uniform thickness under the electron microscope (Fig. 5). Each side of the plates is approximately one micron in length with a thickness of about 0.05 micron. Corners between edges of most plates are blunt, but in some instances edges are sharp enough for measurement of angles between them. Five measurements gave mean values of $65.5 \pm 0.5^\circ$ and $114.5 \pm 0.5^\circ$.

CHEMICAL ANALYSIS

Two chemical analyses of basaluminite (Table 1) were made. Material for chemical analyses was prechecked by X-ray diffraction, and no impurities were detected. Traces of gypsum, iron oxides and greenish-brown material (allophane?) were observed under the petrographic microscope. Recalculated data indicate the chemical composition of basaluminite is close to the empirical formula, $Al_4SO_4(OH)_{10} \cdot 5H_2O$, given by Hollingworth and Bannister (1950). As noted, weight loss from hydrobasaluminite to basaluminite is 47 percent, which includes loss of molecular water in the hydrobasaluminite and loss of adsorbed water. Therefore, it is unlikely that hydrobasaluminite contains more than 28 moles of water. Thirty-six molecular waters were assigned to hydrobasaluminite by Hollingworth and Bannister (1950) and twelve molecular waters assigned by Sunderman and Beck (1964) do not agree with this study.

TABLE 1. CHEMICAL ANALYSES OF BASALUMINITE FROM KANSAS (ANALYST, O. K. GALLE)

	1	1a	2	2a	3
SiO	1.4		1.4		
Al ₂ O ₃	43.8	47.1	44.8	45.8	44.0
Fe ₂ O ₃	1.0		1.0		
CaO	2.4		1.0		
MgO	0.1		0.1		
K ₂ O	0.1		0.1		
Na ₂ O	tr.		tr.		
SO ₃	17.0	15.5	17.0	17.3	17.2
H ₂ O ^a	32.8	37.4	34.2	36.9	38.8
Total	98.6	100.0	100.0	100.0	100.0

1 and 2 basaluminite from Kansas, containing gypsum, allophane (?) and iron oxides.

1a and 2a recalculated excluding gypsum, allophane (?) and iron oxides.

3 calculated for $2Al_2O_3 \cdot SO_3 \cdot 10H_2O$.

^a water content by difference.

TABLE 2. X-RAY POWDER DATA OF HYDROBASALUMINITE, BASALUMINITE AND THE THERMAL PRODUCTS OF BASALUMINITE

1	2 ^a		3		4 ^a		5 ^a		6		7		8		9		
	d(A)	I ^b	d(A)	I	d(A)	I	d(A)	I	d(A)	I ^b							
12.62	vvsB	2.6	vvs	9.30	vvsB	9.4	vs	8.5	vvs	8.29	vvsB	6.10	vw	4.48	w	3.47	vs
9.34	w	8.08	m	7.81	vw	7.18	vwvw	6.90	ms	6.77	m	4.93	w	3.86	w	2.55	vvs
8.13	m	6.18	s	7.30	sm	6.73	w	5.97	m	5.92	s	4.46	vw	3.49	vs	2.37	s
6.24	m			6.80	sm	5.92	m	4.90	ms	4.98	m	4.25	w	3.34	vw	2.16	vw
5.89	s			5.90	sm	5.27	m	4.36	vs	4.71	m	3.48	vw	2.85	s	2.082	vvs
5.26	s	5.29	s	5.30	sm	4.68	s	4.14	ms	4.41	vs	3.34	s	2.69	vw	1.960	m
4.98	vw			4.99	vw	4.68	s	3.72	vw	4.13	m	2.96	m	2.47	w	1.867	vw
4.68	vs	4.70	s	4.67	vs	4.13	vw	3.46	mw	3.69	w	2.57	vw	2.32	sm	1.739	s
4.20	sm	4.23	ms	3.88	sm	3.87	m	3.20	w	3.45	w	2.25	w	2.21	sm	1.600	vvs
3.92	sm	4.09	ms	3.65	s	3.68	ms	2.92	ms	3.35	vw	1.897	w	2.083	m	1.5449	w
3.67	vs	3.73	s	3.44	s	3.44	vw	2.76	w	3.04	vw	1.815	w	1.991	m	1.4876	m
3.46	sm	3.43	m	3.22	w	3.20	vw	2.51	vw	2.97	vw	1.743	w	1.943	vw	1.4024	s
3.21	m	3.21	w	3.14	vw	2.90	w	2.68	w	2.88	m	1.541	vw	1.866	sm	1.3716	vs
3.06	m	3.07	s	2.94	m	2.82	w	2.55	vw	2.65	w	1.446	sm	1.746	sm	1.3348	vw
2.95	m			2.83	m	2.71	mw	2.48	m	2.55	w	1.593	vw	1.646	sm	1.2755	vw
2.81	vw	2.83	mw	2.72	mw	2.45	mw	2.40	w	2.46	m	1.559	vw	1.589	m	1.2360	sm
2.71	vw			2.55	vw	2.45	mw	2.30	vw	2.40	w	1.517	vw	1.517	vw	1.1889	m
2.53	sm	2.57	m	2.46	m	2.38	vw	2.19	m	2.42	mw	1.487	w	1.487	w	1.1459	m
2.38	w	2.41	m	2.39	vw	2.26	m	2.10	vw	2.172	m	1.420	vw	1.420	vw		
2.24	w	2.25	m	2.28	vw	2.26	m	2.02	vw	2.081	w	1.394	vw	1.394	vw		
2.18	m	2.22	w	2.177	s	2.18	mw	2.02	vw	2.007	vw	1.318	w	1.318	w		
2.08	w	2.10	ms	2.072	vw	2.06	w	1.921	s	1.907	m	1.275	w	1.275	w		
2.057	w	2.06	w	2.036	w	2.02	w	1.851	w	1.850	w	1.2138	w	1.2138	w		
2.014	vw			1.963	w	1.958	vw	1.753	w	1.745	vw	1.1648	w	1.1648	w		
1.989	w	1.96	mw	1.886	s	1.880	ms	1.689	mw	1.681	vw						
1.825	w	1.835	ms	1.841	w	1.835	mw	1.665	w	1.626	vw						
1.778	vw	1.793	m	1.770	m	1.762	mw	1.602	mw	1.626	vw						
1.726	w	1.729	mw	1.682	vw	1.678	vw	1.500	w	1.5922	vw						
1.684	vw	1.680	vw	1.623	m	1.616	mw	1.518	w	1.5039	vw						
1.667	sm			1.5712	vw	1.601	w	1.485	vw	1.4790	vw						
1.5587	vw	1.560	vw	1.5161	vw			1.458	ms								
1.4873	vw	1.500	w	1.4843	vw	1.462	vw	1.426	ms	1.4486	m						
1.4661	m			1.4685	vw	1.4521	w			1.4254	w						
1.4501	m			1.4521	m	1.435	m										
1.4367	m	1.445	m	1.4371	m	1.414	vw										
1.4256	vw			1.4185	vw												
1.4069	vw			1.3905	vw												
				1.3726	vw												
				1.3522	vw												
				1.3322	vw												
				1.3228	vw												
				1.3148	vw												
				1.2995	vw												
				1.2859	vw												
				1.2517	vw												
				1.1850	vw												
				1.1580	vw												

1. Hydrobasaluminite, Kansas. 2. Hydrobasaluminite, England. 3. Basaluminite, Kansas. 4. Basaluminite, England. 5. Metabasaluminite (basaluminite heated to 150°C), England. 6. Basaluminite heated to 250°C. 7. Basaluminite heated to 350°C. 8. Basaluminite heated to 700°C. 9. Basaluminite heated to 950°C.
 a. Adopted from Hollingworth and Bannister (1950, p. 8).
 b. Scale of decreasing intensities: vvs, vs, s, sm, m, w, vw, and vvw from visual estimation, B Broad line.

X-RAY DATA

Fine powdered samples of hydrobasaluminite, basaluminite, and the thermal products of basaluminite were sealed in thin glass capillaries (0.2 mm diameter) and X rayed. X-ray photographs were taken with a Debye-Scherrer 114.6 mm camera, using nickel-filtered copper radiation. The X-ray unit was operated at 35kv and 18ma with an exposure time of 10 hours. X-ray data for the Kansas and England material are given in Table 2.

DIFFERENTIAL THERMAL ANALYSIS

Differential thermal analyses were made on hydrobasaluminite and basaluminite. A mixture of alumina and calcined kaolinite was used as

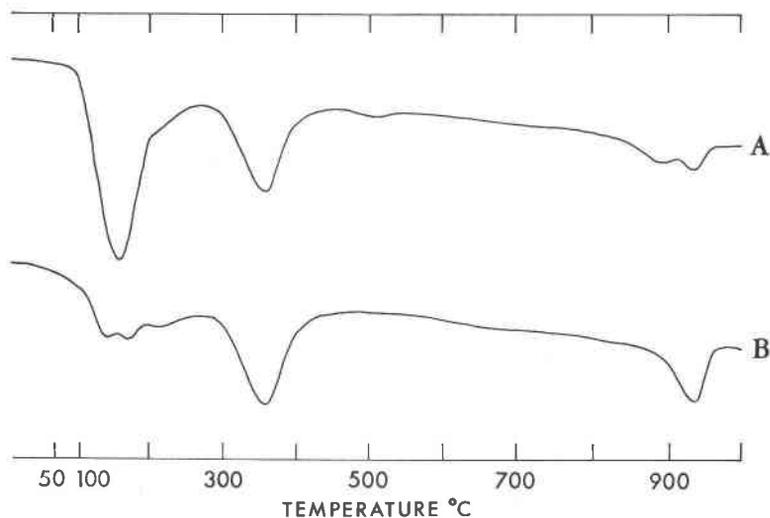


Fig. 6. Differential thermal curves of hydrobasaluminite (A) and basaluminite (B).

reference. Samples were heated at 10° per minute in a ceramic holder.

All peaks on the DTA curves of hydrobasaluminite and basaluminite are endothermic (Fig. 6). Hydrobasaluminite has peaks at 155°C, 220°C, 355°C, 890°C, and 940°C, and basaluminite at 125°C, 170°C, 220°C, 355°C, and 940°C.

INFRARED SPECTRA

Infrared spectra of basaluminite were obtained with a Perkin-Elmer Model 521 spectrophotometer, using KBr disks containing about 0.3 percent sample. Disks were prepared using the method described by Adler and Kerr (1965). Because this technique cannot be applied to a

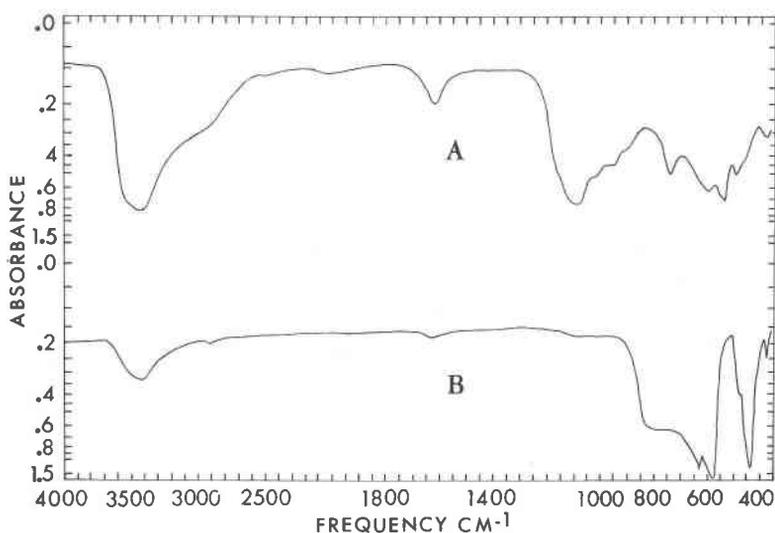


FIG. 7. Infrared spectra of basaluminite (A) and basaluminite heated to 975°C (B).

wet sample, hydrobasaluminite could not be analyzed by this technique. Basaluminite shows typical sulfate absorption bands in the regions 580 to 670 cm^{-1} and 1050 to 1200 cm^{-1} (Fig. 7A). Sulfate adsorption bands do not appear in the spectrum of basaluminite sample heated to 975°C (Fig. 7B). Weak bands for water in the high frequency regions indicate the sample basaluminite heated to 975°C contained some adsorbed water.

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