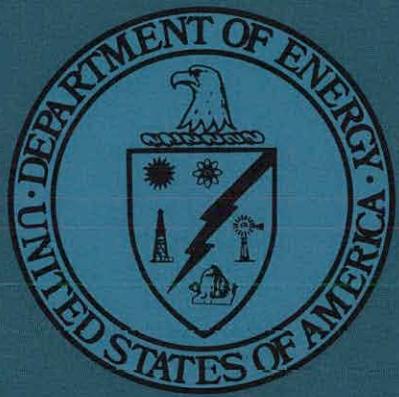


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THERMAL BEHAVIOR OF DAWSONITE

BY

Francis J. Keenan, John Howatson, and John Ward Smith

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REPORT OF INVESTIGATIONS

THERMAL BEHAVIOR OF DAWSONITE

By Francis J. Keenan, John Howatson, and John Ward Smith

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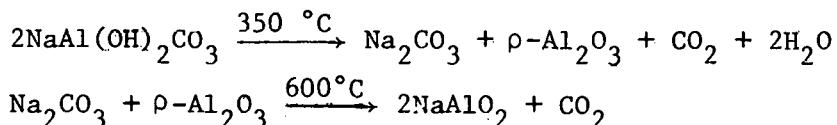
THERMAL BEHAVIOR OF DAWSONITE

by

Francis J. Keenan¹, John Howatson², and John Ward Smith³

ABSTRACT

Evidence for the dawsonite decomposition reaction sequence



is presented. Synthetic dawsonite was heated at temperatures from 250°-800°C and studied by X-ray powder diffraction and infrared spectroscopy. From 350°-550°C sodium carbonate and a "low temperature form" of alumina were the main products. Hydrolysis experiments showed that this heretofore unidentified alumina product is rho-alumina. At temperatures of 600°C and above, the sodium carbonate and rho-alumina react in an incomplete solid state reaction to form crystalline sodium aluminite.

INTRODUCTION

The aluminum-containing mineral dawsonite [$\text{NaAl(OH)}_2\text{CO}_3$] occurs in massive amounts in association with Green River Formation oil shale of Colorado's Piceance Creek Basin (Smith and Milton, 1966; Smith *et al.*, 1972; Beard *et al.*, 1974). The dawsonite is accompanied by smaller amounts of an aluminum hydroxide mineral tentatively identified as nordstrandite. These minerals could provide a source of extractable alumina in excess of six billion tons (Beard *et al.*, 1974), enough to supply the total United States alumina requirements for hundreds of years and to free this country from its current almost total dependence on foreign sources (Nielson, 1969).

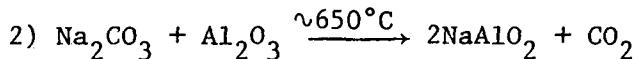
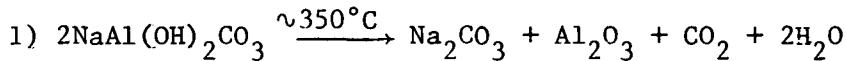
Piceance Creek dawsonite occurs almost exclusively in microcrystalline form in intimate mixture with the other components of oil shale rather than as discrete beds. Consequently the extraction of alumina can best be accomplished by base extraction of the porous spent shale remaining after production of the shale oil by retorting (Smith and Young, 1975). Optimizing such a process requires detailed knowledge of the thermal behavior of dawsonite.

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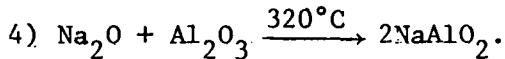
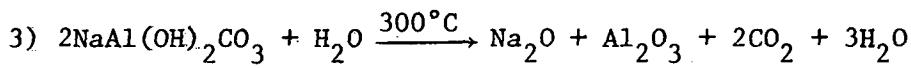
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Support for the thermal decomposition reaction sequence



has resulted from the research of a number of investigators. Beck (1950) first studied the decomposition of natural dawsonite using DTA but did not mention the identity of the solid product formed during the release of CO_2 and H_2O . Loughnan and See (1967) on the basis of DTA and TGA proposed reaction 1) as the correct pathway at temperatures between 290–330°C. Since they were working with dawsonitic sandstone, reaction 2) was not observed. Smith (1972) and Smith and Young (1975) studied African Olduvai Gorge dawsonite using DTA and TGA and agreed with reaction 1) but reported 360°C as the decomposition temperature. They also stated that sodium carbonate peaks were found in X-ray diffraction patterns until sodium aluminate formed at 700°C according to reaction 2). Harris *et al* (1971) reported the formation of an X-ray amorphous product at 375°C followed by sodium aluminate crystallization at 700°C. These results were based on X-ray diffraction and thermal analysis of synthetic dawsonite. Huggins and Green (1973) working with both synthetic and natural dawsonite also found that an X-ray amorphous product forms at 400°C but the IR spectrum of this material contained sodium carbonate peaks. By 700°C, NaAlO_2 was X-ray detectable.

In contrast to the thermal behavior observed by the above researchers, several investigators have proposed different reaction pathways. Savage and Bailey (1968) applied DTA to natural dawsonite and reported the formation of sodium aluminate at 370°C. Kim and Ishikawa (1974) studied synthetic dawsonite and reported the formation of an X-ray amorphous sodium aluminate gel $[\text{NaAlO(OH)}_2]$ at 360°C which crystallized at 650°C. They based their results on X-ray diffraction, infrared spectroscopy and thermal analysis. However, inspection of their presented IR spectra reveals the presence of a carbonate ion peak at 1450 cm^{-1} even from dawsonite heated to 1000°C. Haas and Atwood (1975) proposed that synthetic dawsonite decomposed directly to NaAlO_2 at 300°C with only a slight amount decomposing according to reaction 1). Their conclusion was based on carbonate ion analysis of the calcined material. Finally, Szczepanik and Rudnicki (1978) stated that dawsonite decomposed according to the following reaction scheme:



In summary, there appears to be little agreement as to the identity of the initial thermal decomposition product of dawsonite. However, the validity of the above reports is difficult to assess due to the lack of sufficient experimental detail and proper characterization of the starting material.

This study was undertaken to decide which of the reported decomposition pathways is correct. Identification of the thermal decomposition products of well-characterized synthetic dawsonite over a range of

temperatures was carried out using a combination of X-ray diffraction, infrared spectroscopic and chemical methods. Particular emphasis was placed on determining the nature of the low temperature X-ray amorphous aluminum containing product.

EXPERIMENTAL

Synthesis of dawsonite

Dawsonite was prepared by a new synthetic method. A solution containing 0.00347 moles aluminum nitrate, 0.175 moles sodium hydroxide, 0.500 moles sodium carbonate and 0.333 moles urea in one liter of water was heated at 93°C for about 24 hours. The urea slowly decomposed to produce CO_2 leading to homogeneous precipitation of microcrystalline dawsonite. After filtration the product was washed several times with hot water and then dried at 110°C for two hours.

This synthetic dawsonite compared well with natural dawsonite, including that occurring in Green River Formation oil shale, when studied using X-ray powder diffraction (Smith and Milton, 1966; J.C.P.D.S. Powder Diffraction File-Card 19-1175) and infrared spectroscopy (Jackson *et al*, 1972; Estep and Karr, 1968). Table 1 lists the measured X-ray powder diffraction peaks of this starting material along with their relative intensities. The top spectrum in Figure 1 depicts the infrared spectrum obtained on the synthetic dawsonite. Listed in Table 2 are peak widths of the 5.68 \AA peak measured at half-maximum taken from powder diffraction diagrams of both synthetic and natural dawsonite. For comparison similar data collected by Jackson *et al* (1972) are presented. These data indicate that this synthetic is of comparable crystallinity to that of both oil shale and Olduvai Gorge dawsonite but is much better crystallized than the commercial dawsonite studied by Jackson *et al* (1972).

Nitrogen B.E.T. surface area measurements yielded a surface area of $30 \text{ m}^2/\text{g}$ as compared to $107 \text{ m}^2/\text{g}$ for dawsonite prepared by Kim and Ishikawa (1974). SEM micrographs revealed that this material consisted of needle-like particles ranging from 0.3-2.0 microns in diameter and up to 10 microns in length. This is similar to material made by Jackson *et al* (1972). Chemical analysis of this synthetic dawsonite revealed that it contained 18.58 percent aluminum as compared to the theoretical value of 18.74 percent.

Thermal decomposition

One hundred milligram samples of dawsonite were heated in air in a nichrome wirewound tube furnace. The samples were held in shallow platinum pans. The furnace temperature was controlled to $\pm 1.0^\circ\text{C}$.

Hydrolysis

Hydrolysis experiments were performed on samples decomposed at 400°C for thirty minutes. In a typical experiment, decomposed dawsonite was washed with five 25 ml portions of hot water. The remaining solid was divided into several portions. One portion was immediately dried at

Table 1. Powder X-ray diffraction data
for synthetic dawsonite

<u>hkl</u>	<u>2θ</u>	<u>I/I₀</u>	<u>d, Å</u>
110	15.60	100	5.68
200	26.34	17	3.38
121	26.83	15	3.32
130	28.77	8	3.10
211	32.03	81	2.792
040	34.25	28	2.616
112	35.76	26	2.509
231	40.51	7	2.225
202	41.94	27	2.152
240	43.62	8	2.073
150	45.37	26	1.997
051	46.31	15	1.959
042	47.62	3	1.908
013	49.55	4	1.838
312	52.74	24	1.734
400	54.06	20	1.695
242	55.18	23	1.663
152	56.55	8	1.626
260	59.76	7	1.546
062	62.77	6	1.479
422	66.92	12	1.397
352	69.70	9	1.348
044	77.32	3	1.233

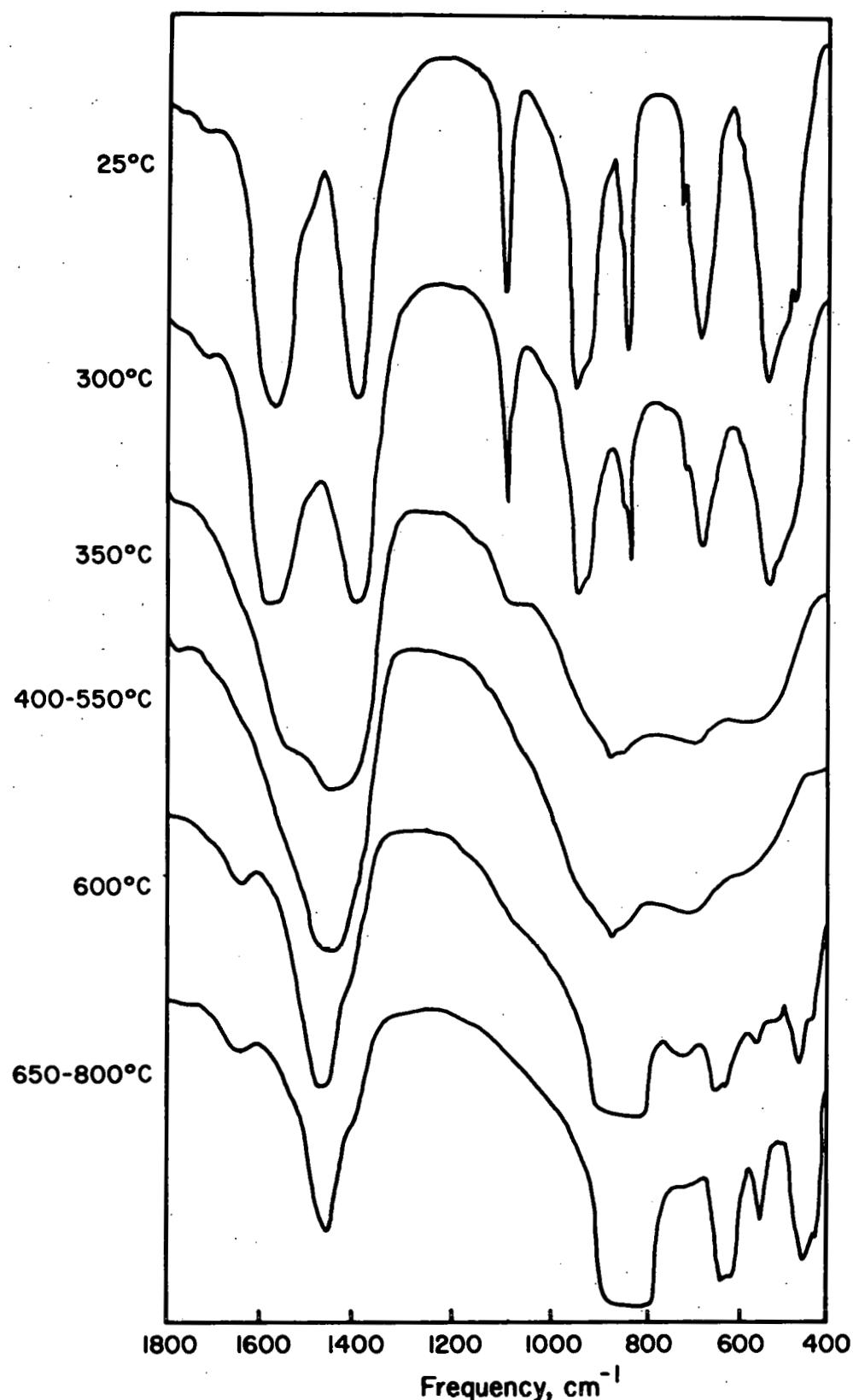


Figure 1. Infrared spectra of dawsonite heated at various temperatures for 25 minutes.

Table 2. Peak widths of synthetic and natural dawsonites
at half-maximum of 5.68\AA peak.

	<u>Sample</u>	<u>Peak width, degrees 2θ</u>
This study	10% dawsonite oil shale	0.16
	Olduvai Gorge	0.28
	Synthetic	0.45
Jackson <u>et al</u> (1972)	Oil shale	0.175
	Olduvai Gorge	0.300
	Bureau of Mines, No 28A	0.150
	Commercial	1.263

110°C for one hour. The other portions were immersed in water and kept at a constant temperature of 25°C for various lengths of time. The slurries were filtered and the solid was dried at 110°C for two hours.

Analysis

X-ray diffraction data were obtained using a Picker X-ray powder diffraction camera (114.6mm diameter) and CuK α radiation with a Ni filter. Standard exposure time was eight hours. Intensity data and peak width measurements for both synthetic and natural dawsonite were taken on a Norelco powder diffractometer using CuK α radiation and a graphite monochromator at a scan rate of 2° 2θ per minute. Infrared data were obtained on a Perkin-Elmer model 621 infrared spectrophotometer using a scan time of 15 minutes. Potassium bromide was used as the matrix material with a ratio of 2 mg sample to 300 mg KBr. Surface area measurements were made using a nitrogen adsorbing gravimetric high-vacuum system incorporating a Cahn microbalance. SEM photographs were taken by a JSM-U3 scanning electron microscope at 3000x magnification. Chemical analysis for aluminum was performed on a Instrumental Laboratories model 251 atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Table 3 and Figure 1 contain complete X-ray powder diffraction and infrared spectroscopic data, respectively, obtained on the product resulting from the thermal decomposition of dawsonite on heating for twenty-five minutes at discrete temperatures up to 800°C. This data is summarized in Table 4. The first crystallographic indication of change occurred at 300°C with the appearance of one new, unidentified diffraction peak ($d=1.89\text{\AA}$). At 350° decomposition was almost complete with only the most intense dawsonite peak ($d=5.68\text{\AA}$) detected. A second unidentified peak ($d=1.65\text{\AA}$) was observed at this temperature. At 400°C the dawsonite was completely decomposed. The disappearance of dawsonite peaks was accompanied by the development of sodium carbonate peaks (J.C.P.D.S. Powder Diffraction File-Card 19-1130). However, no peaks were observed for the low temperature forms of alumina described by Tertian and Papee (1958) such as ρ , η , χ and $\gamma\text{-Al}_2\text{O}_3$.

Since the infrared spectrum of the carbonate ion varies with its mode of coordination to other atoms, infrared spectroscopy also provided useful information about the decomposition of dawsonite to sodium carbonate. In addition, information about the formation of "low temperature" aluminas was obtained. The dawsonite structure contains chains in which the aluminum atoms are linked by a combination of bridging OH and bridging bidentate CO₃²⁻ groups (Freuh and Golightly, 1967; Corazza *et al.*, 1977; Keenan, F.J. and J. Howatson, unpublished work). As the dawsonite decomposed on heating, the splitting of the doubly degenerate v_3 ionic carbonate absorption observed for bidentate carbonate at 1575 cm⁻¹ and 1390 cm⁻¹ reverted to a single peak at 1450 cm⁻¹. In addition the carbonate absorption at 1090 cm⁻¹ observed for dawsonite disappeared since it is forbidden for the more symmetric ionic carbonate (Serna *et al.*, 1977). Also the Al-O absorptions at 675 cm⁻¹ and in the 550-400 cm⁻¹ region disappeared with the appearance of a broad band in the 900-600 cm⁻¹ region that is characteristic of the "low temperature" aluminas

Table 3. X-ray data for dawsonite thermal decomposition products.^I

250°C		300°C		350°C		400°C	
d, Å	hkl-Assign						
5.68	110-daw	5.67	110-daw	5.68	110-daw	2.964	002-NaC
3.38	200-daw	3.39	200-daw	2.964	002-NaC	2.618	020-NaC
3.32	121-daw	3.32	121-daw	2.611	020-NaC	2.546	310-NaC
3.09	130-daw	3.09	130-daw	2.543	310-NaC	2.365	112-NaC
2.789	211-daw	2.784	211-daw	2.368	112-NaC	2.254	202-NaC
2.611	040-daw	2.604	040-daw	2.254	202-NaC	2.181	221-NaC
2.505	112-daw	2.505	112-daw	2.179	221-NaC	2.034	221-NaC
2.230	231-daw	2.225	231-daw	1.957	402-NaC	1.953	402-NaC
2.154	202-daw	2.154	202-daw	1.896	unknown	1.896	unknown
2.074	240-daw	2.065	240-daw	1.881	222-NaC	1.710	222-NaC
1.996	150-daw	1.994	150-daw	1.651	unknown	1.681	203-NaC
1.951	051-daw	1.953	051-daw			1.646	unknown
1.835	013-daw	1.897	unknown				
1.731	312-daw	1.833	013-daw				
1.694	400-daw	1.731	312-daw				
1.660	242-daw	1.692	400-daw				
1.617	152-daw	1.659	242-daw				
1.548	260-daw	1.618	152-daw				
1.536	350-daw	1.543	260-daw				
1.477	062-daw	1.476	062-daw				
1.417	440-daw	1.394	422-daw				
1.395	422-daw	1.353	262-daw				
1.355	262-daw	1.339	352-daw				
1.343	352-daw	1.228	044-daw				
1.289	204-daw						
1.274	134-daw						
1.257	343-daw						
1.233	044-daw						

Table 3. Continued

<u>450°C</u>		<u>500°C</u>		<u>550°C</u>		<u>600°C</u>	
<u>d, Å</u>	<u>hkl-Assign</u>	<u>d, Å</u>	<u>hkl-Assign</u>	<u>d, Å</u>	<u>hkl-Assign</u>	<u>d, Å</u>	<u>hkl-Assign</u>
2.960	002-NaC	2.964	002-NaC	2.974	002-NaC	4.26 ²	101-NaA
2.615	020-NaC	2.611	020-NaC	2.611	020-NaC	2.955	102-NaA
2.543	310-NaC	2.543	310-NaC	2.539	310-NaC	2.678	200-NaA
2.368	112-NaC	2.368	112-NaC	2.377	112-NaC	2.620	020-NaA
2.262	202-NaC	2.257	202-NaC	2.261	202-NaC	2.571	112-NaA
2.181	221-NaC	2.184	221-NaC	2.176	221-NaC	2.365	112-NaC
1.896	unknown	1.951	402-NaC	1.896	unknown	2.262	202-NaC
1.649	unknown	1.885	222-NaC	1.713	222-NaC	2.181	221-NaC
		1.653	unknown	1.648	unknown	1.961	122-NaA
						1.885	220-NaA
						1.765	203-NaA
						1.592	302-NaA
						1.478	132-NaA
						1.415	214-NaA
						1.362	322-NaA

Table 3. Continued

<u>650°C</u>		<u>700°C</u>		<u>750°C</u>		<u>800°C</u>	
<u>d, Å</u>	<u>hkl-Assign</u>						
4.25 ²	101-NaA	4.24 ²	101-NaA	4.24 ²	101-NaA	4.24 ²	101-NaA
2.950	102-NaA	2.945	102-NaA	3.31	111-NaA	3.31	111-NaA
2.692	200-NaA	2.689	200-NaA	2.950	102-NaA	2.941	102-NaA
2.615	020-NaA	2.613	020-NaA	2.695	200-NaA	2.687	200-NaA
2.575	112-NaA	2.567	112-NaA	2.618	020-NaA	2.611	020-NaA
2.374	112-NaC	2.368	112-NaC	2.566	112-NaA	2.563	112-NaA
2.254	202-NaC	2.257	202-NaC	2.383	210-NaA	2.386	210-NaA
2.179	221-NaC	2.179	221-NaC	2.256	211-NaA	2.249	211-NaA
1.965	122-NaA	2.139	202-NaA	2.142	202-NaA	2.147	202-NaA
1.874	220-NaA	1.955	122-NaA	1.985	113-NaA	1.985	113-NaA
1.767	203-NaA	1.881	220-NaA	1.953	122-NaA	1.957	122-NaA
1.596	302-NaA	1.764	203-NaA	1.875	220-NaA	1.877	220-NaA
1.524	312-NaA	1.682	213-NaA	1.816	221-NaA	1.812	221-NaA
1.502	132-NaA	1.598	302-NaA	1.764	203-NaA	1.764	203-NaA
1.470	204-NaA	1.526	312-NaA	1.598	302-NaA	1.599	302-NaA
1.418	214-NaA	1.500	132-NaA	1.527	312-NaA	1.528	312-NaA
1.362	322-NaA	1.472	204-NaA	1.500	132-NaA	1.499	132-NaA
1.286	* -NaA	1.460	024-NaA	1.472	204-NaA	1.472	204-NaA
		1.418	214-NaA	1.457	024-NaA	1.460	024-NaA
		1.363	322-NaA	1.418	214-NaA	1.418	214-NaA
		1.304	* -NaA	1.362	322-NaA	1.362	322-NaA
		1.285	* -NaA	1.303	* -NaA	1.303	* -NaA
		1.250	* -NaA	1.283	* -NaA	1.284	* -NaA
				1.254	* -NaA	1.256	* -NaA
				1.176	* -NaA	1.177	* -NaA
				1.125	* -NaA	1.121	* -NaA

¹Heating time=25 minutes²Doublet unresolved

*hkl value not assigned

daw=dawsonite

NaC=sodium carbonate

NaA=sodium aluminate

Table 4. Results of thermal decomposition of dawsonite*

Temperature	X-ray diffraction	IR spectrum
25°C	23 peaks dawsonite	dawsonite
250°C	28 peaks dawsonite	dawsonite
300°C	23 peaks dawsonite 1 peak unknown	dawsonite
350°C	8 peaks Na_2CO_3 1 peak dawsonite 2 peaks unknown	Na_2CO_3 alumina
400°C	10 peaks Na_2CO_3 2 peaks unknown	Na_2CO_3 alumina
450°C	6 peaks Na_2CO_3 2 peaks unknown	Na_2CO_3 alumina
500°C	8 peaks Na_2CO_3 1 peak unknown	Na_2CO_3 alumina
550°C	7 peaks Na_2CO_3 2 peaks unknown	Na_2CO_3 alumina
600°C	12 peaks NaAlO_2 3 peaks Na_2CO_3	NaAlO_2 Na_2CO_3
650°C	15 peaks NaAlO_2 3 peaks Na_2CO_3	NaAlO_2 Na_2CO_3
700°C	20 peaks NaAlO_2 3 peaks Na_2CO_3	NaAlO_2 Na_2CO_3
750°C	26 peaks NaAlO_2	NaAlO_2 Na_2CO_3
800°C	26 peaks NaAlO_2	NaAlO_2 Na_2CO_3

*Time of heating = 25 minutes

reported by Stegmann *et al* (1974). The observed changes in the infrared spectra are entirely consistent with the formation of sodium carbonate and some form of alumina.

No significant additional changes were observed with increasing temperatures up to 600°C. At 600°C both the X-ray pattern and IR spectrum changed considerably. The X-ray pattern contained twelve peaks due to $\beta\text{-NaAlO}_2$ (Ampian, 1964) plus three peaks due to sodium carbonate. The latter were the most intense sodium carbonate peaks that were not coincident with sodium aluminate peaks. Also, both unidentified peaks had vanished. The IR spectrum showed several bands extending from 900-460 cm^{-1} which were very similar to peaks reported by Schroeder and Lyons (1966) for NaAlO_2 . In addition, the carbonate band at 1450 cm^{-1} remained but it had narrowed significantly. A weak peak emerged at 1630 cm^{-1} which was not identified.

The X-ray patterns of samples heated at 650-800°C showed continuous crystalline development of $\beta\text{-NaAlO}_2$ with 26 peaks found at 800°C. The IR spectra of samples heated above 600°C changed only slightly except for continued narrowing of the carbonate ion band at 1450 cm^{-1} accompanied by a small decrease in intensity. However, this peak is still at 80 percent absorbance for the 800°C sample indicating the continued presence of sodium carbonate.

These results agree most closely with the work of Smith and Young (1975) and clearly indicated that dawsonite decomposes in a two-step reaction. Dawsonite initially decomposed according to reaction (1) to yield Na_2CO_3 and a "low temperature form" of alumina. At about 600°C reaction (2) proceeded to form NaAlO_2 . However, reaction (2) was not quantitative under the conditions investigated. We found no evidence of other reactions occurring in this temperature range as claimed by Savage and Bailey (1968), Kim and Ishikawa (1974), Haas and Atwood (1975) and Szczepanik and Rudnicki (1978).

Listed in Table 5 are the IR and X-ray diffraction results of samples of decomposed dawsonite hydrolyzed for various periods of time. The X-ray pattern of the sample after washing with water yielded seven broad peaks which were consistent with the pattern for boehmite gel (Tertian and Papee, 1958). The IR spectrum showed the absence of carbonate ion and was similar to the spectrum published for boehmite (Stegmann *et al*, 1974). Heating of the boehmite gel at 500°C for 20 minutes resulted in $\eta\text{-Al}_2\text{O}_3$.

The IR spectra taken on samples exposed to water for from one to twelve days indicated splitting of the O-H stretching band after one day with more pronounced splitting as the exposure to water increased. After twelve days exposure, the O-H peak was split into five peaks with additional peaks at 1015 and 970 cm^{-1} . The resultant spectrum was very similar to spectra presented for bayerite, $\text{Al}(\text{OH})_3$ (Stegmann *et al*, 1974; Vivien *et al*, 1973). X-ray diffraction patterns showed 16 peaks due to bayerite after one day and 22 peaks after twelve days.

Yamaguchi and Chiu (1968) attempted to hydrolyze β , η , and $\gamma\text{-Al}_2\text{O}_3$ using pure water and various basic solutions. They found that only

Table 5. Results of hydrolysis of decomposed dawsonite*

Exposure to H ₂ O	X-Ray diffraction	IR spectrum
before wash	7 peaks Na ₂ CO ₃	Na ₂ CO ₃
		Al ₂ O ₃
after wash	7 peaks boehmite gel	similar to boehmite
1 day	16 peaks bayerite	bayerite
3 days	17 peaks bayerite	bayerite
7 days	18 peaks bayerite	bayerite
12 days	22 peaks bayerite	bayerite

*Heated at 400°C for 30 minutes

ρ - Al_2O_3 will hydrolyze under any of the conditions investigated. Rho-alumina was found to transform to boehmite gel followed by bayerite when exposed to room temperature water. Tertian and Papee (1958) studied the entire alumina series and performed hydrolysis experiments with two low-temperature forms of alumina ρ and χ - Al_2O_3 . They found that ρ - Al_2O_3 will rehydrate quantitatively to bayerite when exposed to liquid water at 25°C for 14 days. Chi-alumina possessed only a slight inclination to rehydrate under the same conditions. Rho-alumina also has a very limited X-ray diffraction pattern that consists of only one peak at 1.40Å. Depending upon formation conditions even this one peak may not be present. Therefore, the presence of ρ - Al_2O_3 would be very difficult to detect via X-ray diffraction. Kim and Ishikawa (1974) also noted the formation of bayerite as the hydrolysis product of decomposed dawsonite. However, they believed that sodium aluminate gel was the source material rather than some form of alumina.

Since ρ - Al_2O_3 is the only low-temperature form of alumina which readily hydrolyzes to bayerite, and since it has the most limited powder pattern of the aluminas, the X-ray amorphous alumina product formed from dawsonite at 400°C is ρ - Al_2O_3 . Since ρ - Al_2O_3 does not become unstable with respect to η - Al_2O_3 until 600°C (Tertian and Papee, 1958), the alumina product present from 350-550°C is most likely rho-alumina. It was expected that η - Al_2O_3 would be found above 600°C. However, its presence was not detected, probably because of the solid state reaction with sodium carbonate. In trying to study the thermal behavior of this ρ - Al_2O_3 phase as a separate compound, an attempt was made to dissolve out the sodium carbonate with water, but this led to the formation of pseudoboehmite as discussed above. In conclusion, it appears that the intermediate alumina compound is ρ - Al_2O_3 instead of χ - Al_2O_3 as originally postulated by Smith and Young (1975).

CONCLUSIONS

The decomposition of dawsonite has been confirmed to be a two-step process. The first reaction occurs at about 350°C, producing a solid mixture. Sodium carbonate is one component of the mixture, and the heretofore unidentified alumina component is rho-alumina. The second reaction is a solid state reaction between sodium carbonate and rho-alumina at 600°C producing crystalline sodium aluminate. Because this is a solid state reaction, it does not proceed to completion. These results on synthetic dawsonite agree most closely with the results of Smith and Young (1975) on natural dawsonite with the exception of the identification of the X-ray amorphous alumina product as rho-alumina.

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