

HYDROLYSIS OF ALUMINUM-TRI-(SEC-BUTOXIDE) IN IONIC AND NONIONIC MEDIA

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Abstract—The hydrolysis of aluminum-tri-(sec-butoxide), ASB, in ionic and nonionic media is shown to be a useful method for the synthesis of aluminum minerals. Infrared and X-ray analysis were used to identify the reaction products. Pseudoboehmite is formed at low water to aluminum ratios. At higher water content, transformation of pseudoboehmite occurs with bayerite as the final phase. Dawsonite-type minerals are produced when ASB is hydrolyzed in the presence of sodium, potassium, or ammonium bicarbonate. Infrared evidence suggests that the carbonate group is more perturbed than indicated by the proposed crystal structure. A compound with a structure like the pyoaurite-sjögrenite group was obtained when ASB reacted with a lithium carbonate solution. The infrared spectrum indicates the possible existence of bicarbonate and carbonate ions between the brucite-like layers.

INTRODUCTION

Many of the reactions that proceed in natural surface deposits are so slow that their duplication in the laboratory is impractical. A common approach to this problem has been the use of elevated temperatures in the synthesis. These extreme laboratory conditions make extrapolation to natural synthesis questionable. The low temperature synthesis of minerals, such as aluminum hydroxide, dawsonite and aluminosilicates, has been demonstrated using aluminum amalgam (Šarc-Lahodny, 1964; Chesworth, 1971). However, the rate of this reaction is slow and difficult to control.

A better approach to the synthesis of aluminum minerals can be obtained by the hydrolysis of aluminum alcoholates in controlled media. Aluminum-tri-(sec-butoxide), ASB, was used in this study as it is a convenient representative of this class of compound. ASB has been used in the production of aluminum hydrous oxide (Catone and Matijevic, 1974) and aluminum hydroxide (Harris and Sing, 1957; Bye and Robinson, 1961; Aldcroft *et al.*, 1969), as well as in the production of aerogels (Teichner *et al.*, 1976). The utility of the hydrolysis of ASB in the synthesis of mineralogical specimens will be illustrated by the effect of water on the crystallization rate of aluminum hydroxide and the reactions which occur when alkaline carbonates and bicarbonates are present during hydrolysis.

EXPERIMENTAL

ASB, obtained from Chattem Chemical Co., was checked as Nujol mulls by infrared spectroscopy. Since no absorption bands due to molecular water or hydroxyl groups were present, the compound was used as received. Experiments were carried out at 25°C under a nitrogen atmosphere in order to limit exposure to carbon dioxide and water vapor. ASB solutions, 15% w/v, were prepared in benzene or anhydrous isopropanol. The solvent used was not observed to affect the hydrolysis reaction. After the reaction, the products were stored in a desiccator at 0% relative humidity and analyzed periodically. For analysis, the products were washed with anhydrous iso-propanol or benzene, filtered, and dried at 50°C.

The hydrolysis reaction in nonionic medium was carried out by using deionized water at different H₂O/Al molar ratios ranging from 2 to 24. Solutions of sodium, potassium, or ammonium bicarbonate were used based on the solubility of each bicarbonate salt in order to obtain various Al/HCO₃ molar ratios. Only single products were obtained when 1:1 or greater Al/HCO₃ ratios were used. Mixtures of aluminum hydroxide and dawsonite-type compounds were obtained at lower ratios. The use of other anions such as nitrate or sulfate as the sodium, potassium, or ammonium salts produced initially amorphous aluminum hydroxide which later developed into pseudoboehmite.

ASB was also hydrolyzed in the presence of lithium carbonate at a Al/CO₃ ratio of 1. Due to the low solubility of lithium carbonate, a saturated solution in equilibrium with solid was used. The precipitate

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was washed with water to remove excess lithium carbonate prior to analysis.

The precipitates were characterized by X-ray powder diffraction using a General Electric XRD-5 diffractometer.

Infrared analysis was performed using KBr pellets or as deposits on AgCl windows. Samples were run on a Perkin-Elmer 180 Spectrophotometer. H by D exchange under vacuum (10^{-4} mm Hg) was carried out by using an infrared cell similar to that described by Angell and Shaffer (1965).

RESULTS AND DISCUSSION

Reactions in nonionic medium

Amorphous aluminum hydroxide to pseudoboehmite transformation. At molar ratios of water to aluminum of 3 or greater, aluminum hydroxide is immediately precipitated. X-ray powder diffraction patterns (Figure 1A) show that the initial precipitate is amorphous. The presence of a broad reflection between 18 and 30° indicates a repetitive interatomic distance of $3\text{--}5 \text{ \AA}$.

The amorphous character of the initial precipitate is also observed in the infrared spectrum (Figure 2A). The hydroxyl groups vibrate between $3700\text{--}2800 \text{ cm}^{-1}$ for stretching vibrations and $1100\text{--}900 \text{ cm}^{-1}$ for bending vibrations. The broad absorption band between 700 and 400 cm^{-1} indicates Al—O vibrations. In addition, molecular water is also present in the initial precipitate as evidenced by an absorption band at 1640 cm^{-1} . The poorly defined peak at 840 cm^{-1} is due, at least in part, to the presence of carbonate ion, even though the precipitation was carried out under nitrogen atmosphere (Serna *et al.*, in press).

The amorphous aluminum hydroxide is unstable and X-ray powder diffraction peaks at 3.18 , 2.34 and 1.83 \AA are observed (Fig. 1C) as pseudoboehmite develops during aging (Calvet *et al.*, 1953).

The absence of the equivalent interatomic distance in pseudoboehmite of the 020 plane in boehmite at

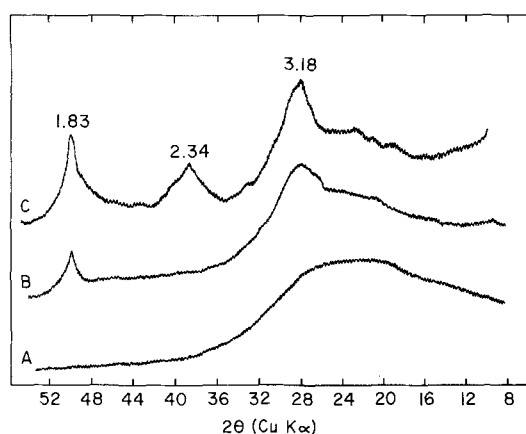


Figure 1. X-ray diffractograms of the hydrolysis product of ASB precipitated at $3\text{H}_2\text{O}/\text{Al}$ and aged at 25°C : A, initial; B, 1 week; C, 2 weeks.

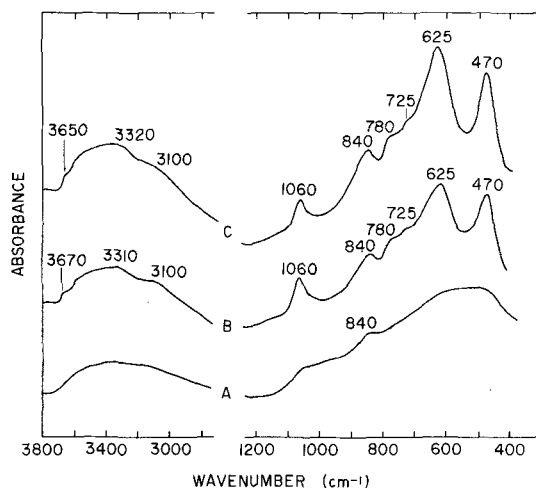
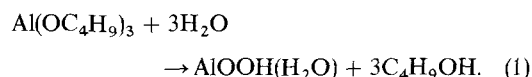


Figure 2. Infrared spectra of the hydrolysis product of ASB precipitated at $3\text{H}_2\text{O}/\text{Al}$ and aged at 25°C : A, initial; B, 1 week; C, 2 weeks.

6.1 \AA has been previously observed and was interpreted as due to the retention by the pseudoboehmite surface of water or ions (Papée *et al.*, 1958). The absence of the reflection at approximately 6 \AA in some pseudoboehmites is still not clear, since hydrolysis of ASB in the presence of sodium nitrate or sodium sulfate produced pseudoboehmite in which the reflection at 6.1 \AA was present. In addition, the hydrolysis of ASB at higher water ratio shows the presence of a small reflection at approximately 6 \AA (Figure 3). The absence in some pseudoboehmites of this reflection and the presence of molecular water have raised questions about the description of pseudoboehmite as a colloidal boehmite. Therefore, the reaction at low water content may be written as:



The infrared spectrum (Figure 2B) also indicates that pseudoboehmite develops during aging for 1

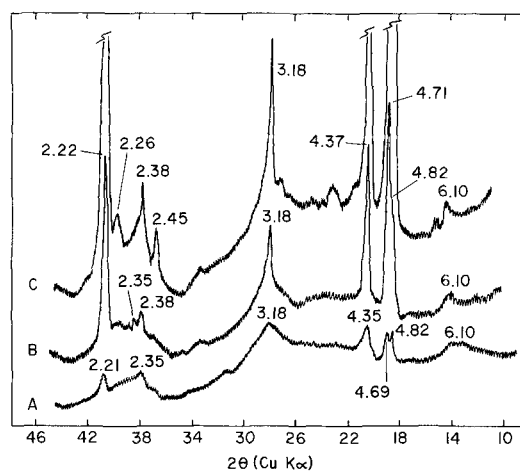


Figure 3. X-ray diffractograms of the hydrolysis product of ASB precipitated at $24\text{H}_2\text{O}/\text{Al}$ and aged at 25°C : A, initial; B, 1 week; C, 2 weeks.

Table 1. Infrared absorption bands, cm^{-1} , of the hydrolysis products of ASB at $\text{H}_2\text{O}/\text{Al}$ ratios of 3 and 24

Product at $3\text{H}_2\text{O}/\text{Al}$	Boehmite,* assignment	Product at $24\text{H}_2\text{O}/\text{Al}$	Bayerite†
		3650	3655
		3620‡	
		3545	3550
		3520‡	
		3460	3470
		3430	3410
3310	3297, OH		
3100	3090, OH		
1060	1080, OH	1060§	
		1025	
		975	972
780	755, OH	760	770
725		730	720
625	618, AlO_6	630	630
		585	580
		555	555
	522, AlO_6	530	525
470		475	475
	410, Al—O	430	428

* Fripiat *et al.* (1967).

† Elderfiel and Hem (1973).

‡ Gibbsite.

§ Pseudoboehmite.

week at 25°C (Jungmann *et al.*, 1964). Although the interpretation of the infrared spectrum of pseudoboehmite has not been established, the assignment of some bands can be made based on comparison to boehmite (Table 1).

Pseudoboehmite to bayerite transformation. When ASB is hydrolyzed at a $\text{H}_2\text{O}/\text{Al}$ ratio of 24, the trans-

formation of pseudoboehmite to bayerite occurs rapidly (Fig. 3). The initial precipitate shows the presence of pseudoboehmite by broad reflections at 3.18 and 6.10 Å as well as small amounts of bayerite as indicated by the reflections at 4.69, 4.35, 2.35 and 2.21 Å. During aging, the broad reflection due to pseudoboehmite decreases and an increase in the reflections of bayerite at 4.71, 4.37, 3.18, 2.45, 2.38 and 2.22 Å occur. Some gibbsite is also present as noted by the reflection at 4.82 Å.

The transformation of pseudoboehmite to bayerite at higher water content is also demonstrated by the infrared spectra shown in Figure 4. The hydroxyl stretching vibrations of pseudoboehmite at 3300 and 3100 cm^{-1} decrease in intensity during aging as the more sharply defined absorption bands of bayerite develop. In addition, the decreasing intensity of the absorption bands at 1060 and 625 cm^{-1} suggests a transformation from pseudoboehmite to bayerite. The reaction product after 1 week is mainly bayerite, although evidence of gibbsite is seen at 3618 and 3545 cm^{-1} (Nail *et al.*, 1976).

The formation of crystalline aluminum trihydroxide from an aqueous suspension of pseudoboehmite was observed by Aldcroft *et al.* (1969) and by McHardy and Thomson (1971). The proposed mechanism was based on the dissolution of the pseudoboehmite.

There is wide disagreement concerning the relative stability of gibbsite/bayerite and boehmite (Kittrick, 1969; Chesworth, 1972). Thermodynamic evidence (Chesworth, 1972) indicates that boehmite can be more stable than gibbsite at low water content or in the presence of impurities. This view is supported

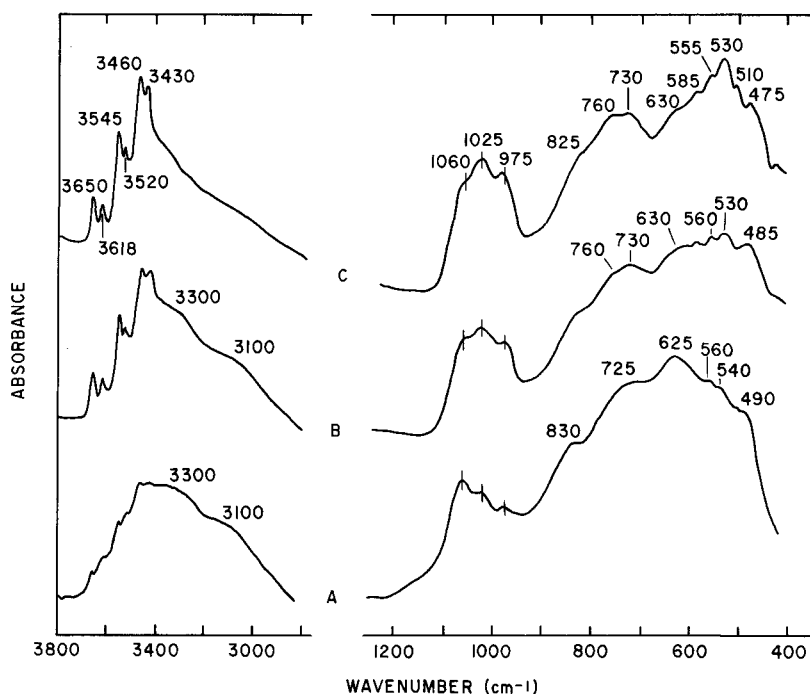


Figure 4. Infrared spectra of the hydrolysis product of ASB precipitated at $24\text{H}_2\text{O}/\text{Al}$ and aged at 25°C : A, initial; B, 1 week; C, 2 weeks.

Table 2. X-ray data of dawsonite-type minerals, $XAl(OH)_2CO_3$, spacing in Å

Natural dawsonite*	X					hkl
	Na	Na/NH ₄	K	K/NH ₄	NH ₄	
5.70	5.64	5.78	5.57	5.67	5.78	(110)
		4.03	4.09	4.07	4.03	
3.38	3.35	3.29	3.34	3.38	3.39	(200)
3.00			3.17	3.25	3.27	(130, 302)
2.79	2.76	2.87	2.82	2.85	2.92	(211)
					2.88	
2.61				2.63		(040)
2.50	2.49	2.56	2.52		2.56	(112)
2.23		2.22			2.24	(141, 231)
2.15	2.15	2.18	2.16	2.17	2.19	(202)
2.06		2.03			2.2	(240, 132)
1.989	1.97	1.98	1.98	1.99	1.99	

* Frueh and Golightly (1967).

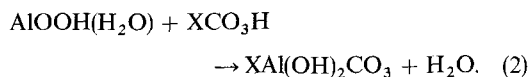
by the present experiments as pseudoboehmite was the stable phase at the lower H_2O/Al ratio. That pseudoboehmite is more stable than bayerite under high salt concentration has been demonstrated by Hsu (1967).

Reaction in ionic medium

Dawsonite-type structure. Dawsonite, $NaAl(OH)_2CO_3$, was first synthesized by hydrolyzing sodium aluminate in the presence of carbon dioxide (Seiyama *et al.*, 1967). Potassium and ammonium dawsonite have also been synthesized (Besson *et al.*, 1973; Hem and White, 1975).

Dawsonite was formed within several hours after the hydrolysis of ASB in the presence of stoichiometric quantities of sodium bicarbonate. The hydrolysis of ASB in the presence of potassium or ammonium bicarbonate also resulted in the formation of a dawsonite-type structure. In addition, ammonium sodium dawsonite and ammonium potassium dawsonite were synthesized by using a mixture of the bicarbonate salts indicating the existence of a solid series. X-ray data for the dawsonite-type compounds are given in Table 2.

As pseudoboehmite is the initial product of the hydrolysis of ASB, dawsonite-like compounds could be produced by the following reaction:



The low solubility of bicarbonate salts required a large excess of water for solution. As noted previously, pseudoboehmite converts to aluminum hydroxide in the presence of excess water. Thus, bicarbonate salts with high solubility such as NH_4HCO_3 produced more crystalline dawsonite-like compounds than $NaHCO_3$, the bicarbonate salt used having the lowest solubility.

The infrared spectra of the synthetic dawsonite was carefully studied in view of the differences in interpretation found in the literature for the molecular vibrations of the carbonate ion (White, 1974). Seiyama *et al.* (1976) first assigned the infrared bands of dawsonite in terms of bicarbonate because during synthesis, dawsonite was formed at pH conditions which favor bicarbonate ion. Thus, the absorption band at 1098 cm^{-1} was considered to be due to the hydroxyl group of the bicarbonate ion.

Frueh and Golightly (1967) determined the crystal structure of dawsonite and reported that carbonate ion was present almost without distortion. However, the two strong infrared absorption bands around 1500 cm^{-1} were considered carbonyl vibrations. A later study (Estep and Karr, 1968) assigned the band at 1500 cm^{-1} to hydroxyl bending vibrations and only the band at 1400 cm^{-1} to the carbonyl group.

The infrared spectra of dawsonite and deuterated dawsonite are shown in Figure 5. Comparison of the spectra indicate that the absorption bands at 1565, 1400, 1095, 840 and 725 cm^{-1} arise from carbonate

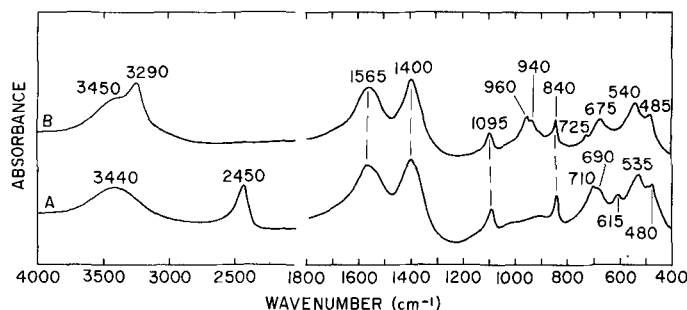


Figure 5. Infrared spectra of synthetic dawsonite: A, deuterium dawsonite; B, dawsonite.

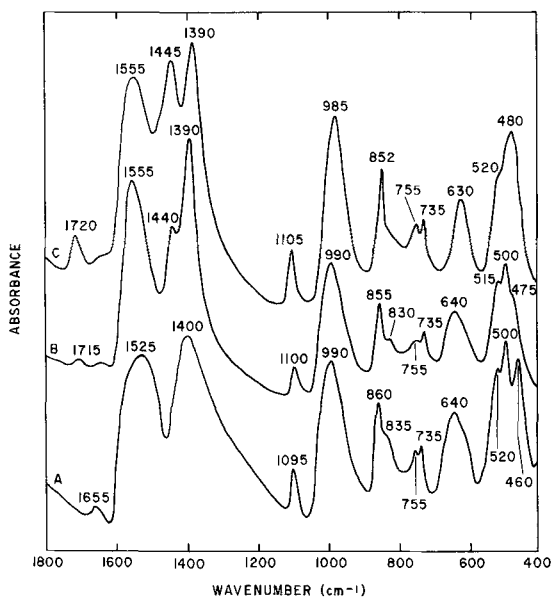


Figure 6. Infrared spectra of synthetic dawsonites: A, potassium dawsonite; B, potassium ammonium dawsonite; C, ammonium dawsonite.

and that no bicarbonate is present. The replacement of H by D in the structure produces the shift of the OH-stretching from 3290 to 2450 cm^{-1} and identifies the bands at 960 and 940 cm^{-1} as OH-bending vibrations. These bands appear at 710 and 690 cm^{-1} in the infrared spectrum of deuterium dawsonite.

It is interesting to note that although two OH-bending vibrations were observed for dawsonite, there is only one OH-stretching vibration at 3290 cm^{-1} . However, potassium dawsonite and ammonium dawsonite only present one OH-stretching and one OH-bending vibration at 3400 and 990 cm^{-1} or 3430 and 985 cm^{-1} , respectively. The infrared spectra of dawsonite-type minerals reported by Besson *et al.* (1973) show analogous features.

The infrared vibrations at lower wavenumbers must arise from Al—O vibrations. In the 550–400 cm^{-1} region, absorptions seem to arise from nearly pure Al—O vibrations as no important differences are observed between sodium, potassium, or ammonium dawsonite (Figures 5B, 6A, 6C). However, the Al—O vibration at 675 cm^{-1} in sodium dawsonite was observed at 640 cm^{-1} in potassium dawsonite and at

Table 3. Symmetry sites for the atoms in dawsonite

Site symmetry	Wyckoff's notation	Atom sites
C_{2h} (2)	a	
C_{2h} (2)	b	Al
C_{2h} (2)	c	Na, K, or NH_4
C_{2h} (2)	d	
C_{2v} (2)	e	C, O_I
C_2 (4)	f	
C_2 (4)	g	
C_s (4)	h	O_{II}
C_s (4)	i	OH
C_1 (8)	j	

630 cm^{-1} in ammonium dawsonite suggesting that this vibration is strongly affected by the nature of the monovalent cation.

An interpretation of the molecular vibrations of carbonate in dawsonite can be made based on the crystal structure proposed by Frueh and Golightly (1967) in which the space group assigned was Imma (D_{2h}^{28}) with 2 molecules per Bravais cell. The symmetry sites of the different atoms in dawsonite are presented in Table 3. The fact that the carbonate ion lies in a site of lower symmetry, C_{2v} , than the unperturbed carbonate, D_{3h} , results in the removal of the degeneracy of the ν_3 and ν_4 vibrations and ν_1 will become infrared active (Table 4). The site group to factor group correlation is also shown in Table 4. The splitting of the carbonate ν_4 vibration is not observed in dawsonite because of the presence of Al—O vibrations, but it is clearly observed in potassium and ammonium dawsonite at 735 and 755 cm^{-1} , respectively (Figures 6A, 6C).

The absorption band at 830 cm^{-1} in potassium and ammonium dawsonite and in some natural samples (Estep and Karr, 1968) cannot be assigned at present.

The wide splitting of the carbonate ν_3 vibration (165 cm^{-1}) is supported by the crystal structure in which one oxygen is only hydrogen bonded while the other two oxygen atoms are bonded to two sodium atoms and one aluminum atom in octahedral coordination. Theoretical calculations for the carbonate ion in bidentate coordination has given splitting for ν_3 as great as 300 cm^{-1} (Fujita *et al.*, 1962). The infrared spectrum would suggest that the carbon to oxygen angles and/or bond distances must be some-

Table 4. Correlation for the carbonate ion in dawsonite

Molecular group, D_{3h}	Site group, C_{2v}	Observed absorption bands (cm^{-1})	Factor group, D_{2h}
ν_1 (symm. stretch) A_1'	A_1 (IR)	1095	B_{1u} (IR)
ν_3 (asymm. stretch) E' (IR)	A_1 (IR)	1565	B_{1u} (IR)
	A_1 (IR)	1400	B_{1u} (IR)
ν_4 (in plane bend.) E' (IR)	B_2 (IR)	725	B_{2u} (IR)
	B_2 (IR)	a	B_{2u} (IR)
ν_2 (out plane bend.) A_2'' (IR)	B_1 (IR)	840	B_{3u} (IR)

* Obscured by Al—O vibrations. Observed in K and NH_4 dawsonite at 755 and 735 cm^{-1} .

Table 5. X-ray diffraction data of the hydrolysis product of ASB with lithium carbonate compared to magnesium aluminum hydroxy carbonates

Precipitate		Manasseite		Hydrotalcite	
<i>d</i> (Å)	<i>I</i> _{relative}	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₁	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₁
7.5	s	7.67	100	7.69	100
4.35	vw				
3.78	s	3.83	20	3.88	70
		2.60	50		
2.50	s	2.49	30	2.58	20
		2.34	40	2.30	20
2.22	w (broad)	2.17	40		
1.91	w (broad)	2.00	40	1.96	20

what different in order to explain the ν_3 splitting. This is in contrast to the crystal structure proposed by Frueh and Golightly which assigns almost equal bond distances and angles to the carbonate ion.

Molecular absorptions are also observed for the ammonium ion in ammonium dawsonite (Figures 6B, 6C). The ammonium ion is also in a low site of symmetry, C_{2h} (Table 3). However, the effective symmetry of the ion must be lower since C_{2h} is not a subgroup of T_d . A comparison of the symmetry sites of C_{2h} and T_d indicates that ammonium could be in dawsonite with C_2 symmetry. This lower symmetry accounts for the presence of the absorption at 1720 cm^{-1} (ν_2) which is inactive in the unperturbed ammonium ion (Figures 6B, 6C). The absorption at 1445 cm^{-1} is the ν_4 vibration of the ammonium ion.

Pyroaurite-sjögrenite-type structure. The room temperature hydrolysis of ASB in the presence of lithium carbonate produces a type of mineral similar to the pyroaurite-sjögrenite group (Table 5). Besson *et al.* (1974) have synthesized lithium aluminum hydroxy carbonate by boiling mixtures of aluminum hydroxide and lithium carbonate. Nevertheless, the presence of a monovalent cation along with aluminum in the brucite-like layers of these minerals is unusual since the general formula for the pyroaurite-sjögrenite group is $\{M_1^{2+}_x M_2^{3+}(\text{OH})_2\}(\text{CO}_3)_{x/2}(\text{H}_2\text{O})_{(1-3x)/(2-\Delta)}$, where Δ is below 0.125 and x has a maximum value of 0.33 (Taylor, 1973).

The infrared spectrum of the hydrolysis product of ASB in the presence of lithium carbonate is shown

in Figure 7 along with a natural hydrotalcite from Dypindel, Norway. Infrared spectra of hydrotalcite and related minerals have been published by Mump-ton *et al.* (1965), but neither band assignments nor specific vibrational frequencies were given. Comparison of the infrared spectra in Figure 7 shows stronger hydrogen bonds for the hydroxyl vibrations (3450 cm^{-1}) in the synthetic samples than in natural hydrotalcite. This difference may be related to the lower d_{001} of the synthetic sample.

Somewhat different features are observed in the region of the carbonate vibrations for both samples. Two broad absorption bands at 1625 and 1375 cm^{-1} are observed in the natural hydrotalcite. Deuterium exchange under vacuum caused the absorption band at 1625 to shift to 1585 cm^{-1} indicating that this band is due to carbonyl vibrations rather than molecular water (Figure 7C). The absorption band at 1375 cm^{-1} appears as two bands at 1385 and 1340 cm^{-1} and a new broad band appears around 1060 cm^{-1} following deuteration under vacuum.

Miyata (1975) has synthesized hydrotalcite-like compounds containing different anions. Absorption bands at 1370 – 1390 and 1680 – 1700 cm^{-1} in a synthetic hydrotalcite with interlayer nitrate ions were interpreted in terms of unidentate-bidentate coordination. This interpretation seems unlikely as it implies that strong covalent bonds exist between inter-layer ions and the brucite-like surface. It is more reasonable to assign the absorption bands at 1625 cm^{-1} in natural hydrotalcite to bicarbonate ion

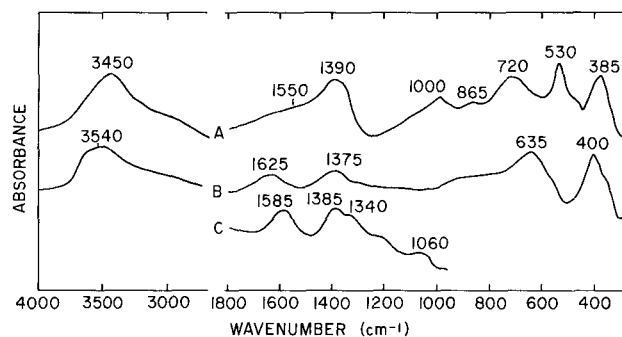


Figure 7. Infrared spectra of hydrotalcites: A, synthetic lithium hydrotalcite; B, natural hydrotalcite; C, deuterated natural hydrotalcite.

and the band at 1375 cm^{-1} to carbonate ion. The splitting (45 cm^{-1}) of the band at 1375 cm^{-1} under vacuum may be due to a small perturbation of carbonate ion as a consequence of evacuation. The appearance of the band at 1060 cm^{-1} is in agreement with this perturbation as it probably represents the ν_1 vibration which is inactive for unperturbed carbonate ion.

In the synthetic lithium hydrotalcite (Figure 7A), a broad absorption band at 1390 cm^{-1} is observed with a shoulder at 1550 cm^{-1} . Because of the absorption band at 1000 cm^{-1} , Besson *et al.* (1974) suggested that bicarbonate anions are in the interlayers of lithium hydrotalcite. The infrared spectrum of bicarbonate ion is not well understood since bicarbonate is usually found as a hydrogen bonded polymer. Monomeric bicarbonate ion has been isolated by Bernitt *et al.* (1965); however, the frequencies reported are significantly different than those observed in lithium hydrotalcite (Figure 7A). Absorption bands of the potassium bicarbonate dimer were reported at 1648, 1628, 1400, 1368 and 1002 cm^{-1} (Bernitt *et al.*, 1965). These bands agree fairly well with those observed in Figure 7A, suggesting that bicarbonate may exist as a dimer in the lithium hydrotalcite interlayer. An alternative explanation is the presence of unperturbed carbonate anions in the interlayer. In this case, the absorption band at 1000 cm^{-1} would be due to the vibrations of the hydroxyl groups coordinated to the cations in the octahedral layers. Attempts to produce a deuterated sample of lithium hydrotalcite were unsuccessful, as were attempts to replace the interlayer ions by washing at room temperature with 0.5 N NaNO_3 or NaCl .

The infrared spectra in the low infrared region reflects the differences in chemical composition between the synthetic lithium hydrotalcite and natural hydrotalcite. Although no assignments can be made at present, the most striking difference is the presence of an absorption at 530 cm^{-1} in synthetic lithium hydrotalcite which must involve some contribution from the lithium cation.

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