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INFRARED INVESTIGATION OF BASIC DOUBLE-CARBONATE HYDRATE MINERALS

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ABSTRACT

The infrared spectra of dundasite, strontiodresserite, dresserite, and hydrodresserite corroborate the occurrence of hydrogen bonding in the minerals. The hydroxyl groups are linked through H-bonds and the frequency of hydroxyl stretching vibrations indicates that the hydrogen bonds are of variable strength. The H-bond strength falls in the order: dundasite > strontiodresserite > dresserite > hydrodresserite. Hydrogen bonding to the carbonate groups produces bicarbonate-like spectral behavior in the minerals. Such behavior implies the structural formulae $BaAl_2O_2(OH)_2(HCO_3)_2 \cdot 3H_2O$ for hydrodresserite, and $MAl_2O_2(OH)_2(HCO_3)_2 \cdot H_2O$ for dundasite, dresserite, and strontiodresserite (M = Pb, Ba, and Sr, respectively). Vibrational evidence also exists for the presence of hydrogen-bond linkages of metal-oxygen units. Structural water was detected in the minerals, but no definite evidence was found for water coordination through the formation of aquo complexes.

The thermal decomposition of hydrodresserite produces a dresserite-like structurally disordered intermediate compound. Definite vibrational similarities exist between dresserite and hydrodresserite from 22 to 275°C; although complete conversion of hydrodresserite to dresserite is not indicated by infrared vibrational analysis, X-ray diffraction studies do indicate such a transition.

SOMMAIRE

Les spectres infrarouges de dundasite, strontiodressérite, dressérite et hydrodressérite confirment la présence de ponts hydrogène dans ces minéraux. Les groupes hydroxyle sont reliés par des ponts hydrogène, et la fréquence des vibrations d'étirement de l'hydroxyle indique que la force de liaison du pont hydrogène est variable. En ordre de force de liaison décroissante des ponts hydrogène, on a la série: dundasite>strontiodressérite>dressérite>hydrodressérite. Un pont hydrogène qui aboutit à un groupe carbonate produit, dans ces minéraux, un comportement spectral semblable à celui du bicarbonate. Un tel comportement implique les formules structurales suivantes: hydrodresséirte = $BaAl_2O_2(OH)_2(HCO_3)_2 \cdot 3H_2O$; dundasite, dressérite et strontiodressérite = $MAl_2O_2(OH)_2(HCO_3)_2 \cdot H_2O$ (M = Pb, Ba et Sr, respectivement). Certaines vibrations pourraient étayer l'existence de ponts hydrogène dans des liaisons oxygène-métal. On a établi la présence d'eau dant la structure des minéraux ci-dessus, sans pouvoir prouver que cette eau soit coordonnée par formation de complexes aqueux.

La décomposition thermique de l'hydrodressérite donne un composé intermédiaire structuralement désordonné semblable à la dressérite. De 22 à 275°C, il existe des analogies certaines au point de vue des vibrations entre la dressérite et l'hydrodressérite. La conversion de l'hydrodressérite en dressérite, établie par diffraction X, serait incomplète d'après l'analyse des spectres infrarouges.

(Traduit par la Rédaction)

INTRODUCTION

Infrared data are not available for dundasite, $PbAl_2(CO_3)_2(OH)_4 \cdot H_2O$, and the recently discovered minerals dresserite, $BaAl_2(CO_3)_2(OH)_4 \cdot H_2O$, strontiodresserite, $SrAl_2(CO_3)_2(OH)_4 \cdot H_2O$, and hydrodresserite, $BaAl_2(CO_3)_2(OH)_4 \cdot 3H_2O$. Since the minerals are compositionally analogous and are probably structurally similar, one would expect close correspondence in spectral features. The absorption bands have been assigned with reference to the infrared investigation by Frueh & Golightly (1967) of dawsonite, $NaAl(CO_3)(OH)_2$. The infrared studies of Huang & Kerr (1960) and White (1974) on the carbonates cerussite, $PbCO_3$, witherite, $BaCO_3$, and strontianite, $SrCO_3$, were also useful in assigning carbonate absorption frequencies.

Dundasite, strontiodresserite and dresserite are orthorhombic. However, the space group of dundasite is *Pbnm* (Cocco *et al.* 1972) whereas that of dresserite is *Pbmm*, *Pb*2_1*m* or *Pbm*$_2$ (Jambor *et al.* 1977b). The space group of strontiodresserite has not been determined but may be the same as that of dresserite. Dawsonite is also orthorhombic, so that similarity of spectral features related to mutually occurring O-H, CO_3, Al-O, and H_2O vibrations is expected. Likewise, spectroscopic similarities between dresserite (orthorhombic) and hydrodresserite, which is triclinic (Jambor *et al.* 1977a), should appear due to their compositional rather than structural likeness.

Hydrogen bonding in dawsonite was found by Frueh & Golightly (1967) from X-ray diffraction and infrared evidence. In dundasite, Cocco *et al.* (1972) determined hydrogen bonding from X-

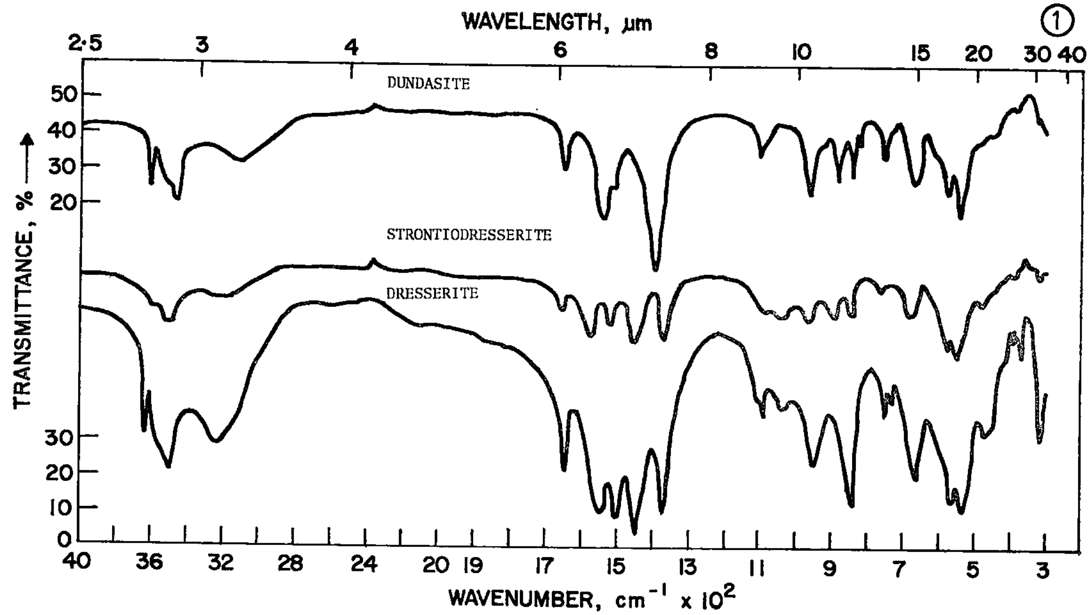

FIG. 1. Infrared spectra of dundasite, strontiodresserite and dresserite.

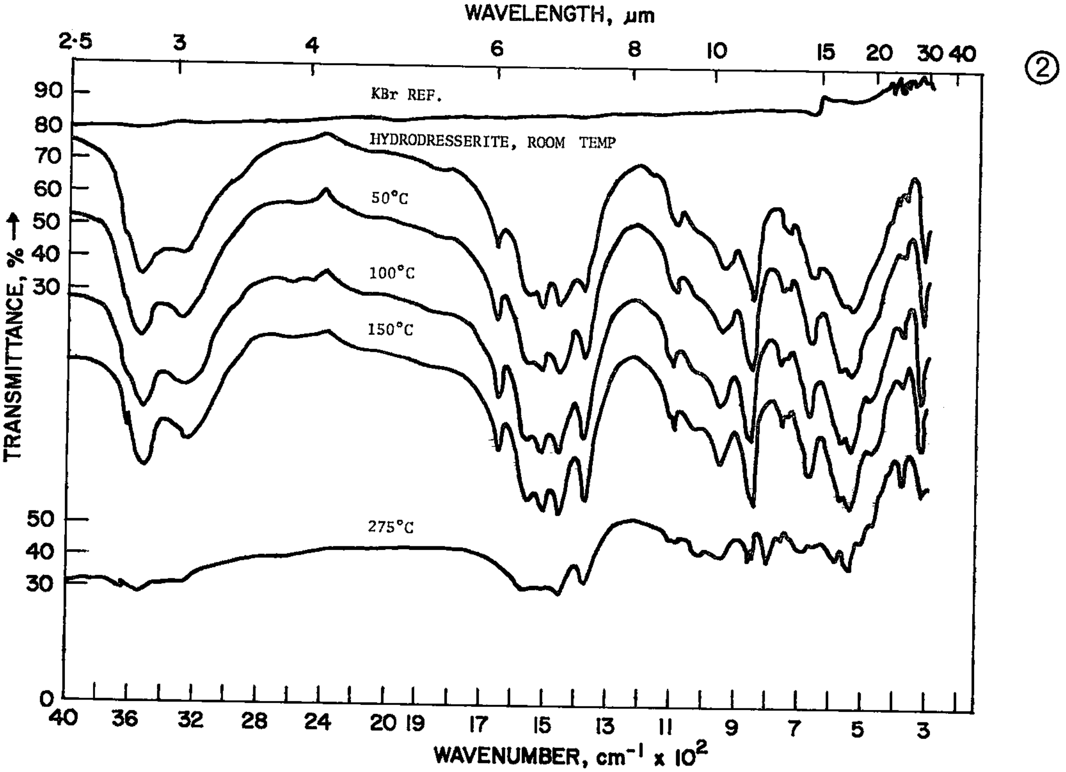

FIG. 2. Infrared spectra of hydrodresserite heated to 50, 100, 150, and 275°C.

ray diffraction studies. Structural framework hydrogen bonding rather than cation coordination occurs with water molecules. Hydrodresserite is a metastable mineral which desorbs water and converts to dresserite, in some cases via an intermediate phase (Jambor *et al.* 1977a). Their

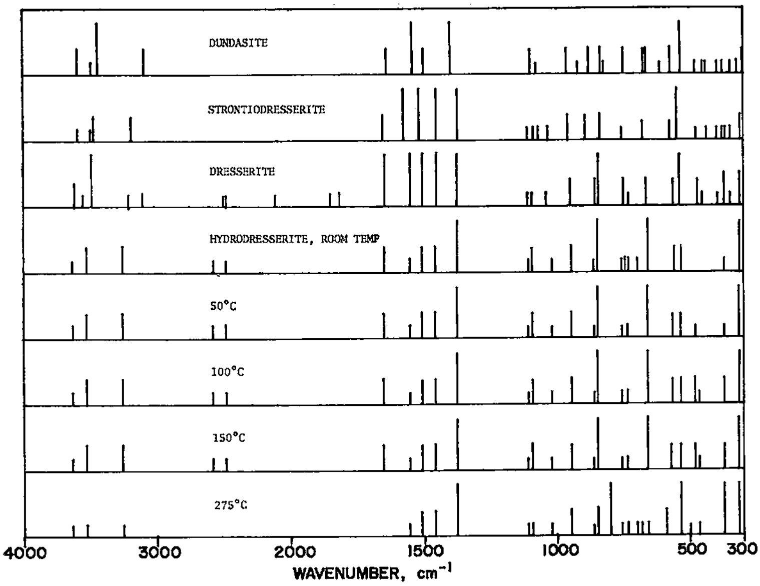

FIG. 3. Band-height diagram of dundasite, strontiodresserite, dresserite, hydrodresserite, and heated hydrodresserite.

X-ray data and heating experiments indicate that the breakdown of hydrodresserite is complex. Spectral data indicate that all compounds formed in the breakdown are structurally similar; after heating to 275°C, the spectra seem to indicate a disordered dresserite-type compound.

EXPERIMENTAL METHOD

The mineral samples were hand-picked under a binocular microscope and checked by X-ray diffraction patterns. Dundasite from Mt. Dundas, Tasmania, was obtained from the National Mineral Collection, Ottawa (Ref. No. 13112). The strontiodresserite, dresserite, and hydrodresserite were from St-Michel, Montreal Island, Quebec, the only locality known. The specimens were prepared for infrared analysis by the standard KBr pressed-pellet technique. The KBr was dried at 140°C for 24 hours prior to use and 0.5 wt. % of sample was added, except for strontiodresserite, for which only 0.2 wt. % was available.

To determine the decomposition pattern, a single hydrodresserite disk was deposited sequentially in an oven at temperatures of 50, 100, 150, and 275°C, held at temperature for one hour, and cooled in a stream of dry nitrogen prior to infrared analysis. The thermal limits of KBr prevented investigation at higher temperatures. On the assumption that pellitization pressures might cause decomposition of the hydrodresserite, a second specimen of the mineral was prepared as a suspension in nujol. The room-temperature KBr and nujol spectra were identical, and therefore only the KBr spectra are reported here.

The IR spectra were registered with a Beckman IR-12 infrared spectrophotometer in the 300-4000 cm^{-1} region using a scanning speed of 40 cm^{-1}/min. The spectra were standardized against polystyrene absorptions, and reproducibility of duplicate spectra was within ±2 cm^{-1} in the 300-2000 cm^{-1} region and ±5 cm^{-1} in the 2000-4000 cm^{-1} region. The spectra of dundasite, strontiodresserite and dresserite are illustrated in Figure 1; those of unheated and heated hydrodresserite appear in Figure 2. Figure 3 shows the band intensities, as determined by the band heights only, in terms of their absorbance relative to the strongest band for that mineral and corrected for differences in sample concentration. Figure 3 also indicates the resolution of certain bands, which is not immediately evident in the spectra as reproduced in Figures 1 and 2.

SPECTRAL COMPOSITION

Spectral features are discussed assuming relatively minor interaction between ionic species in each mineral. The spectra consist of characteristic lattice modes plus sharp spectral bands indicating the presence of distinct internal modes for hydroxyl, water, and carbonate groups. Spectral assignments for dundasite, strontiodresserite, and dresserite are compiled in Table 1; those of hydrodresserite and its thermal products appear in Table 2.

TABLE 1. INFRARED ABSORPTION FREQUENCIES OF DUNDASITE, STRONTIODRESSERITE AND DRESSERITE

Dundasite	Strontiodresserite	Dresserite	Assignment
303(m)	312(m)	313(m)	lattice modes, H_2O librations, M-OH or Al-O-Al deformations
324(w)			
350(w)	350(w)	350(w)	
	370(sh)	372(m)	
382(w)	382(w)		
397(w)	400(w)	395(w)	
440(w)	440(sh)	455(sh)	
455(w)			
485(w)	481(w)	470(m)	ν_{M-O}
542(s)	550(s)	535(s)	
576(m)	578(m)	566(m)	
615(sh)			
667(m)		668(m)	$\nu_{4(CO_3^{2-})}$
675(m)	680(m)		
		730(w)	
753(m)	760(w)	750(m)	ν_{AlO}
826(w)			
843(m)	841(m)	840(s)	$\nu_{2(CO_3^{2-})}$
		858(m)	
883(m)	893(m)		
925(sh)			
965(m)	962(m)	952(m)	$\nu_{HO\cdots Al}$
	1035(w)	1040(w)	OH bridge?
	1070(sh)		
1083(sh)	1093(w)	1088(w)	$\nu_{1(CO_3^{2-})}$
1102(m)	1112(w)	1108(sh)	
1396(vs)	1370(vs)	1375(vs)	$\nu_{3(CO_3^{2-})}$
	1455(vs)	1450(vs)	
1503(m)	1517(s)	1505(s)	
1540(s)	1576(s)	1550(s)	
1643(m)	1653(m)	1644(s)	ν_{HOH}
		1815(sh)	harmonics of unknown origin
		1850(sh)	
		2110(sh)	
		2480(vw)	
		2500(vw)	
		3120(sh)	ν_{OH} + H-bonding
3100(m)	3200(m)	3230(s)	
3446(s)	3480(m)	3490(vs)	
3510(sh)	3510(sh)	3560(sh)	
3600(m)	3600(w)	3625(m)	

TABLE 2. INFRARED ABSORPTION FREQUENCIES OF HYDRODRESSERITE AND ITS THERMAL PRODUCTS*

Frequency cm^{-1}	Final Product Temp. and Absorption Band Intensity After Cooling					Assignment
	Room Temp.	50°C	100°C	150°C	275°C	
315	s	s	s	s	s	lattice modes, H_2O librations, M-OH or Al-O-Al deformations
373	w	w	m	m	s	
465	-	-	sh	sh	w	
480	-	sh	m	m	-	ν_{M-O}
500	-	-	-	-	sh	
535	m	m	m	m	s	
	565(m)	568(m)	570(m)	572(m)	586(m)	
660	s	s	s	s	w	$\nu_{4(CO_3^{2-})}$
682	-	-	-	-	w	
700	sh	-	-	-	sh	
734	w	w	w	w	sh	
741	w	-	-	-	-	ν_{AlO}
755	sh	w	w	w	w	
800	-	-	-	-	s	
848	s	s	s	s	m	$\nu_{2(CO_3^{2-})}$
860	sh	sh	sh	sh	m	
950	m	m	m	m	m	$\nu_{HO\cdots Al}$
1020	sh	sh	sh	w	w	OH bridge?
1090	w	w	w	w	w	$\nu_{1(CO_3^{2-})}$
1110	sh	sh	sh	sh	sh	
1375	s	s	s	s	s	$\nu_{3(CO_3^{2-})}$
1455	m	m	m	m	m	
1505	m	m	m	m	m	
1550	m	m	m	m	m	
1650	m	m	m	m	-	ν_{HOH}
2480	sh	sh	sh	sh	-	harmonics of unknown origin
2580	sh	sh	sh	sh	-	
3260	m	m	m	m	w	ν_{OH} + H-bonding
3530	m	m	m	m	w	
3635	w	w	w	w	w	

*X-ray identification of products for this temperature range are given in Table 5 of Jambor *et al.* (1977a).

sh = shoulder w = weak m = medium s = strong v = very

M=Pb, Sr, Ba for dundasite, strontiodresserite, and dresserite, respectively.

Hydroxyl and water vibrations

Spectral bands with frequencies exceeding 3000 cm^{-1} are assigned to OH vibrations. Hydrogen bonds modify the oscillations by reducing their frequencies proportionate to the hydrogen-bond strength. The data indicate at least three distinct hydroxyl vibrations in the 3200, 3500, and 3600 cm^{-1} ranges. As Cocco *et al.* (1972) have shown, four distinct OH sites exist in dundasite, as well as water of hydration, so that at least four OH frequencies may be assigned readily. The 3200 cm^{-1} vibrations are strongly affected by hydrogen bonding, reducing their absorptions approximately 450 cm^{-1} from the OH^- free-ion frequency. From the relative hydroxyl frequencies, the strength of hydrogen bonds is in the order dundasite>strontiodresserite>dresserite>hydrodresserite. Additional splitting occurs at 3446 and 3510 cm^{-1} for dundasite and at 3480 and 3510 cm^{-1} for strontiodresserite, whereas dresserite splits at 3120, 3230 cm^{1-} and 3490, 3560 cm^{-1}. However, such splitting does not occur for triclinic hydrodresserite, and appears to be influenced by hydrogen-bond strength.

Absorption arising from bridging of two metallic ions by hydroxyl groups may occur at frequencies less than 1100 cm^{-1}. Such bridging occurs in lead complexes studied by Maroni & Spiro (1967), in dawsonite (Frueh & Golightly 1967) and in dundasite (Cocco *et al.* 1972). The 950-965 cm^{-1} bands in the present minerals are assigned to the H-O• • • Al bending mode (Frueh & Golightly 1967).

Structural-water bending vibrations were observed in the 1650 cm^{-1} region. Librational modes due to rotational oscillations of uncoordinated water may account for some of the bands at less than 600 cm^{-1}. Such librational modes are generally quite weak because of restrictive interatomic interactions.

Carbonate vibrations

The medium to very strong vibrations in the 1370-1576 cm^{-1} region are assigned to the ν_3 asymmetric stretching mode of the carbonate group. The strong splitting of ν_3 produces multiple bands in a wide spectral range. The magnitude of splitting is a consequence of low symmetry, differences in environment of the carbonate oxygens, and the formation of hydrogen bonds to the CO_3^{2-} group. In dundasite, two distinct CO_3^{2-} environments exist, and the low symmetry of these environments split the doubly degenerate ν_3 mode to yield two frequencies for each site. In dawsonite and dundasite, two C-O bond lengths are equal and longer than the other, implying two H-bonds which increase the bond lengths. As such bonding produces vibrational structure similar to that of the bicarbonate ion, HCO_3^-, a suitable structural formula could possibly be $NaAlO(OH)HCO_3$ for dawsonite (Seiyama *et al.* 1967) and $PbAl_2O_2(OH)_2(HCO_3)_2 \cdot H_2O$ for dundasite. Analogous structural formulae are postulated for strontiodresserite, dresserite, and possibly hydrodresserite.

Vibrations assigned to the carbonate v_1 symmetric stretching mode appear in the frequency range 1083-1112 cm^{-1}. These bands are infrared-active due to the asymmetry resulting from two unequal carbonate C-O bond lengths and the formation of hydrogen bonds. The observation of two frequencies is consistent with the presence of two distinct carbonate environments. As noted by White (1974), the v_1 intensity increases in the order aragonite (Ca), strontianite (Sr), witherite (Ba), and cerussite (Pb) for the aragonite-type structures. The same intensity increase with cation mass is present for strontianite (Sr), dresserite (Ba), and dundasite (Pb). The out-of-plane bending mode v_2 occurs with medium to strong intensity in the frequency range 840-893 cm^{-1}. Again, doubling occurs as a result of the presence of two distinct CO_3^{2-} environments.

Medium to strong vibrations in the 660-734 cm^{-1} spectral range are characteristic of the v_4 in-plane bend of CO_3^{2-}. Except for weak bands at 730 cm^{-1} in dresserite, and 700 and 734 cm^{-1} in hydrodresserite, little evidence of site-group splitting occurs. In their investigation of the aragonite-type carbonates, Huang & Kerr (1960) found v_4 splitting in strontianite, but not in witherite or cerussite.

In addition to the preceding assignment of fundamentals, additional carbonate vibrations likely appear in the spectral region less than 500 cm^{-1}. These include lattice vibrations but cannot be assigned without confirmatory evidence. Difference bands involving two or more carbonate fundamentals are not expected where the lowest fundamental frequency involved is greater than 600 cm^{-1}.

Metal–oxygen vibrations

From the study of dawsonite by Frueh & Golightly (1967), the singlet band in the 950-965 cm^{-1} region is assigned to the H-O • • • Al bending mode arising from hydrogen bonds directed toward oxygen coordinated to aluminum. This is within the usual spectral range of *M*-OH deformation vibrations. In their crystal-structure determination of dundasite, Cocco *et al.* (1972) showed that aluminum is octahedrally coordinated to 4 hydroxyls and 2 oxygen atoms, thereby supporting such an assignment.

A single band in the 741-760 cm^{-1} region is tentatively assigned to an Al-O stretching vibration. Such an assignment is supported by the work of Stegmann *et al.* (1973) on AlO_6 stretching vibrations in orthorhombic boehmite, AlO(OH), and by Stubičan & Roy (1961) in their studies of aluminosilicates.

Medium to strong absorption in the 470-578 cm^{-1} region is characteristic of metal–oxygen stretching vibrations. According to Barnes *et al.* (1944), the fundamental absorption frequency for a pair of atoms that can be considered to be in isolation from the rest of the crystal, as a first approximation, is given by

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{k_o}{\mu}}$$

where μ = reduced mass of participating atoms, k_o=force constant, c=velocity of light, and v= vibrational frequency in cm^{-1}. If one considers the *M*-O structures of strontiodresserite and dresserite (SrO and BaO, respectively), and assumes constant k_o, then the frequency ratio strontiodresserite:dresserite is 1.03:1.00. This ratio is very close to that of the paired 470-578 cm^{-1} bands of this study. They are therefore assigned to the Sr-O and Ba-O stretching vibrations of strontiodresserite and dresserite. Similarly, the bands at 485, 542, 576 cm^{-1} are assigned to the Pb-O vibrations of dundasite and 535, 565 cm^{-1} are assigned to the BaO vibrations of hydrodresserite.

The medium to strong oscillation occurring below 320 cm^{-1} may arise from Al-O-Al or *M*-OH deformation or from a lattice vibration. A more definite assignment is impossible with the available data.

THERMAL STUDY OF HYDRODRESSERITE

The v_{OH} bands at 3260, 3540, and 3635 cm^{-1} remain at relatively constant intensity upon heating up to 275°C. At 275°C, the band intensities are greatly diminished due to partial sample decomposition with loss of hydroxy and volatilization of structural water. Water loss is indicated by the disappearance of the 1650 cm^{-1} band at 275°C. The 1020 cm^{-1} band intensity increases with temperature and remains weak but present even at 275°C, indicating relatively strong bridging by hydroxyls. However, the $v_{HO...Al}$ deformation at 950 cm^{-1} increases in intensity to 150°C, but is considerably weaker at 275°C. Again, hydrogen-bond strength increases to 150°C but decreases substantially upon subsequent sample decomposition.

The carbonate v_3 absorptions at 1375 and 1455 cm^{-1} increase in intensity to 150°C but are considerably weaker at 275°C. Intensity enhancement at the lower temperatures (room temperature to 150°C) is a result of pronounced splitting due to hydrogen bonding and to progressive formation of a more ordered crystal structure. Diminution at 275°C arises from partial decomposition of the carbonate with release of carbon dioxide. The same effects occur with the ν_1, ν_2, and ν_4 carbonate vibrations in the spectral ranges 1090-1110, 848-860, and 660-734 cm^{-1}, respectively. Enhanced splitting of the carbonate ν_2 vibrations at 275°C is probably due to the presence of non-equivalent carbonate groups.

The ν_{BaO} band at 565-586 cm^{-1} increases in frequency with temperature, probably because of progressively increasing crystallinity. Such crystallinity changes likely account for frequency shifts throughout the spectral region of analysis.

In general, the spectra of hydrodresserite vary relatively little by heating to 150°C. After heating to 275°C, the background absorption appears very high; this may be due to "fogging" of the KBr by desorbed water retained in trace amounts undetectable by infrared.

For dresserite which formed by the breakdown of hydrodresserite at room temperature, the XRD study by Jambor *et al.* (1977a) showed that crystallinity increased with time plus temperature up to 100°C. Examination of the spectra of Figures 1 and 2 and the band-height diagram (Fig. 3) indicates rather marked spectral differences between dresserite, and hydrodresserite and its thermal products. The dresserite has 32 absorption bands whereas hydrodresserite and its thermal products have 25. The additional 7 bands in dresserite are all of very weak intensity and may arise from trace impurities or undefined harmonics. No definite assignment of these bands can be made. However, the spectral positions of the main hydroxyl, carbonate, AlO and *M*O vibrations closely coincide, although intensities vary to some degree. One exception is that the band at 800 cm^{-1} in the 275°C product does not occur with the other thermal products or dresserite. This band is possibly due to an AlO stretching vibration.

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