

INFRARED CHARACTERIZATION OF WATER AND HYDROXYL ION IN THE BASIC MAGNESIUM CARBONATE MINERALS

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ABSTRACT

Infrared spectra in the 0.5-50 μm range have been measured on nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), artinite ($\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$) and hydromagnesite ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$). The CO_3^{2-} internal vibrations are sharp in hydromagnesite and unexpectedly broad and diffuse in artinite and nesquehonite. The OH^- stretching region contains a sharp band indicative of a weak, well defined hydrogen bond in all three minerals. There is also a broad band characteristic of moderately strong and less well defined hydrogen bonds in all three. In addition hydromagnesite has two sharp intense bands not present in the other two minerals. The artinite spectrum is interpretable by Jagodzinski's structure and nesquehonite appears to be similar. Hydromagnesite should have a distinctly different structure. There is no evidence for bicarbonate groups in nesquehonite.

INTRODUCTION

The moonmilk minerals are a series of basic magnesium carbonates. They are found in a number of environments but have been most extensively studied from cave localities, mainly by researchers in Europe. In cave occurrences the minerals take the form of pasty white masses with the texture of cottage cheese. There has been a resurgence of interest in these materials because of their peculiar structures. The structure of artinite was recently determined by Jagodzinski (1965). The structures of the other minerals are unknown but structural determinations are now underway. Table 1 presents a listing of the minerals and a summary of available crystallographic information.

The purpose of the present paper is to examine the infrared spectra of these minerals, particularly the vibrations characteristic of water and hydroxyl ion, with the object of providing a reference against which the proposed structures can be tested. The proposed artinite structure relies heavily on coupling by hydrogen bonds. The infrared spectrum is particularly sensitive to hydrogen bonding and should provide a valuable supplement to less sensitive diffraction methods. Infrared data on these minerals are sparse. The spectrum of hydromagnesite is known (Baron *et al.*, 1959; Pobeguín, 1959). Mumpton *et al.* (1965) list spectra of both hydromagnesite and artinite.

TABLE 1. THE MAGNESIUM CARBONATE BASIC HYDRATES (MOONMILK MINERALS¹)

Mineral	Formula	Space group cell contents	Lattice parameters	Reference
Nesquehonite	$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$	$P2_1/n$ C_{2h}^5 $Z=4$	$a=7.68 \text{ \AA}$ $b=5.39$ $c=12.00$ $\beta=90.45^\circ$	Kinsolving <i>et al.</i> (1950)
Lansfordite	$\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$	$P2_1/m$ C_{2h}^2 $Z=4$	$a=12.369$ $b=7.529$ $c=7.315$ $\beta=99^\circ 36'$	ASTM Powder Data File, Card No. 18-769
Artinite	$\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$	$C2/m$ C_{2h}^3 $Z=4$	$a=16.561$ $b=6.298$ $c=6.220$ $\beta=99^\circ 09'$	Jagodzinski (1965)
Hydromagnesite	$4 \text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	$C222_1$ D_2^5	$a=18.58$ $b=9.06$ $c=8.42$	Murdoch (1954)

EXPERIMENTAL

The specimen of artinite was a well-crystallized mass of needles on serpentine from San Benito County, California. The individual crystals were 2–4 mm long and no extraneous phases were present.

A number of hydromagnesite specimens from localities at Logan Cave, Utah, Wind Cave, South Dakota, and Butler Cave, Virginia, were examined. All were fine-grained white powders. The materials varied considerably in crystallinity as judged by the sharpness of X-ray diffraction peaks. The specimen from Logan Cave, Utah, contained a considerable percentage of material amorphous to X-rays. The varying crystallinity was not apparent in the infrared spectra.

One specimen of nesquehonite was from the type locality at Nesquehoning, Pa. obtained from the mineral collection of F. A. Genth. The other specimen was a synthetic single crystal grown from silica gel media by S. Sommers.

Lansfordite is not stable at room temperature. The type locality material examined in the Genth collection had converted to nesquehonite.

All infrared spectra were obtained from KBr discs containing about 1 mg of sample. Great care was taken in specimen preparation to assure that all discs were completely transparent. Spectra in the range of 300 to 2000 cm^{-1} were obtained on a Perkin-Elmer Model 621 spectrophotometer.

meter. Spectra in the near infrared region including the hydroxyl stretching region were obtained on a Beckman Model DK-2A spectrophotometer.

RESULTS AND DISCUSSION

The spectra are shown in Figures 1 and 2. The mid-infrared region of Figure 1 is dominated by the vibrational modes of the carbonate ion (Table 2). The various bands in the 3000 cm^{-1} range in figure 2 are all due to O-H stretching motions of water or hydroxyl. The near infrared region was scanned from the region of Figure 2 into the visible. No additional features were observed.

The bands in Figure 2 for all structures divide into one or more very sharp bands at high frequencies and a single broad band with some discernible shoulders at low frequencies. The great variation in the OH stretching frequencies is usually attributed to the varying strength of hydrogen bonding between the OH or H_2O molecules and some adjacent oxygen in the structure. Many attempts have been made to relate this frequency shift to the oxygen-oxygen distance, some with considerable success. The theoretical curve of Lippencott and Schroeder (1955) is shown in Figure 3. On it is superimposed the measured data from known structure hydroxides and oxyhydroxides compiled by Glemser and Hartert (1956) and Schwarzmann (1962). This curve has been used to calculate equivalent oxygen-oxygen distances for the various vibrational frequencies and these are tabulated in Table 3.

Jagodzinski (1965) described the structure of artinite as consisting of octahedra of $\text{Mg}(\text{OH})_3(\text{H}_2\text{O})_2\text{O}$ which are edge-linked into chains with attached CO_3^{2-} groups or attached water molecules. The CO_3^{2-} and H_2O alternate statistically along the b -axis and give rise to diffuse X-ray spots and an effective doubling of the b cell parameter. The chains are cross-linked by means of hydrogen bonds between water molecules and the CO_3^{2-} groups. The main hydrogen bond lengths from the artinite structure are tabulated in Table 3. It can be seen that there is a general agreement between these short hydrogen bonds in the range of 2.7 \AA and the frequencies of the various shoulders of the intense broad infrared band. The statistical nature of the bonding is also in agreement with the breadth of the infrared peak. In contrast, the sharp band at 3610 cm^{-1} implies a long (therefore weak) hydrogen bond. There are interchain distances in artinite with lengths very close to the length calculated from this band. Jagodzinski questions whether such long distances can really be hydrogen bonds but it appears from the small shift of the peak that at least a weak hydrogen bond is formed. These bonds are well defined crystallographically (i.e., are not involved with the statistical distribu-

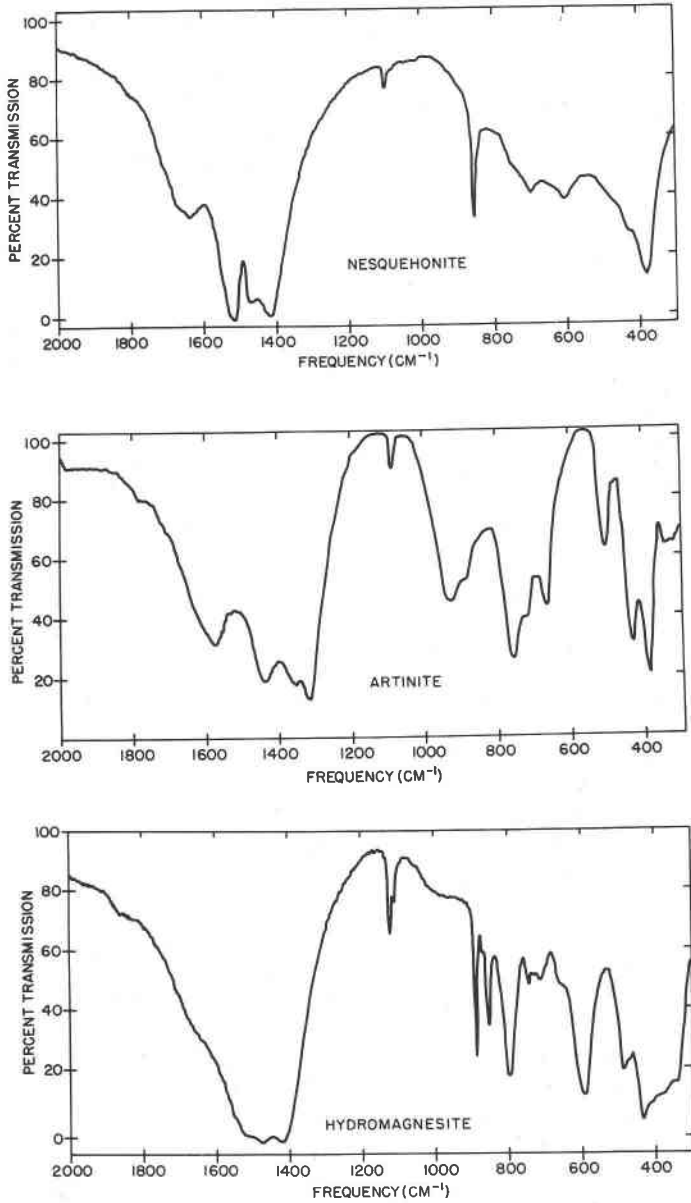


FIG. 1. Infrared spectra of the hydrous magnesium carbonates in the mid-infrared range.

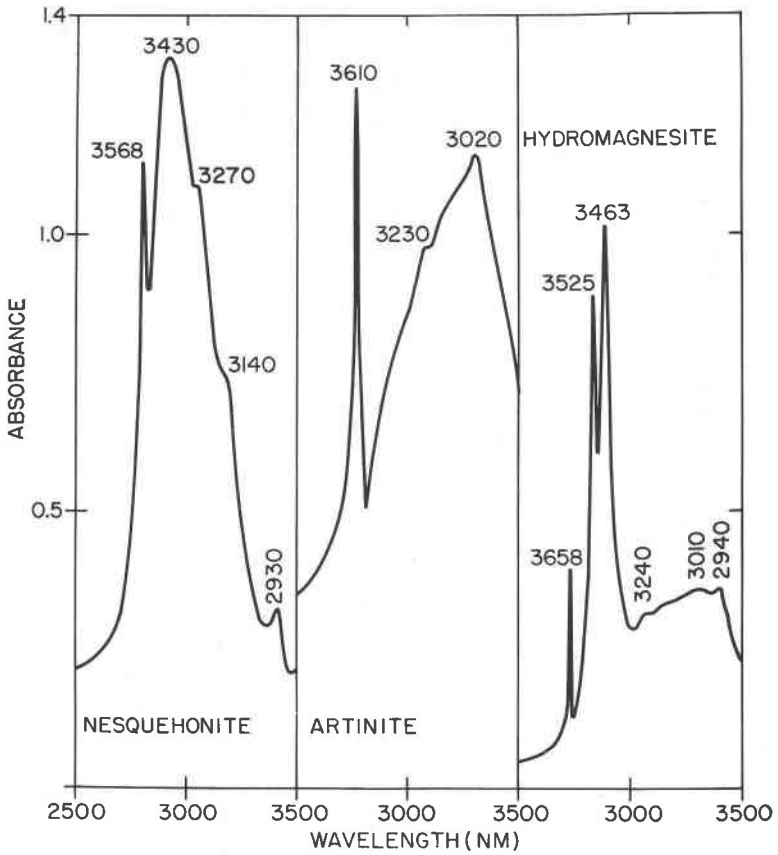


FIG. 2. Spectra of the hydrous magnesium carbonates in the near infrared. The frequencies of the band maxima are given in cm^{-1} .

TABLE 2. FREQUENCIES OF CARBONATE BANDS

Nesquehonite	Artinite	Hydromagnesite	Assignment
1640 cm^{-1}	1575	~ 1650 (?)	H_2O bend
1518	1440	1515	$\nu_3 \text{CO}_3^{-2}$ assym stretch
1470	1355	1475	
1415	1320	1420	
1097	1087	1120	$\nu_1 \text{CO}_3^{-2}$ sym. stretch
		1110	

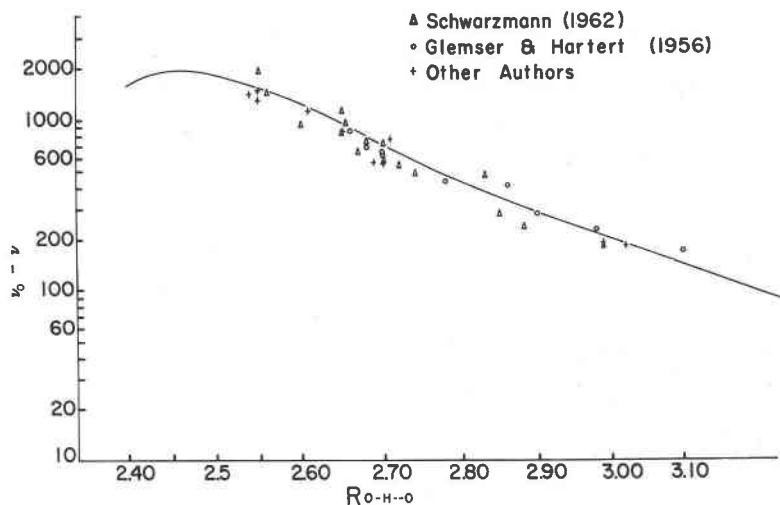


FIG. 3. Relationship between OH frequency shift and O-H . . . O distance. The solid curve is the theoretical relation of Lippencott and Schroeder (1955). Various experimental data for hydroxides, oxyhydroxides, and other hydrogen-bonded inorganic solids are superimposed. $\nu_0 = 3756 \text{ cm}^{-1}$.

tion of water and CO_3^{2-}), and are also in positions where they do not interact. The peak is therefore sharp.

The artinite structure is unique in that it implies a strong participation of the water molecules in the interchain bonding. Some of this is reflected

TABLE 3. CALCULATED^a O-H . . . O DISTANCES

<i>Nesquehonite</i>			
<i>Sharp</i>		<i>Broad</i>	
3568 cm^{-1}	3.03 Å	3430	2.87 Å
		3270	2.78
		3140	2.73
		2930	2.68
<i>Jagodzinski structure</i>			
		<i>Cross-Chain</i>	
		<i>In-Chain</i>	
<i>Artinite</i>			
3610	3.10	3230	2.76
		3020	2.69
		3.06 OH(1)-O(1)	2.73 OH(1')-OH(1'')
			2.87 OH(1')-H ₂ O(1')
			2.61 H ₂ O(1'')-CO ₃
			2.72 H ₂ O(1'')-CO ₃
<i>Hydromagnesite</i>			
3658	3.22	3240	2.77
3525	2.97	3010	2.70
3463	2.90	2940	2.68

^a Calculation from Lippencott-Schroeder curve of figure 3.

in the H_2O bending mode near 1600 cm^{-1} which has shifted to lower frequencies.

The CO_3^{2-} stretching modes are split into three components implying that not only is the CO_3^{2-} site distorted but that there are several crystallographically distinct CO_3^{2-} groups in the structure (see papers by Adler and Kerr, 1963a and 1963b, for a more complete discussion of the infrared spectra of carbonate ions in crystals). The bending modes are broad and indistinct in strong contrast to usual carbonate spectra where the bending modes are quite sharp. This is a collaboration of the statistical positioning of the carbonate ions in the Jagodzinski structure.

The infrared spectrum of nesquehonite is very similar to that of artinite and may imply a similar structural arrangement. The sharp band is a bit lower in frequency implying a shorter hydrogen bond length for some unperturbed hydrogen bond. The broad group of bands is also present but it peaks at higher frequencies. The range of implied strong hydrogen bond lengths in nesquehonite, however, is much the same as for artinite as indicated in Table 3. There is no evidence that nesquehonite contains bicarbonate groups as has been claimed. The bicarbonate ion usually hydrogen bonds very strongly and the characteristic infrared frequencies are shifted to the range of $2200\text{--}2500\text{ cm}^{-1}$ (see Nakamoto, Margoshes, and Rundle, 1955, for a description of the infrared spectra of NaHCO_3 and KHCO_3).

The infrared spectrum of hydromagnesite is distinctly different. The internal modes of the carbonate ion are split, indicating site distortion and distinct kinds of carbonate ions, but the bands are sharp and well resolved, speaking against the active participation of the carbonate groups in the bonding as was the case for artinite. Hydromagnesite is much closer to the more usual carbonate spectra in this respect. The OH^- stretching region is much more complicated. There is a broad absorption band at lower frequencies but it is quite weak. Also occurring is a very sharp band at 3658 cm^{-1} which must be due to an almost free O-H vibration; the hydrogen bond shift is extremely small and the calculation of the 3.22 \AA distance is probably not very accurate. In agreement with the low intensity of these bands, the H_2O bending vibration at 1650 cm^{-1} is also very weak and appears only as a faint shoulder on the side of the CO_3^{2-} stretching band. The dominant feature in the spectrum is the pair of strong sharp bands at 3525 and 3463 cm^{-1} . These have a modest hydrogen bonding shift corresponding to distances of 2.97 and 2.90 \AA . These distances are characteristic of many hydroxides and oxyhydroxides with more open layer structures. These results imply that the hydromagnesite structure is of a different kind than the nesquehonite

and artinite structures, and that much of the water that appears in the usual formula is probably present as OH rather than H₂O. These OH-groups form hydrogen bonds of modest strength which may be of structural importance. The carbonate ions are likely packed in the structure and participate only in ionic bonding.

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