American Mineralogist, Volume 95, pages 1515–1522, 2010

Far infrared spectroscopy of carbonate minerals

**Tatiana N. Brusentsova,[1,]* Robert E. Peale,[1] Douglas Maukonen,[1]
George E. Harlow,[2] Joseph S. Boesenberg,[2] and Denton Ebel[2]**

[1]Department of Physics, University of Central Florida, Orlando, Florida 32816, U.S.A.
[2]Department of Earth and Planetary Sciences, American Museum of Natural History, New York, New York 10024, U.S.A.

Abstract

This study presents far infrared spectra in the range 650–70 cm^{-1} of 18 common and rare carbonate minerals. Mineral samples of known provenance are selected and physically characterized to determine the purity of the crystalline phase and their composition. The fine ground mineral powders are embedded in polyethylene pellets, and their transmittance spectra are collected with a Fourier spectrometer. The far infrared spectra of different carbonate minerals from the same structural group have well-defined similarities. Observed shifts generally manifest the mass effect of the constituent metal cations. Remarkable spectral differences occur for different carbonates in the far IR region and may serve as fingerprints for mineral identification and are more useful identifiers of carbonate species than those in any other infrared range. For some of the minerals studied here, like kutnohorite, artinite, gaylussite, and trona, no far infrared spectra to that extend (up to 70 cm^{-1}) have been found in literature.

Keywords: IR spectroscopy, far infrared, transmittance spectra, carbonate minerals

Introduction

The vibrational spectrum of a carbonate mineral consists of mid-infrared (IR) internal modes due to bending and stretching within the carbonate anion and far IR lattice modes. The far IR modes probes lattice vibrations and are unique for a specific crystalline structure, differing significantly for different polymorphs of the same chemical compound in different crystalline forms. The spectral region where lattice vibrations occur is below 600 cm^{-1} (Nyquist and Kagel 1971; White 1974). The far IR is an ideal spectral range when it comes to distinguishing between different minerals. For distinguishing carbonates with IR spectra, far-infrared data are indispensible. One situation where mineral identification using IR spectroscopy is of greatest use is in the astronomical analysis of cosmic dust. Successfully launched in 2009, Herschel Space Observatory will collect the spectra from the interstellar objects in the far IR and sub-millimeter range (167–15 cm^{-1}). This will substantially enhance astronomical observations in this range (Rowan-Robinson 2009). These spectra will provide the information about the distribution of different mineral species in space, which in turn allows to deduce information on physical conditions and the possible presence of water in its different states. Only since the past 10 years has far IR spectroscopy become a usable tool for identifying the mineral dust composition around the astronomical objects (Chiavassa et al. 2005). Since that time, attempts to identify some common minerals that possess prominent far IR features observed in dust found around various astronomical objects are being undertaken. Among those minerals the carbonates group is especially interesting. The presence of carbonate grains within interplanetary dust particles was demonstrated by Sandford (1986) and Tomeoka and Buseck (1986) by means of laboratory analysis. Kemper et al. (2002a, 2002b) attributed the 109 and 161 cm^{-1} emission bands in spectra of planetary nebula NGC 6302 collected by the Infrared Space Observatory (ISO) to calcite and dolomite. Similar emission bands between 111 and 91 cm^{-1} were found by Chiavassa et al. (2005) in 17 out of 32 ISO spectra of proto stars and were again attributed to the presence of calcite. All these data encourage an extensive laboratory infrared studies of terrestrial carbonate minerals to the far IR range.

All information on vibrational spectroscopy of carbonate minerals up to 1973 has been reviewed in White (1974). Also, measured and calculated vibration frequencies for all carbonate groups are presented in Gadsden (1975), although in this publication only peak frequencies are given, rather then the full spectra themselves. Within the mid-IR range, the vibrational spectra of naturally occurring carbonate minerals have been extensively studied down to 625 cm^{-1} (Huang et al. 1960; Adler and Kerr 1962, 1963a, 1963b; Chester et al. 1967; Hunt et al. 1950; Weir et al. 1961). IR spectra of many carbonate minerals in the range between 400 to 4000 cm^{-1} with specified characteristic frequencies are given in Moenke (1962, 1966). A study of three possible carbonate polymorphs (aragonite, calcite, and vaterite) is reported in Weir et al. (1961).

Only a few far IR spectral data on naturally occurring carbonate minerals of sufficient quality to be useful for application to astronomical data analysis can be found in the literature. There is a substantial work on 10 anhydrous normal carbonates (Morandat et al. 1967), where the far IR spectra (400–12 cm^{-1}) together with the assignments for all the lattice vibrations are provided. Absorption spectra of 7 anhydrous normal carbonates in 500–30 cm^{-1} range are presented in Angino (1967). However, all these spectra contain gaps around 350 and 140 cm^{-1}, which

---

* E-mail: brust455@inbox.ru

0003-004X/10/0010–1515$05.00/DOI: 10.2138/am.2010.3380

distorts the overall spectral pattern. Far IR spectra between 200 to 50 cm^{-1} of 3 carbonates (dawsonite, calcite, and dolomite) are presented in Karr et al. (1969). IR spectra (mass absorption coefficients) of dolomite, calcite, aragonite, magnesite, siderite, and ankerite in the range of 5000–50 cm^{-1} also are presented in Kemper et al. (2002a, 2002b), but with no peak frequencies specified. Moreover, data presented as mass absorption coefficient, while suitable for astrophysics, is less useful for mineral identification where the raw data are in the form of transmittance. A detailed IR investigation of the Cd- and Mg-carbonate solid solutions has been performed in the range of 50–2000 cm^{-1} (Bromiley et al. 2007). In Bessière-Morandat et al. (1970), the vibrational features (no full spectra) in the range of 5000–67 cm^{-1} for four hydroxyl-containing carbonates (hydrocerussite, hydromagnesite, azurite, and malachite) are tabulated and assigned to different virbrational modes. The vibrational modes of azurite and malachite with the assignments in the region of 5000 to 60 cm^{-1} (again without presentation of the spectra themselves) are also reported in Goldsmith and Ross (1968). IR spectra of three hydrated and hydroxyl-containing carbonates (nesquehonite, artinite, and hydromagnesite) in the 2000–350 cm^{-1} range have been reported in White (1971). The spectra of 23 carbonate compounds between 3800 and 45 cm^{-1} are presented by Nyquist and Kagel (1971). Most are represented by chemical reagents, and no assignments or peak frequencies are specified. Also, the 200–45 cm^{-1} region is poorly resolved, which makes the main characteristic features in the far IR range difficult to identify. Far IR transmittance spectra (4000 to 30 cm^{-1}) of various alkaline earth double carbonates (huntite, alstonite, norsethite, baritocalcite, and benstonite) are reported in Scheetz and White (1977), and the assignments for lattice vibrations are provided. All references, compiled to the best of our knowledge, containing data on far IR spectra for carbonates minerals considered in this paper, are given in the Table 1.

According to (Kolrausch 1943) the lowest fundamental vibration (ν_4) of CO_3^{2-} is situated at 680 cm^{-1}, so that all absorption bands reported here may be attributed to lattice vibrations. We determine frequencies of the main peaks in our spectra and compare them to previously published values, where available. The substantial differences in the values of main peak frequencies, which can be found in the literature, may be partially explained by the variations in chemical composition.

EXPERIMENTAL DETAILS

Carbonate samples (Table 2) were selected from the mineral collection of the American Museum of Natural History (AMNH). Most samples were extracted from specimens as macroscopic crystals by visual inspection under a stereo microscope to manually select those with similar morphology and absence of visible zoning, exsolutions, or inclusions.

All samples were examined to establish their identity, major-element composition, and chemical homogeneity. X-ray diffraction analyses of macroscopic grains were performed using a Rigaku DMAX/Rapid microdiffraction system, using incident-monochromatized Cu*K*α radiation, operating at 46 kV and 40 mA. Subsequent search/matching was carried out using JADE software (Materials Data, Inc.) referenced to the ICDD PDF-2 diffraction database file. The lattice parameters extracted from powder XRD data are given in Table 2.

Chemical composition and impurity content were analyzed by electron microprobe analysis (Cameca SX100) of polished grain mounts. Backscattered electron imaging was used for a basic assessment of homogeneity and existence of included phases, and energy dispersive spectrometry was used to confirm the phases present as well as to identify any included phases. Both individual point analyses and traverses were carried out on single grains. Traverses were particularly valuable in evaluating compositionally zoning and were typically ~1 mm long with 10 points. All samples considered in this study have acceptable purity (near end-member composition) and homogeneity. The impurities determined by electron microprobe analysis are presented in the Table 2, in the form of molar percentage of the carbonates of a corresponding metal. Complete data is available from the data website for this project: http://research.amnh.org/users/debel/pub/LAP-data/.[1]

All the carbonates were further ground in a McCrone Micronizer cylindrical mill to powders with intended average particle size of ~5 μm or less. Particle sizes were verified by scanning electron microscopy of dispersed powders. Sufficiently small particle size is important to minimize scattering (Coleman 1993; Brügel 1962), whose signature is a sloping transmittance baseline. Also, the effective thickness [$d = m/(\rho \cdot A)$, where m is mineral mass per pellet, ρ is mineral mass density, and A is the area of the IR sample pellet cross-section] of a dilute dispersion of minerals in a sample matrix should not be less than the individual particle size.

IR transmittance measurements were made on suspensions of mineral particles in polyethylene (PE) pellets 3 cm in diameter and 1 mm thick containing ~700 mg of PE powder (Mitsui Chem MIPELON XM-220 PE microparticles with 30 μm average size), which has high far IR transparency and low melting temperature (136 °C). To avoid saturation of the absorption features in transmittance the total effective thickness must be no more than several micrometers. This condition is satisfied by mineral content of ~3–9 mg per pellet (~0.5–1.2 wt%; Brügel 1962).

A fine distribution of mineral particles in the PE is achieved by thoroughly mixing the desired mineral powder with incremental additions of PE powder using an agate mortar and pestle. The mixture is transferred to a Teflon Pelletier and leveled by plunger rotation. Hot pressing at a controlled temperature of ~150 °C for 30 min

---

[1] Deposit item AM-10-059, project data. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 1. References on the previously published studies, which contain far IR spectra

Mineral	Chemical formula	Previously published IR data below 400 cm^{-1}
Ankerite	$Ca(Fe_{0.28}Mg_{0.65})(CO_3)_2$	Kemper et al. (2002a, 2002b)
Aragonite	$CaCO_3$	Morandat et al. (1967); Kemper et al. (2002a, 2002b)
Artinite	$Mg_2(CO_3)(OH)_2 \cdot 3H_2O$	White (1971)
Calcite	$CaCO_3$	Morandat et al. (1967); Angino (1967); Karr et al. (1969); Nyquist and Kagel (1971); Kemper et al. (2002a, 2002b)
Cerussite	$PbCO_3$	Morandat et al. (1967); Angino (1967); Nyquist and Kagel (1971)
Dolomite	$CaMg(CO_3)_2$	Morandat et al. (1967); Karr et al. (1969); Kemper et al. (2002a, 2002b)
Gaylussite	$Na_2Ca(CO_3)_2 \cdot 5H_2O$	–
Huntite	$CaMg_3(CO_3)_4$	Scheetz and White (1977)
Hydromagnesite	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$	Bessière-Morandat et al. (1970); White (1971)
Hydrozincite	$Zn_5(CO_3)_2(OH)_6$	Nyquist and Kagel (1971)
Kutnohorite	$Ca_{0.78}Mn_{1.13}(CO_3)_2$	–
Magnesite	$MgCO_3$	Morandat et al. (1967); Angino (1967); Kemper et al. (2002a, 2002b); Bromiley et al. (2007)
Rhodochrosite	$MnCO_3$	Morandat et al. (1967); Angino (1967); Nyquist and Kagel (1971)
Siderite	$FeCO_3$	Angino (1967); Kemper et al. (2002a, 2002b)
Smithsonite	$ZnCO_3$	Morandat et al. (1967)
Strontianite	$SrCO_3$	Morandat et al. (1967); Angino (1967); Nyquist and Kagel (1971)
Trona	$Na_3(HCO_3)(CO_3) \cdot 2H_2O$	–
Witherite	$BaCO_3$	Morandat et al. (1967); Angino (1967); Nyquist and Kagel (1971)

Table 2. Mineral samples, formula, unit-cell parameters, impurities (mol%), and mineral concentration in IR samples (wt%)

Mineral, AMNH cat. no., locality	Formula	Crystal system, Space group	Unit-cell constants (Å)			Impurities, mol%	IR %
			a	*b*	*c*		
Calcite-structure carbonates							
Magnesite 99133, Bajia, Brazil	$MgCO_3$	Tri., $R\bar{3}c$	4.631	–	15.012	Fe < 1, Ca < 1	0.90
Calcite 102282, Canada	$CaCO_3$	Tri., $R\bar{3}c$	4.990	–	17.061	–	0.90
Rhodochrosite 46075, South Africa	$MnCO_3$	Tri., $R\bar{3}c$	4.792	–	15.657	Mg < 2.5, Ca < 1	0.45
Siderite 48283, Minas Gerais, Brazil	$FeCO_3$	Tri., $R\bar{3}c$	4.679	–	15.260	Mg ~ 37, Mn ~ 1.4, Ca < 1	0.45
Smithsonite 71389, New Mexico	$ZnCO_3$	Tri., $R\bar{3}c$	4.658	–	15.045	undefined	0.90
Aragonite-structure carbonates							
Aragonite 110828, Spain	$CaCO_3$	Orthor., *Pmcn*	4.968	7.983	5.748	Sr < 1	0.90
Strontianite 8514, Germany	$SrCO_3$	Orthor., *Pmcn*	5.092	8.373	6.001	Ca ~ 5	0.90
Witherite 63364, Czechoslovakia	$BaCO_3$	Orthor., *Pmcn*	5.299	8.908	6.423	Sr < 1.4	1.34
Cerussite 94104, Namibia	$PbCO_3$	Orthor., *Pmcn*	5.200	8.531	6.167	–	0.90
Dolomite-structure carbonates							
Huntite 30249, South Australia	$CaMg_3(CO_3)_4$	Tri., *R*32	9.497	–	7.813	Na < 1, Sr < 1	0.45
Dolomite 26224, Styria, Austria	$CaMg(CO_3)_2$	Tri., $R\bar{3}$	4.801	–	15.967	Fe < 1	0.45
Ankerite 63808, New York, U.S.A.	$Ca(Fe_{0.28}Mg_{0.65})(CO_3)_2$	Tri., $R\bar{3}$	4.813	–	16.065	Mn < 1.4	0.90
Kutnohorite 92090, Franklin, New Jersey, U.S.A.	$Ca_{0.78}Mn_{1.13}(CO_3)_2$	Tri., $R\bar{3}$	4.850	–	16.206	Zn < 1.2, Mg < 2.5, Fe < 1.4	0.90
Hydroxyl-containing carbonates							
Hydrozincite 19191, Italy	$Zn_5(CO_3)_2(OH)_6$	Monocl., *C*2/*m*	13.512	6.272	5.409	Na < 4.2, Pb ~ 0.5	0.90
Hydromagnesite 34974, Canada	$Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$	Monocl., *P*21/*c*	10.079	8.927	8.338	–	0.90
Artinite 44829, California, U.S.A.	$Mg_2\,(CO_3)(OH)_2{\cdot}3H_2O$	Monocl., *C*2/*m*	16.548	3.151	6.221	–	0.90
Hydrated carbonates							
Gaylussite 30027, California, U.S.A.	$Na_2Ca(CO_3)_2{\cdot}5H_2O$	Monocl., *C*2/*c*	14.344	7.780	11.202	–	–
Acid carbonates							
Trona 24389, Wyoming, U.S.A.	$Na_3(HCO_3)(CO_3){\cdot}2H_2O$	Monocl., *C*2/*c*	20.422	3.492	10.331	–	–

Note: The uncertainty in lattice parameters ~0.0005 Å, in mineral concentrations ~10%.

transforms the powder to a uniform pellet. The resulting pellets are translucent in the visible spectral range and sufficiently transparent microscopically to inspect them for the presence of large particles. All the pellets prepared during this study will be archived in the AMNH mineral collection (Department of Earth and Planetary Sciences, Division of Physical Sciences) and made available for loan.

A Bomem DA8 vacuum-bench Fourier spectrometer was used to collect far IR transmittance spectra. A globar source viewed through 12 and 3 μm Mylar pellicle beamsplitters by a DTGS FIR detector provided 70–650 cm^{-1} spectral range for measurements. A spectral resolution of 4 cm^{-1} suffices for far IR mineral features. Each measured spectrum consists of the superposition of 1000 scans, giving a collection time for each of about 30 min. Transmittance is obtained by dividing the sample spectra by a blank PE pellet spectrum.

The above described method of polyethylene pellets was not suitable for two of the mineral samples investigated, namely gaylussite [$Na_2Ca(CO_3)_2{\cdot}5(H_2O)$] and trona [$Na_3(CO_3)(HCO_3){\cdot}2(H_2O)$]. These two minerals appeared to decompose while hot pressing the sample pellets. This has been verified by XRD of the powder-like mineral sample before and after heating at similar conditions. For measuring far infrared spectra of trona and gaylussite, their powders were dispersed over Scotch tape and a plain tape was used as a reference for obtaining a transmittance spectrum.

RESULTS AND DISCUSSION

Calcite-structure carbonates

Transmittance spectra of the calcite-group carbonates are presented in Figure 1. There are 5 active IR lattice vibrations for calcite-type carbonates: 3 vibrations relative to the center of gravity represented by the anti-translatory vibrations of class E_u (when all the CO_3 ions are vibrating in parallel or perpendicular opposite directions to the phase of the cations), and 2 librations of the carbonate anion of class A_{2u} (Morandat et al. 1967; Couture 1947; Cabannes 1942).

The magnesite ($MgCO_3$) spectrum reveals three strong separate peaks at 228, 256, and 306 cm^{-1}, one strong broad band at 380 cm^{-1}, and a shoulder at 439 cm^{-1}. These four bands are the primary lattice vibrations of magnesite, similar to those reported previously (Morandat et al. 1967; Angino 1967), with slight variations of the corresponding frequencies (Table 3). The weak absorption bands below 200 cm^{-1} reported by Morandat et al. (1967) were not observed. In Moenke (1962), a double-structured strong peak appears at about 425 cm^{-1}, which makes a good connection with our 380–439 cm^{-1} feature.

The far IR spectrum of calcite ($CaCO_3$) has been widely reported. Two strong separate peaks at 110 and 228 cm^{-1}, an adjacent medium peak at 98 cm^{-1}, and one broad strong band at 319 cm^{-1} with a shoulder at 360 cm^{-1} are in good agreement with previous researchers (Morandat et al. 1967; Angino 1967; Scheetz and White 1977; Nyquist and Kagel 1971) (Table 3).

The spectrum of manganese carbonate (rhodochrosite, $MnCO_3$) contains a very characteristic triplet of strong, well-resolved peaks (160, 177, and 205 cm^{-1}) and a broad strong peak at 308 cm^{-1} with a shoulder at 352 cm^{-1}, which coincide well with those reported previously (Angino 1967; Morandat et al. 1967) (Table 3), and with a downturn at the 400 cm^{-1} limit of the spectrum in Moenke (1962).

For siderite ($FeCO_3$) there are two broad bands: one at 230 cm^{-1} with a prominent shoulder at 195 cm^{-1} and a broad strong band at 378 cm^{-1}. Similar far IR bands are demonstrated in the siderite spectra by others (Angino 1967; Kemper et al. 2002a, 2002b), but ours are shifted to longer wavelength (Table 3).

The spectrum of smithsonite ($ZnCO_3$) contains two strong broad bands, at 202 and 309 cm^{-1} with a shoulder at 360 cm^{-1}, like those reported in Morandat et al. (1967) (Table 3). Additionally, one medium peak at 461 cm^{-1} with a shoulder at 486 cm^{-1} is found, which has not been reported previously. The origin of these peak might indicate the presence of some hydrozincite [$Zn_5(CO_3)_2(OH)_6$] within our smithsonite sample, since the spectrum of hydrozincite contains a prominent peak at 467 cm^{-1} (see below). A mid-IR spectrum of smithsonite in Moenke (1962) contains a definite slope starting from 450 to 400 cm^{-1}, which hints at a possible peak right below 400 cm^{-1}. We also find two weak peaks at 98 and 109 cm^{-1}, which have not been reported previ-

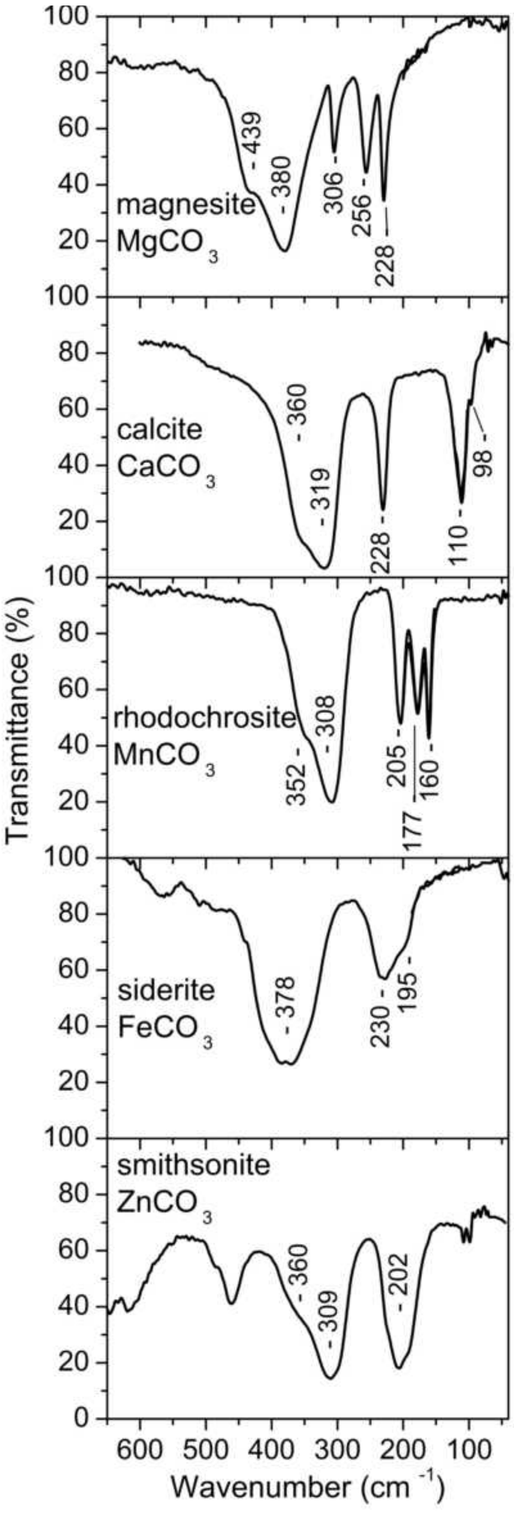

FIGURE 1. Far IR spectra of the calcite-structure carbonates.

ously. The only bands on the spectrum, which should be attributed to smithsonite itself, are those at 360–309 and 202 cm^{-1}. The other features at the spectrum are due to the contaminants.

For the carbonates, it has been observed previously that IR bands shift to longer wavelengths with an increase in atomic number of the metal cation (Morandat et al. 1967). For the calcite group this effect is observed in the broad band, which shifts from 380 cm^{-1} (magnesite, $MgCO_3$) to 319 cm^{-1} (calcite, $CaCO_3$) and then to 308 and 309 cm^{-1} for rhodochrosite ($MnCO_3$) and smithsonite ($ZnCO_3$), respectively (Fig. 1). The fact that a corresponding band in siderite's ($FeCO_3$) spectrum is, opposite to the expectations, shifted to higher frequencies (378 cm^{-1}) should be due to a considerably high content of $MgCO_3$ solid solution (~37 mol%) in the siderite sample (Table 2).

Aragonite-structure carbonates

Normal vibrations for the aragonite structure have been determined by Couture (1947), and there are 11 far-IR active lattice vibrations predicted (Morandat et al. 1967; Couture 1947; Cabannes 1942). Among these, seven are modes around the center of gravity, representing the anti-translatory vibrations (Morandat et al. 1967). The other four modes are librations of the CO_3 group (Morandat et al. 1967; Narayanan et al. 1958), which lead to large change of polarizability and produce several peaks (both in IR and Raman spectra) (Narayanan et al. 1958) at wavelengths beyond those for anti-translatory vibrations. Only a portion of the 11 predicted peaks is clearly observed in the experimental spectrum given in Angino (1967) and Morandat et al. (1967). The remaining modes most likely are unresolved and contribute to the structure in the broad band.

For aragonite ($CaCO_3$), the strong broad band peak is at 263

TABLE 3. Far IR absorption bands of calcite-structure carbonates: comparison with previous works

Mineral	Our work	Prior works
Magnesite	–	158W*, 164W†
	–	187W(Sh)†
	228S	231S*, 230S†
	256S	263S*, 256S†
	306S	303S*, 306S†
	380bS	380bS*, 387bS†
	439S(Sh)	440S(Sh)†
Calcite	98M	–
	110S	106S*, 106S†, 120S‡, 110S§
	–	190(Sh)†
	228S	229S*, 228S†, 230S‡, 230S§
	319bS	312bS*, 315S†, 320S‡, 325bS§
	360S(Sh)	–
Rhodochrosite	160S	157S*, 162S†, 160S§
	177S	181S*, 180S†, 175S(Sh)§
	205S	198S*, 205S†, 205S§
	–	264W(Sh)†
	308bS	316S*, 312S†, 325bS§
	352S(Sh)	
		395M(Sh)†
		465S†
Siderite	–	165W(Sh)†
	–	184S†
	195M(Sh)	208S†
	–	215W†
	230M	–
	–	300W(Sh)†
	–	330S†
	378bS	
Smithsonite	–	165W(Sh)*
	202bS	200bS*
	309bS	307bS*
	360M(Sh)	–

Note: S = Strong, M = Medium, W = Weak, Sh = Shoulder, b = broad.
* Morandat et al. (1967).
† Angino (1967).
‡ Scheetz and White (1977).
§ Nyquist and Kagel (1971).

cm^{-1} and has a sharp adjacent peak at 215 cm^{-1}, in agreement with Morandat et al. (1967), where the corresponding broad strong band at 267 cm^{-1} has been attributed to anti-translatory vibrations of the carbonate group. This broad band is a superposition of overlapping peaks separated by about 20 cm^{-1} and attributed to anti-translatory vibrations (B_{1u}, B_{2u}, B_{3u}) (Morandat et al. 1967; Couture 1947; Narayanan et al. 1958). The librations of CO_3 groups are responsible for a peak at 110 cm^{-1} and the peak at 215 cm^{-1} (Morandat et al. 1967) (Table 4).

A strong, broad-structured band with bumps at 140, 180, 210, 227, and 267 cm^{-1} appears in the strontianite ($SrCO_3$) spectrum, which agrees well with Morandat et al. (1967) and Nyquist and Kagel (1971), and especially with Angino (1967) (Table 4; Fig. 2). Two peaks identified at 227 and 210 cm^{-1} are attributed to anti-translatory vibrations [238 and 212 cm^{-1} by Schaeffer et al. (1926)]. The two lowest peaks at 140 and 180 cm^{-1} may be attributed to librations of CO_3 groups, in analogy to aragonite (Morandat et al. 1967).

For witherite ($BaCO_3$), our observations contrast with previous studies. We observe only a single, broad-structured band between 250 and 100 cm^{-1}, whereas in Nyquist and Kagel (1971) additional weak peaks at 355 and 315 cm^{-1}, in Scheetz and White (1977) a weak shoulder at 300 cm^{-1}, and in Angino (1967) a weak band at 319 cm^{-1} are found (Table 4). The bumps on the broad band at 137, 155, 182, 205, and a shoulder at 230 cm^{-1}, are similar to those reported in the above mentioned sources (Table 4). The better resolved peaks at 137 and 155 cm^{-1} are due to the librations of CO_3 groups. They also appear in the Raman spectrum of witherite at 136 and 154 cm^{-1}, as reported in Narayanan et al. (1958). Peaks at 205 and 182 cm^{-1} correspond to anti-translatory vibrations, as identified for the similar features at 215 and 182 cm^{-1} by Schaeffer et al. (1926).

TABLE 4. Far IR absorption bands of aragonite-structure carbonates

Mineral	Our work	Prior works
Aragonite	110W	106S*
	–	165W*
	215S	216S*
	–	235S*
	263bS	267S*
Strontianite	140W	137W*, 145W†, 143W§
	–	165M*
	180M(Sh)	186S*, 180W(Sh)†, 180S(Sh)§
	210S(Sh)	–
	227S	222bS*, 220W†, 225bS§
	267M(Sh)	270b(Sh)†
Witherite	–	90WM†
	–	122W§
	–	128W§
	137M(Sh)	137M*, 138M†, 130M(Sh)‡, 143W(Sh)§
	155M(Sh)	156M*, 157M†, 165M‡, 170S§
	182S(Sh)	185W(Sh) †
	205S	203bS*, 200S†
	230S(Sh)	243S*, 240W(Sh)†, 220S‡, 220bS§
		319W†, 300W(Sh)‡, 315W§
		355W§
Cerussite	–	120b(Sh)†
	136bS	140bS*, 130W(Sh)†, ~145bS§
	–	175S†
	–	210M(Sh)†
	–	276M†
	–	315M†
	–	–
	–	380W†
	–	396W†
	–	–
	–	470S†

Note: S = Strong, M = Medium, W = Weak, Sh = Shoulder, b = broad.
* Morandat et al. 1967.
† Angino (1967).
‡ Scheetz and White (1977).
§ Nyquist and Kagel (1971).

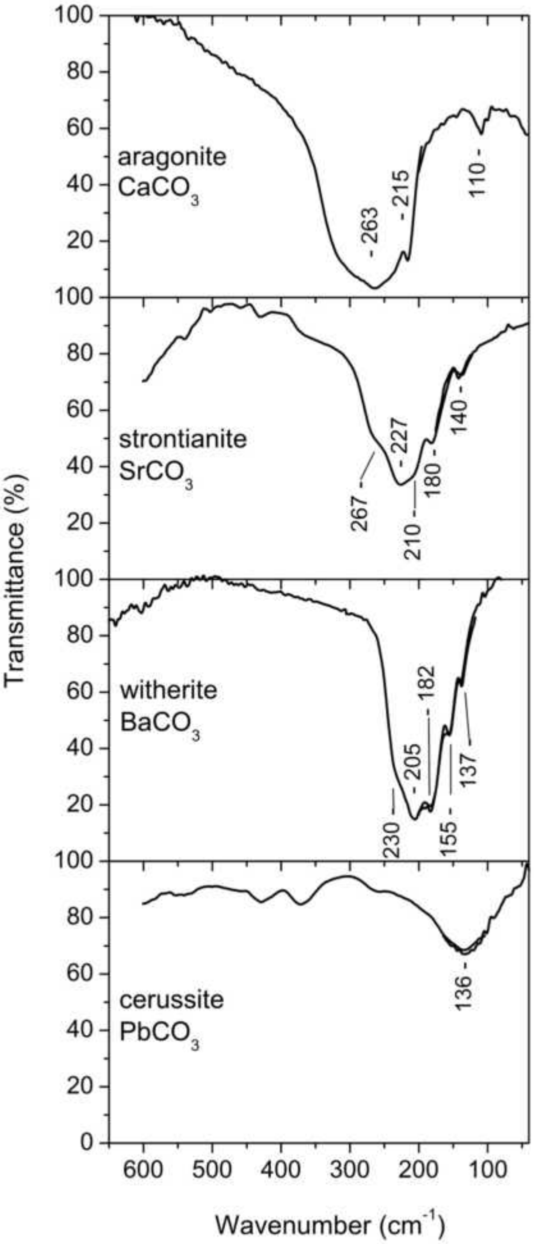

FIGURE 2. Far IR spectra of the aragonite-structure carbonates.

Cerussite ($PbCO_3$) has one broad band at 136 cm^{-1} with no resolvable structure, which agrees with Morandat et al. (1967) and Nyquist and Kagel (1971), who report this band peaking at 140 and 145 cm^{-1}, respectively (Table 4; Fig. 2).

The four aragonite-structure carbonates studied here all reveal a prominent broad band that shifts to longer wavelength with increase of the atomic number of the metal cation, as also seen in Morandat et al. (1967). The broad band at 263 cm^{-1} for aragonite ($CaCO_3$) shifts to 227 cm^{-1} for strontianite ($SrCO_3$), then to 205 cm^{-1} for witherite ($BaCO_3$), and finally to ~136 cm^{-1} for cerussite ($PbCO_3$) (Fig. 2).

A general characteristic feature for the aragonite-group minerals is a substantial decrease in frequency separation between the two CO_3 librations with increase in atomic number of the cation within the aragonite-strontianite-witherite series. This feature has been noted previously (Couture 1947; Narayanan et al. 1958) and can be observed in our spectra. The widths of separations are 105, 40, and 18 cm^{-1}, respectively (Fig. 2).

Anhydrous ordered double carbonates (dolomite group)

For dolomite-group carbonates shown in Figure 3, we expect one more lattice vibration than for the calcite-group (Morandat et al. 1967). This gives six IR active vibrations in the far IR range: four anti-translatory vibrations (of class E_u) and two librations (of class A_{2u}) of the carbonate anion (Morandat et al. 1967; Couture 1947; Cabannes 1942).

The spectrum of huntite [$CaMg_3(CO_3)_4$] in the current study is very similar to that in Scheetz and White (1977), showing the same peaks at comparable wavenumbers (Table 5). The only difference is a weak pair at 185 and 155 cm^{-1}, which is not reported in Scheetz and White (1977).

Dolomite [$CaMg(CO_3)_2$], like calcite, has been thoroughly investigated (Scheetz and White 1977; Morandat et al. 1967; Couture 1947; Yamamoto 1975). The spectrum reported here features a strong peak at 160 cm^{-1} with a prominent shoulder at 173 cm^{-1} compared to 157 and 162 cm^{-1} reported by Morandat et al. (1967). The strong peak at 263 cm^{-1} is identical to the one reported by Morandat et al. (1967), whereas a medium peak at 322 cm^{-1} compares to 327 cm^{-1}, and a strong broad band at 370 cm^{-1} with a shoulder at 408 cm^{-1} is found at 362 cm^{-1} without a shoulder in that study (Table 5).

The far IR spectrum of ankerite [$Ca(Fe_{0.28}Mg_{0.65})(CO_3)_2$] (Table 5) has been previously presented (Kemper et al. 2002a, 2002b), but without specifying the frequencies of the main peaks.

The spectrum of kutnohorite [$Ca_{0.78}Mn_{1.13}(CO_3)_2$] has not been previously reported to our knowledge. Three broad bands are observed at 138 (with a shoulder at 153 cm^{-1}), 204, and 320 cm^{-1} (with a shoulder at 260 cm^{-1}) (Table 5).

In the dolomite group, as with the previously discussed carbonates groups, we observe the effect of atomic number for the constituent metal cation in the series from huntite to kutnohorite (Fig. 3; Table 1). As the average atomic number of metal cation increases, the broad band shifts to longer wavelengths: from 400 [huntite, $CaMg_3(CO_3)_4$] to 370 cm^{-1} [dolomite, $CaMg(CO_3)_2$],

TABLE 5. Far IR absorption bands of dolomite-structure carbonates

Mineral	Our work	Prior works
Dolomite	–	157S(Sh)*
	160S	162S*
	173M(Sh)	–
	263S	263S*
	322M	327S(Sh)*
	370bS	362bS*
	408S(Sh)	
Huntite	79W	77M†
	117W	115S†
	155W	–
	185W	–
	214S	214S†
	228W	228W†
	249S	246S†
	282S	280S†
	363S(Sh)	365M†
	382S(Sh)	385S†
	400S	402S†
	443S	450(Sh)†
	512W	519W†
Kutnahorite	138bM	
	153M(Sh)	
	204M	
	260M(Sh)	
	320bS	
Ankerite	154S	–
	166M(Sh)	
	220W(Sh)	
	259M	
	320S(Sh)	
	356bS	

Note: S = Strong, M = Medium, W = Weak, Sh = Shoulder, b = broad.
* Morandat et al. (1967).
† Scheetz and White (1977).

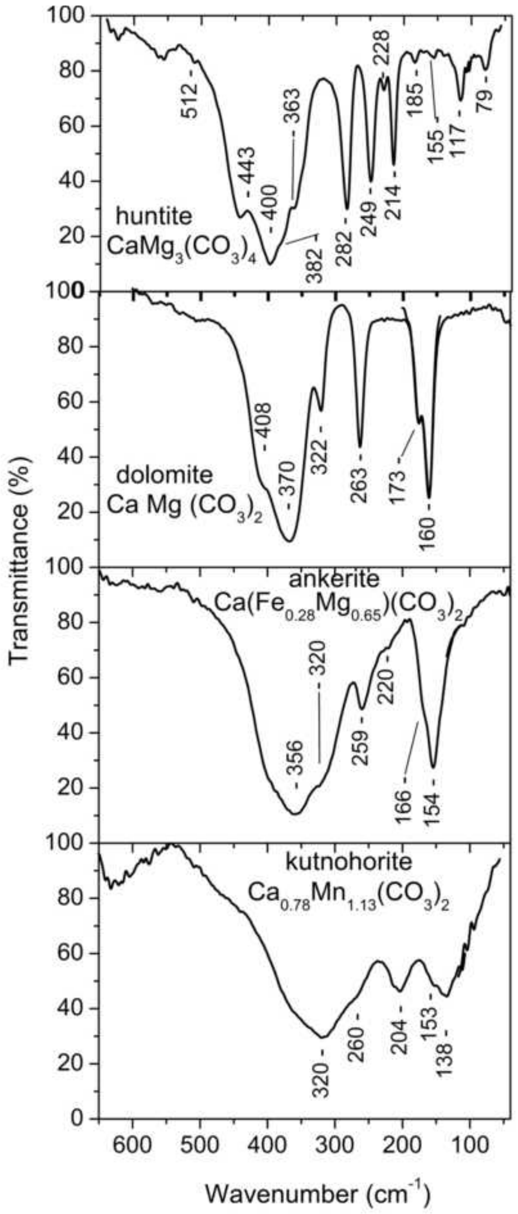

FIGURE 3. Far IR spectra of the dolomite-structure carbonates.

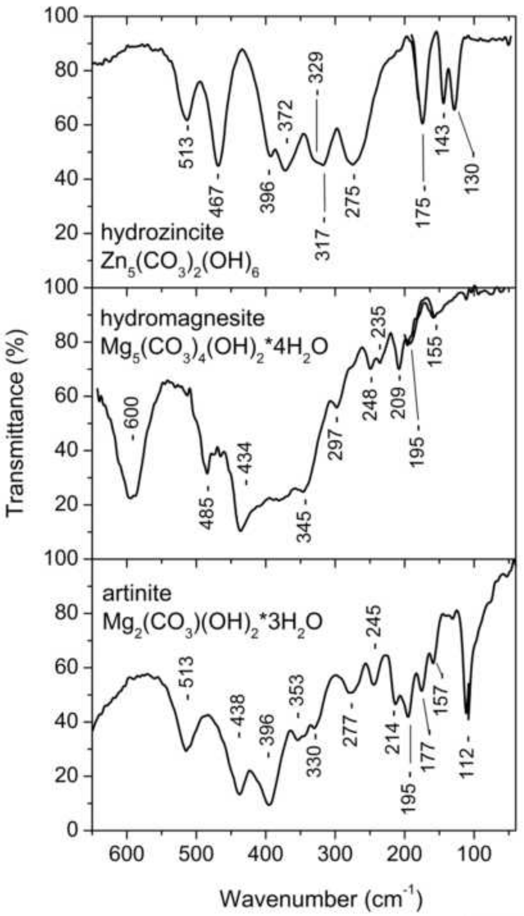

FIGURE 4. Far IR spectra of hydroxyl-containing carbonates.

then to 356 cm^{-1} [ankerite, $Ca(Fe_{0.28}Mg_{0.65})(CO_3)_2$], and finally to 320 cm^{-1} [kutnohorite, $Ca_{0.78}Mn_{1.13}(CO_3)_2$].

Hydroxyl-containing carbonates

According to Bessière-Morandat et al. (1970) and Goldsmith and Ross (1968), the spectrum below 600 cm^{-1} for the hydroxyl-containing group of carbonates, which here includes both hydrated and non-hydrated varieties, exhibits both valence-type (ν) and deformation-type (δ) lattice vibrations along the cation-oxygen and cation-hydroxyl bonds. The former are situated between 600 and 330 cm^{-1}, and the latter appear at longer wavelengths.

Our spectra are presented in Figure 4. There are peaks at 513, 467, and 396 cm^{-1} on our spectrum of hydrozincite [$Zn_5(CO_3)_2(OH)_6$], which is in a good agreement with strong peaks at about 525 and 470 cm^{-1}, and a hint of a peak about to occur right below 400 cm^{-1} on the spectrum in Moenke (1962). There is also good agreement with the hydrozincite far IR spectrum in Nyquist and Kagel (1971), except we resolve several more bands in the range 375–170 cm^{-1} (Table 6).

The spectrum of hydromagnesite [$Mg_5(CO_3)_4{\cdot}(OH)_2{\cdot}4H_2O$] has almost the same peaks mentioned in Bessière-Morandat et al. (1970) with very close agreement in frequencies (Table 6). However, Bessière-Morandat et al. (1970) don't provide the spectrum itself, but only the peak frequencies with their assignments. A broad, unresolved superposition of peaks between 434 and 345 cm^{-1} appears on our spectrum. Only strong peaks at 434 and 345 cm^{-1} [428 and 337 cm^{-1} in Bessière-Morandat et al. (1970)] are clear, and it is difficult to resolve here the other two peaks at 410 and 368 cm^{-1} mentioned by them. One peak at 235 cm^{-1} on our spectrum has not been reported in Bessière-Morandat et al. (1970). In the range of 650–350 cm^{-1} for hydromagnesite, our spectrum strongly resembles that in White (1971). In Moenke (1962), there is a strong peak at about 520 cm^{-1} and a doublet between 450 and 400 cm^{-1}, which agree poorly with our 600 cm^{-1} peak [590 cm^{-1} in Bessière-Morandat et al. (1970) and 600 cm^{-1} in White (1971)].

For artinite [$Mg_2(CO_3)(OH)_2{\cdot}3H_2O$], we find peaks at 513 and 438 cm^{-1} (Table 6), which differ considerably from those shown in Moenke (1962). Our spectrum in the range 650–350 cm^{-1} looks similar to the spectrum of artinite in White (1971). No other far IR spectra for artinite at wave numbers below 350 cm^{-1} have been found in literature.

Hydrated and acid carbonates

No far IR spectra of gaylussite [$Na_2Ca(CO_3)_2{\cdot}5H_2O$] or trona [$Na_3(HCO_3)(CO_3){\cdot}2H_2O$] have been found in the literature. Since these minerals apparently tend to undergo decomposition under heating up to 150 °C (which is a part of the preparation conditions for making PE pellets), the resulting far IR spectra of such decomposed samples were represented by broad, poorly resolved

TABLE 6. Far IR absorption bands of the hydroxyl-containing carbonates

Mineral	Our work	Prior works
Hydrozincite	–	107W(Sh)*
	130M	125S*
	143M	143S*
	175M	170S*
	275S	–
	317S	–
	329S	–
	372S	375S*
	396S	–
	467S	465S*
	513M	520S*
Hydromagnesite	155W	155M†
	195W	191M†
	209M	205M†
	235M	–
	248M	250M†
	297M	290M†
	345S	337M†
	–	368M†
	–	410M†
	434S	428S†
	485S	480M†
	600S	590S†
Artinite	112S	–
	157W	
	177M	
	195M	
	214M	
	245M	
	277M	
	330M	
	345M	
	353M	
	396S	
	438S	
	513M	

Note: S = Strong, M = Medium, W = Weak, Sh = Shoulder, b = broad.
* Bessière-Morandat et al. (1970).
† Nyquist and Kagel (1971).

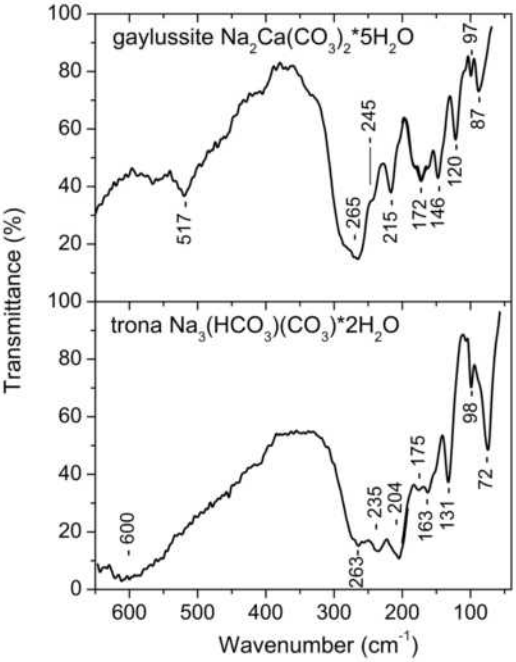

FIGURE 5. Far IR spectra of gaylussite and trona on the sticky tape.

bands (not shown here). In contrast, the spectra obtained using the powder-on-tape method, which doesn't require any heating treatment, appeared to be of sufficient quality and reproducibility (Fig. 5). Remarkably, both of these carbonates show very prominent features below 100 cm^{-1}, which we could only see before in the case of huntite (79 cm^{-1} peak) among all other carbonates studied here. This fact is definitely very characteristic and potentially may serve as a main checkpoint for an even easier identification of these two minerals.

ACKNOWLEDGMENTS

This research was supported in part by NASA-JPL contracts no. 1327221 and 1331440.

REFERENCES CITED

Adler, H.H. and Kerr, P.F. (1962) Infrared study of aragonite and calcite. American Mineralogist, 47, 700–717.

——— (1963a) Infrared spectra, symmetry and structure relations of some carbonate minerals. American Mineralogist, 48, 839–853.

——— (1963b) Infrared absorption frequency trends for anhydrous normal carbonates. American Mineralogist, 48, 124–137.

Angino, E.E. (1967) Far infrared (500–30 cm^{-1}) spectra of some carbonate minerals. American Mineralogist, 52, 137–147.

Bessière-Morandat, J., Lorenzelli, V., and Lecomte, J. (1970) II. Détermination expérimentale et essai d'attribution des vibrations actives en infrarouge de quelques carbonates basiques métalliques a l'état cristallin. Le Journal de Physique, 31, 309–312.

Bromiley, F.A., Boffa Ballaran, T., and Zhang, M. (2007) An infrared investigation of the otavite-magnesite solid solution. American Mineralogist, 92, 837–843.

Brügel, W. (1962) An Introduction to Infrared Spectroscopy. Methuen, London.

Cabannes, J. (1942) Le jeu de la symétrie dans les oscillations fondamentales d'une molécule ou d'un cristal. Revue Scientifique, 80, 407–423.

Chester, R. and Elderfield, H., (1967) The application of infra-red absorption spectroscopy to carbonate mineralogy. Sedimentology, 9, 5–21.

Chiavassa, A., Ceccarelli, C., Tielens, A.G.G.M., Caux, E., and Maret, S. (2005) The 90–110 μm dust feature in low to intermediate mass protostars: Calcite? Astronomy and Astrophysics, 432, 547–557.

Coleman, P. (1993) Practical Sampling Techniques for Infrared Analysis. CRC, New York.

Couture, L. (1947) Etude des spectres de vibrations de monocristaux ioniques. Annales de physique, 2, 5–65.

Gadsden, J.A. (1975) Infrared Spectra of Minerals and Related Inorganic Compounds. Butterworths, U.S.A.

Goldsmith, J.A. and Ross, S.D. (1968) The infra-red spectra of azurite and malachite. Spectrochimica Acta, 24A, 2131–2137.

Huang, C.K. and Kerr, P.F. (1960) Infrared study of the carbonate minerals. American Mineralogist, 45, 311–324.

Hunt, J.M. (1950) Infrared absorption spectra of minerals and other inorganic compounds. Analytical Chemistry, 22, 1478–1497.

Karr Jr., C., and Kovach, J.J. (1969) Far-infrared spectroscopy of minerals and inorganics. Applied Spectroscopy, 23, 219–223.

Kemper, F., Molster, F.J., Jaeger, C., and Waters, L.B.F.M. (2002a) The mineral composition and spatial distribution of the dust ejecta of NGC 6302. Astronomy and Astrophysics, 394, 679–690.

Kemper, F., Jaeger, C., Waters, L.B.F.M., Henning, Th., Molster, F.J., Barlow, M.J., Lim, T., and de Koter, A. (2002b) Detection of carbonates in dust shells around evolved stars. Nature, 415, 295–297.

Kolrausch, K.W.F. (1943) Ramanspektren, 469 p. Becker and Erler, Leipzig.

——— (1962) Mineralspektren I. Akademie Verlag, Berlin.

Moenke, H. (1966) Mineralspektren II. Akademie Verlag, Berlin.

Morandat, J., Lorenzelli, V., and Lecomte, J. (1967) I. Détermination expérimentale et essai d'attribution des vibrations externes actives en infrarouge dans quelques carbonates métalliques a l'état cristallin. Le Journal de Physique, 28, 152–156.

Narayanan, P.S. and Lakshmanan, B.R. (1958) Infrared and Raman spectra of witherite and strontianite. Journal of the Indian Institute of Science, Sec. A, 40, 1, 1–11.

Nyquist, R.A. and Kagel, R.O. (1971) Infrared Spectra of Inorganic Compounds (3800–45 cm^{-1}), 4, p. 75–85. Academic Press, New York.

Posch, Th. and Baier, A., (2007) Carbonates in space: The challenge of low-temperature data. The Astrophysical Journal, 668, 993–1000.

Rowan-Robinson, M. (2009) Probing the cold universe. Science, 325, 546–547.

Sandford, S.A. (1986) Acid dissolution experiments: Carbonates and the 6.8-micrometer bands in interplanetary dust particles. Science, 231, 1540–1541.

Schaeffer, C., Bormuth, C., and Matossi, F. (1926) Das ultrarote Absorptionsspektrum der Carbonate. Zeitschrift für Physik, 39, 648.

Scheetz, B.E. and White, W.B. (1977) Vibrational spectra of the alkaline earth double carbonates. American Mineralogist, 62, 36–50.

Tomeoka, K. and Buseck, P.R. (1986) A carbonate-rich, hydrated, interplanetary dust particle: Possible residue from protostellar clouds. Science, 231, 1544–1546.

Weir, C.E. and Lippincott, E.R. (1961) Infrared studies of aragonite, calcite and vaterite structure in the borates, carbonates, and nitrates. Journal of Research of the National Bureau of Standards, 65A, 173–183.

White, W.B. (1971) Infrared characterization of water and hydroxyl ion in the basic magnesium carbonate minerals. American Mineralogist, 56, 46–53.

——— (1974) The carbonate minerals. In V.C. Farmer, Ed., The Infrared Spectra of Minerals, p. 227–284. Mineralogical Society, London.

Yamamoto, A. (1975) Optically active vibrations and effective charges of dolomite. Spectrochimica Acta, 31A, 1265–1270.

MANUSCRIPT RECEIVED AUGUST 23, 2009
MANUSCRIPT ACCEPTED MAY 4, 2010
MANUSCRIPT HANDLED BY BRIGITTE WOPENKA