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Crystal chemical correlations between the mid and near-infrared in carbonate minerals

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ABSTRACT

Near-infrared (NIR) spectra of carbonates have proved important in many disciplines including planetary exploration. Classically bands in the 4000–6000 cm^{-1} (2.5–1.67 μm) region are assigned to [CO_3^{2-}] internal mode combinations and overtones. However band assignments remain equivocal. This study examines three prominent bands ((*ca* 4505 cm^{-1} (2.219 μm), 4900 cm^{-1} (2.041 μm) and 5145 cm^{-1} (1.944 μm)) from powdered calcite and aragonite group minerals. Results indicate that the bands originate from anharmonic coupling of degenerate internal mode(s) with external (lattice) modes. On this basis it is suggested that NIR data may provide an untapped source of detailed information on lattice mode frequencies and information on the type(s) of the environmental cation(s) in carbonate minerals.

1. Introduction

Carbonate minerals are of appreciable interest in many disciplines including planetary exploration [1–5]. The mid-infrared (MIR) spectra of the [CO_3^{2-}] internal modes of the aragonite (orthorhombic) and calcite (trigonal) groups are well documented as is intra-group wavenumber sensitivity of the carbonate radical to the coordinating divalent cation(s) [6–8]. Although no single physical property of the environmental cation is considered directly responsible for absorption band positions [3] it is widely considered that small shifts of internal modes from the free ion wavenumber reflect small changes in the chemical bonding of the carbonate ion [8]. Various near-infrared (NIR) reflectance and absorption bands have been reported in separate studies in the 4000–6000 cm^{-1} (2.5–1.67 μm) region [9–10] and a range of assignments for calcite and aragonite have been suggested based primarily on combination and overtones of the carbonate radical [1,9,11] although anharmonicity is expected to have quite a large effect on multiple combination tones [11]. To this end this study explores three prominent bands in NIR spectra in an attempt to elucidate the precise relationship between the NIR bands, anharmonicity and, the MIR spectra from which the overtones and combinations emanate.

2. Materials and methods

Fourier transform mid-infrared (MIR) analyses were performed using a Perkin Elmer Spectrum 65. Raman analyses were conducted on lightly ground carbonate mineral powders employing a Perkin Elmer IdentiCheck Raman spectrometer, fitted with a 785 nm laser and continuous (dispersive) CCD detector. The samples were measured in the spectral range 2000–200 cm^{-1}. Each spectrum was collected from 8 scans for 2 s using 70 mW laser power at room temperature. Both techniques show a resolution of 2 cm^{-1} for sharp spectral bands. Near-infrared (NIR) analyses were conducted using a Perkin Elmer Spectrum 100 N spectrometer. Samples were measured in glass vials using NIR reflectance accessory in the range 4000–6000 cm^{-1} region with resolution 16 cm^{-1}. Each spectrum was collected from 5 scans as an interleaved measurement and displayed in absorbance mode. For all three spectroscopic techniques first derivative peak fitting was performed using PeakFit (Jandel, Scientific Software) all values reported show $r^2 > 0.995$.

Six calcite group and four aragonite group powders were analyzed. The MIR and Raman band positions of the internal modes of the carbonate powders agree well with previous reports (Table S1). Hereon experimental band positions are reported in favor of previously published band positions merely to minimize potential uncertainties in band frequencies related to particle size effects and cation substitution schemes within specific powders [21,22] when reporting complementary NIR data. All data was collected at room temperature and acquired at the University of Brighton (United Kingdom).

3. Results and discussion

The NIR spectra consist of a series of variably resolved and commonly overlapping broad bands (Fig. 1) with peaks within wavenumber ranges in which reflectance and absorbance bands have previously been reported [2,9]. Bands in the region of (*ca* 4505, 4900 and

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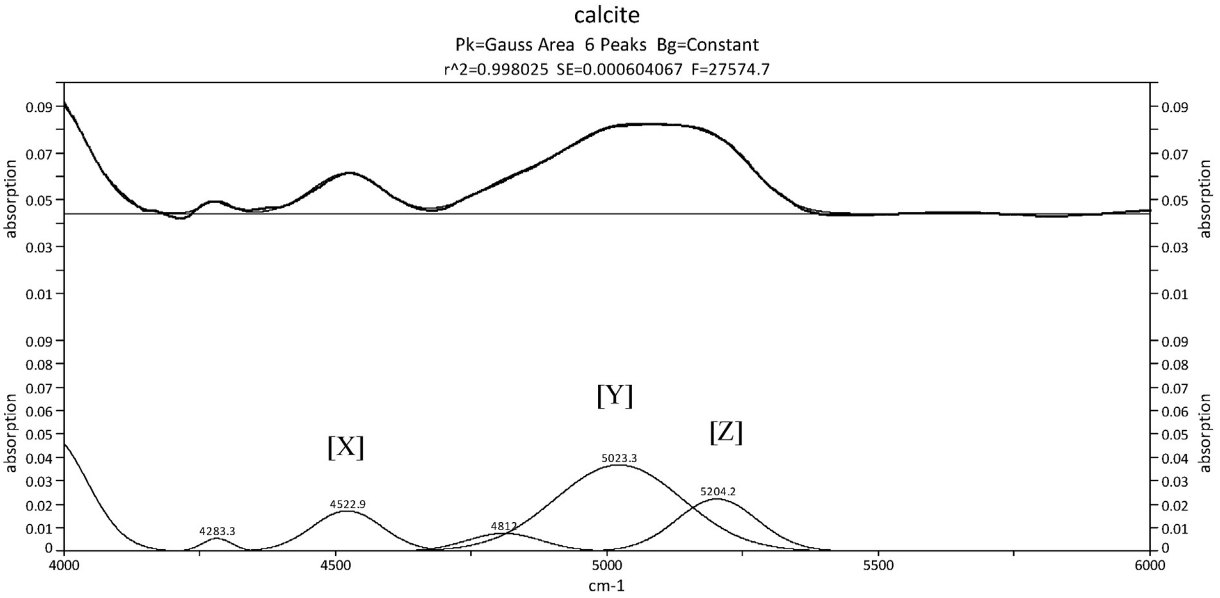

Fig. 1. Peak-fitted NIR spectrum of calcite powder ($r^2 = 0.998$). Labels [X], [Y] and [Z] indicate the relative positions of the three bands examined in this study.

5145 cm^{-1}) labelled [X],[Y],[Z] respectively were resolved for all minerals examined, the relative strengths of absorbance and frequencies varied from spectrum to spectrum (Table 1). The three bands are the focus of this study. The calcite NIR band [Y] wavenumber (5023 cm^{-1}, 1.99 μm) closely coincides with the 2 μm band reported from calcite assigned as $(2v_1 + 2v_3)$ combination band [9]. The closest match to the calcite band [X] wavenumber (measured at 4523 cm^{-1} (2.21 μm)) is reported at 2.16 μm assigned to $(v_1 + 2v_3 + v_4)$ [1,9]. The calcite band [Z] at 5204 cm^{-1} (1.92 μm) closely coincides with the 1.9 μm band assigned to a $(v_1 + 3v_3)$ combination [9].

Fig. 2 shows the calculated values of the combination bands derived from simple summation of MIR data plotted against the NIR frequencies of bands [X], [Y] and [Z]. For all three bands the NIR data deviates variably from a simple harmonic approximation to the MIR-derived values. Further, the disposition of data is such that the divalent cations with the greatest and least atomic masses define the two extremes in wavenumber values for each mineral group and, for bands [X] and [Z] the greatest and least atomic masses for each mineral group coincides with the largest and smallest offset of the NIR wavenumber from the MIR arithmetic totals (Fig. 2).

The wavenumber difference ($\Delta\, x$ cm^{-1}) between values attained by summation of MIR combination band totals and that recorded by NIR for bands [X], [Y], and [Z] respectively are tabulated in Table 2. In total thirteen NIR band ($\Delta\, x$ cm^{-1}) values fall within 16 cm^{-1} of published values for a given mineral-specific lattice mode, with eight readings within ≤4 cm^{-1} of a published lattice mode. For example (Band [X]) the mineral aragonite (Δ 217 cm^{-1}) exactly coincides with the 217 cm^{-1} A_{1g} Raman mode [8]; strontianite (Δ 127 cm^{-1}) coincides with a lattice mode at 128.6 cm^{-1} [24]; magnesite (Δ 162 cm^{-1}) very closely coincides with an E_u lattice mode reported at 158 cm^{-1} [8]; otavite (Δ 124 cm^{-1}) is close to a E_u lattice mode reported at 120 cm^{-1} [8]; calcite (Δ 115 cm^{-1}) closely matches the A_{2u} lattice mode reported between 106 cm^{-1} and 109 cm^{-1} [8,25]. Band [Y] witherite [$BaCO_3$] (Δ 72 cm^{-1}) closely coincides with a lattice mode reported at 76 cm^{-1} [8]; strontianite [$SrCO_3$] (Δ 93 cm^{-1}) closely coincides with a lattice mode reported at 105 cm^{-1} [24]. Band [Z] ($\Delta\, x$ cm^{-1}) values in seven cases (Fig. 1c) closely match reported translational and librational lattice mode frequencies (Table 2).

MIR-measurement of the degenerate v_3 mode from powders is less accurate than the sharper v_1, v_2 and v_4 internal modes. For instance, values obtained from powdered calcite at room temperature show a spread of almost 30 cm^{-1} in separate studies (mean 1422.5 cm^{-1} ($n = 7$) $\pm$ 12.5 cm^{-1}) [8]. Evidently many NIR analyses show $\Delta\, x$ cm^{-1} values which exceed analytical uncertainty related to MIR measurement of v_3 and also coincide exactly or closely with established lattice modes (Table 2). This is interpreted to indicate that subtractive lattice mode components to combinations which contain overtones of the v_3 fundamental exist in the NIR spectra as a consequence of interaction of the motions of the carbonate ion with motion of the entire lattice cell, with the separation in wavenumber due to anharmonic coupling of the internal and lattice fundamentals [26].

Table 1
Near-infrared peak-fitted bands, all reported values are in (cm^{-1}) units. Band [X] wavenumbers corresponds to 2.267–2.174 μm wavelength range, band [Y] to 2.092–1.992 μm and, band [Z] to the 1.968–1.919 μm range.

	4050–4180	4250–4419	[X] 4410–4600	[Y] 4780–5020	[Z] 5080–5210	5475–5750
Cerrusite	4144	4307	4520	4839	5179	5615
Witherite	4182	4391	4526	4874	5181	5538
Strontianite	4097	4256	4531	4935	5234	5597
Aragonite	4062	4343	4471	5059	5217	–
Calcite	–	4283	4523	5023	5204	–
Rhodacrosite	–	4402	4521	5013	5157	–
Otavite	4093	–	4557	4919	5146	5765
Magnesite	4076	4417	4529	5056	5197	–
Siderite	4016	4318	4510	5005	5182	5605
Smithsonite	–	4293	4516	4997	5192	5683