

Raman characterization of synthetic magnesian calcites

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ABSTRACT

Magnesian calcites are important components of sediments and biominerals. Although Raman spectra of calcite, dolomite, and magnesite are well known, those of magnesian calcites deserve further investigation. Nineteen syntheses of magnesian calcites covering the range 0–50 mol% MgCO₃ have been carried out at high pressure and temperature (1–1.5 GPa, 1000–1100 °C). The crystalline run products have been characterized by μ -Raman spectroscopy.

For all lattice and internal modes (L , T , ν_1 , ν_4 , $2\nu_2$) but ν_3 , wavenumbers align closer to the calcite–dolomite line than the calcite–magnesite line. The compositional dependence is strong and regression curves with high correlation coefficients have been determined. Full-width at half maximum (FWHM) plot along parabolas that depart from the calcite–dolomite or calcite–magnesite lines. The limited data dispersion of both shifts and FWHM allow using Raman spectral properties of magnesian calcites to determine the Mg content of abiotic calcites.

A comparison with Raman data from the literature obtained on synthetic magnesian amorphous calcium carbonate (Mg ACC) shows that the wavenumber position of the ACC ν_1 mode is systematically shifted toward lower values, and that their FWHM are higher than those of their crystalline counterparts. The FWHM parameters of crystalline and amorphous materials do not overlap, which allows a clear-cut distinction between crystalline and amorphous materials.

In synthetic magnesian calcites, the shift and FWHM of Raman bands as a function of magnesium can be interpreted in terms of changes of metal–O bond lengths resulting from the replacement of calcium by magnesium. The facts that the wavenumber of magnesian calcites are close to the calcite–dolomite line (not calcite–magnesite), that the FWHM of the T , L , and ν_4 modes reach a maximum around 30 $\pm$ 5 mol% MgCO₃, and that a peak specific to dolomite at 880 cm^{–1} is observed in high-magnesian calcites indicate that dolomite-like ordering is present above $\sim$ 10 mol% MgCO₃. Mg atom clustering in cation layers combined with ordering in successive cation basal layers may account for the progressive ordering observed in synthetic magnesian calcites.

Keywords: Magnesian calcite, dolomite, magnesite, amorphous calcium carbonate, Raman spectroscopy, experimental HP/HT syntheses, dolomite ordering

INTRODUCTION

Calcite is the only CaCO₃ crystalline polymorph that can accommodate substantial amounts of magnesium (Bischoff et al. 1983; Finch and Allison 2007; Long et al. 2012; Mackenzie et al. 1983; Morse et al. 2007; Wang et al. 2012). Magnesian calcites (Mg calcites) are important components of modern and Pleistocene carbonate sediments (Bischoff et al. 1985; Land 1967). In the sediments, they are mostly found as remnants of skeletons of marines invertebrates and as cement (Bathurst 1975; Bischoff et al. 1985; Chave 1954a, 1954b). Since Raman spectroscopy is sensitive to carbonate ion (CO₃^{2–}) vibrations, micro-Raman spectroscopy is classically used to characterize small volumes of crystalline or amorphous carbonate samples. Raman patterns of the different calcium carbonate polymorphs (calcite, aragonite, vaterite, amorphous calcium carbonate) are

well identified; however, the Raman spectral modifications due to variations of chemical composition are less known. The effect of magnesium incorporation in calcite has been thoroughly investigated by Bischoff et al. (1985). These authors characterized the wavenumber shifts and enlargements of the carbonate vibration modes in magnesian calcites as a function of their Mg contents. Carbonate vibration modes of calcite (Cal, CaCO₃), dolomite (Dol, Ca_{0.5}Mg_{0.5}CO₃), and magnesite (Mgs, MgCO₃) show a shift toward higher wavenumber and enlargement as a function of magnesium content. Bischoff et al. (1985) also showed that magnesian calcites display changes of spectral properties aligned along the calcite–magnesite line with slightly positive or negative deviations from linearity for ν_3 and the translational T modes. The full-widths at half maximum (FWHM) of the vibrational Raman bands progressively increase as a function of magnesium contents. However, according to these authors, the shift and FWHM data dispersions are too large to allow the determination

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of calcite Mg contents from their Raman properties. In particular, the Raman shift of the 25 mol% MgCO_3 sample [i.e., the highest magnesium content studied by Bischoff et al. (1985)] diverges from the general tendency. Additional data are needed to clarify these points. In the present study, micro-Raman data obtained on a new series of magnesian calcites synthesized at high pressure and temperature are presented.

Amorphous calcium carbonates (ACC) are widespread in biomineralizing environments, and the formation and transformation of this intermediate and reactive phase are new centers of interest in the biomineralization community (Addadi et al. 2003; Beniash et al. 1997; Benzerara et al. 2006; Politi et al. 2004, 2006; Tao et al. 2009; Wang et al. 2009; Weiner et al. 2005; Weiss et al. 2002). A recent study dealing with the experimental synthesis of ACC with variable magnesium contents (0 to 43 mol% MgCO_3) showed that Raman spectroscopy can be used to determine magnesium contents of ACC (Wang et al. 2012). Indeed, both the position and the FWHM of the fundamental band ν_1 of ACC are linear functions of magnesium content. Below, the data obtained on newly synthesized magnesian calcites will be compared with the data obtained by Wang et al. (2012) to better understand the changes of Raman properties of calcium carbonates as their Mg contents and structure change.

MATERIALS AND METHODS

Experimental syntheses

Nineteen magnesian calcites have been synthesized in the range 2–50 mol% MgCO_3 at high pressure and high temperature in a piston-cylinder apparatus. The starting materials consist of pure synthetic calcite (Alfa Aesar) and natural magnesite from Brumado (Bahia, Brazil). ICP-AES analyses of magnesite indicate trace amounts of Fe (0.15 wt% Fe_2O_3) and Ca (0.22 wt% CaO). The magnesite was ground in a McCrone micronizer agate mortar in ethanol for 30 min. Calcite and magnesite were mixed in appropriate molar proportions and manually ground in an agate mortar with ethanol. After desiccation in an oven at 110 °C, about 60 mg of the mixture was put in a 7 mm high, 5 mm outer diameter gold capsule and welded shut. The gold capsule was placed in a salt-glass assembly (Vielzeuf et al. 2007), pressurized and heated for ~96 h in a piston-cylinder apparatus, at 1000 °C and 1 GPa for compositions in the range 2–30 mol% MgCO_3 , and 1100 °C and 1.5 GPa, for compositions in the range 35–50 mol% MgCO_3 . Large thick-walled capsules and long run durations were chosen to favor attainment of textural and thermodynamic equilibrium and to yield sufficient quantity of crystalline material in a single experiment. After the experiment, the run product was extracted from the capsule, part of it mounted in epoxy and polished for electron microprobe and micro-Raman analyses, while the remaining was ground and kept for X-ray diffraction (XRD) characterization.

Optically clear natural (OCN) calcite, dolomite, and magnesite crystals have also been analyzed to serve as references. OCN calcite comes from a perfect rhombohedron of unknown origin. OCN dolomite and magnesite are from Azcárate Quarry, Eugui, Esteribar (Spain), and Brumado, Bahia (Brazil), respectively.

Analytical methods

Electron microprobe (EMP) analyses. Experimental magnesian calcites were analyzed with a SX100 Cameca electron microprobe (LMV, Clermont-Ferrand). The following analytical conditions were used: 15 kV accelerating voltage, 8 to 20 nA beam current, counting times of 20 s on the peak and 20 s on the background, and 20 μm spot size to minimize crystal damage. All samples were polished with diamond paste down to 0.1 μm , and coated with a ~20 nm thick carbon layer. The compositions in weight percent oxide were measured as CaO and MgO, using synthetic periclase and natural calcite as standards. Since C and O were not independently measured, CO_2 was calculated by stoichiometry from the concentrations of CaO and MgO, considering that all Ca and Mg combine with CO_3 . A sum close to 100 was taken as an indication of a good analysis. Throughout this article, the compositions of magnesian calcites are expressed in mol% MgCO_3 .

Micro-Raman spectroscopy. Samples were analyzed on a Renishaw M-1000 Micro-Raman spectrometer operating with a 514.5 nm argon ion laser, at a spectral resolution of 1 cm^{-1} . A dual-wedge polarization scrambler inserted directly above the objective lens was used to minimize polarization effects. A spot size of about 1 μm was used to respond to spatial constraints associated with the size of the synthetic crystals (100–200 μm). Analytical conditions were chosen to optimize signal to noise ratio: usually 10 scans per spectrum, 10 s per wavelength on the detector, 100% power and a 20 μm slit. Spectral peak positions were periodically calibrated against a silicon standard (at 520.5 cm^{-1}) and rarely varied more than 1 cm^{-1} . Additional measurements in the range 650–950 cm^{-1} were carried out at LMV (Clermont-Ferrand, France) on a Renishaw InVia Micro Raman spectrometer operating with a 532 nm argon ion laser. Analyses were carried out at a spectral resolution of 1 cm^{-1} , in extended mode, with high confocality, 10% power, 10 scans per spectrum, and 15 s exposure time. Spectral peak positions were also calibrated against a silicon standard. All micro-Raman analyses were carried out on polished samples mounted in epoxy. No additional sample preparation was needed for the Raman measurements. Whenever possible, μ -Raman analyses were made on, or close to grains analyzed by electron microprobe (EMP). Spot positioning was made using the 100 $\times$ magnification lens on the microscope. The Renishaw Wire software (<http://www.renishaw.fr/wire>) was used for background removal and wavenumber determination, while Winplotr (Roisnel and Rodríguez-Carvajal 2001) was used for peak FWHM determinations.

RESULTS

Calcite, magnesite, and dolomite optically clear natural (OCN) crystals

Carbonates have six vibration modes composed of two external (or lattice) modes and four internal modes (Couture 1947; White 1974a). Different notations are used in the literature to refer to these vibration modes; they are listed in Table¹ 1 with a brief description of their physical significance. For clarity, the following notation initially used by Cabannes and Aynard (1942), Couture (1947), Kastler and Rousset (1941) and also by Bischoff et al. (1985) will be used throughout the text: translational (T) and librational (rotatory) (L) external modes; ν_1 , ν_2 , ν_3 , and ν_4 internal modes. The notation derived from factor group theory (see Table¹ 1) will be associated to the previous notation only when necessary. The internal vibrations ν_1 , ν_2 , ν_3 , and ν_4 involve bending or stretching of the C-O bonds in the carbonate groups in and out of the plane in the *a* direction (Bhagavantam and Venkatarayudu 1939; Krishnan 1945). Importantly, group theory shows that some silent Raman modes that cannot be found in the first-order spectrum of a crystal can be observed in the second-order spectrum (Dresselhaus et al. 2008). For instance, in calcite and magnesite, ν_2 (at ~880 cm^{-1}) is Raman silent while its overtone $2\nu_2$ (at ~1760 cm^{-1}) is observed (Couture 1947). The external vibrations (T and L) involve relative translations of the metal (e.g., Ca^{2+} or Mg^{2+}) and CO_3^{2-} ions and librations of CO_3^{2-} ions (Couture 1947). Band assignments of lattice modes (L or T) are equivocal, probably as a consequence of mixing (Bischoff et al. 1985). Nevertheless, the notation used by Bischoff et al. (1985) (T: [155–212 cm^{-1}]; L: [282–331 cm^{-1}]) will be used for the sake of simplicity.

The positions of the six active Raman modes in calcite, dolomite, and magnesite OCN crystals are displayed in Figure 1 and Table 2. The doubly degenerate lattice modes T and L and the three internal modes ν_4 , ν_3 , and $2\nu_2$ show a shift toward high

¹Deposit item AM-16-115714, Tables 1 and 3 and Supplemental Figures and Data. Deposit items are free to all readers and found on the MSA web site, via the specific issue's Table of Contents (go to http://www.minsocam.org/msa/ammin/toc/2016/Nov2016_data/Nov2016_data.html).

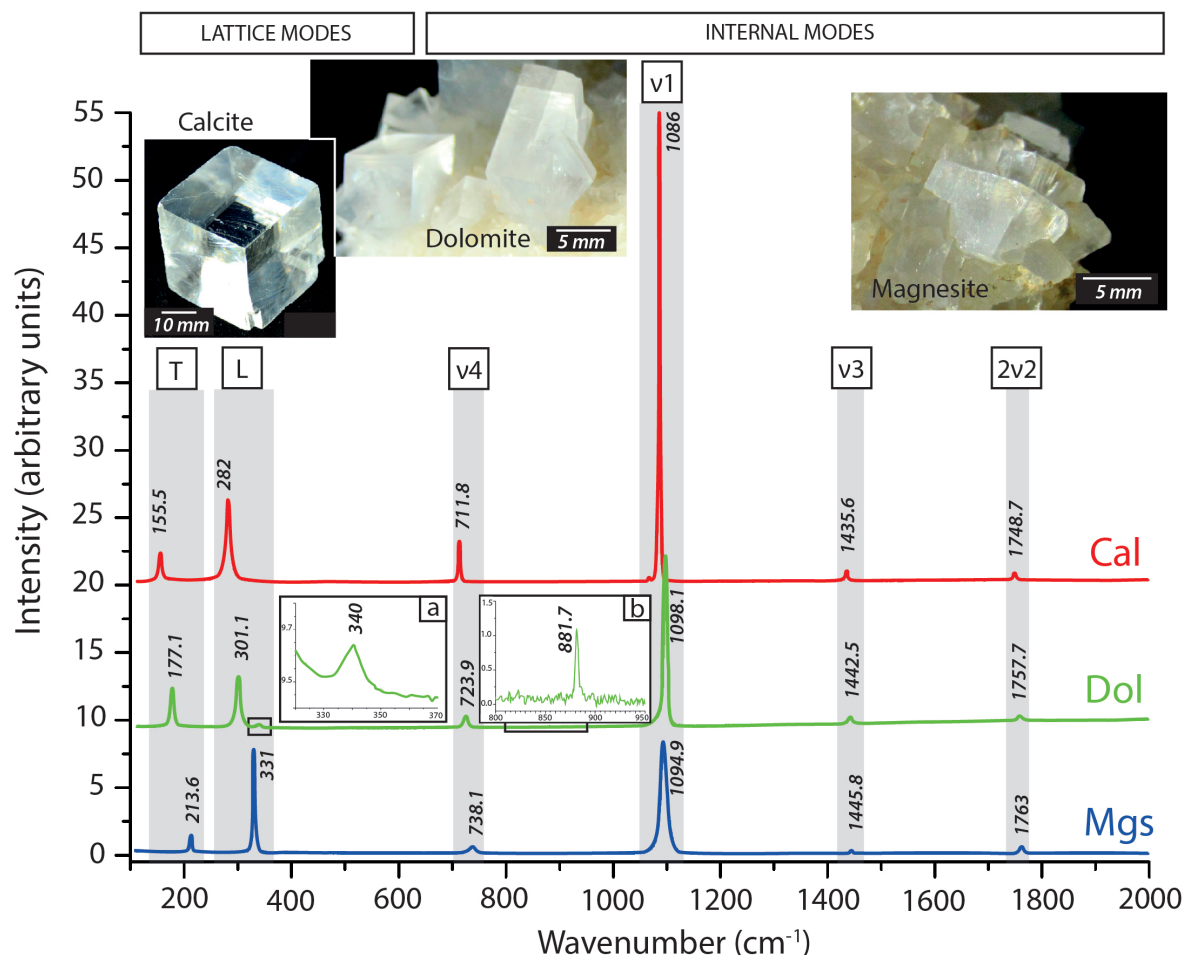


FIGURE 1. Raman spectra of calcite, dolomite, and magnesite optically clear natural (OCN) crystals. Insets **a** and **b** correspond to portions of the dolomite spectrum.

TABLE 2. Wavenumbers and FWHM (in *italics*) of the Raman modes of calcite, dolomite, and magnesite OCN crystals and other reference crystals from the literature (units in cm⁻¹)

	External (or lattice) modes				Internal modes				
	T	230 cm ⁻¹	L	340 cm ⁻¹	v ₄	v ₂	v ₁	v ₃	2v ₂
Calcite									
OCN crystal	155.5	Inactive	282	Inactive	711.8	Inactive	1086	1435.6	1748.7
	6.5		9.7		3.1		3.1	4.7	7.5
Bischoff et al. 1985	154	Inactive	281	Inactive	711	Inactive	1085	1434	1748
	6.2		10.1		3.6		2.5	2.0	3.6
Schauble et al. 2006 (theoretical)	155.5	Inactive	273	310.4 (A _{2g})	711.4	872.5 (A _{2g})	1094.3	1437.6	∅
Dolomite									
Azcárate	177.1		301.1	340	723.9	881.7	1098.1	1442.5	1757.7
OCN crystal	6.1		9.3		9.3		6	7.2	10.4
Bischoff et al. 1985	175		299	335	724	Not observed	1097	1441	1756
	5.5		9.8		9.0		6.1	3.8	4.3
Schauble et al. 2006 (theoretical)	176.2	231.2	295.8	338.3 (A _g)	724.7	876.5	1104.4	1446.6	∅
Magnesite									
Brumado	213.6	Inactive	331	Inactive	738.1	Inactive	1094.9	1445.8	1763
OCN crystal	3.7		4.4		15.8		13.2	6.7	10.1
Bischoff et al. 1985	213	Inactive	329	Inactive	738	Inactive	1093	1444	1762
	4.0		4.9		12.2		12.5	3.1	4.8
Schauble et al. 2006 (theoretical)	208.4	Inactive	324.4	361.7 (A _{2g})	737.7	875.9 (A _{2g})	1103.3	1452.6	∅

wavenumbers from calcite to magnesite, i.e., as Mg increases (Fig. 1). However, this systematic effect is not observed in the non-degenerated ν_1 internal mode, which is less shifted in magnesite than in dolomite. These observations are in agreement with the previous measurements of Bischoff et al. (1985) and, at least qualitatively, with the calculated values of Schauble et al. (2006) using density functional perturbation theory. The singular behavior of ν_1 could be due to the fact that this mode is related to a CO_3^{2-} in-plane vibration (stretch) with little Ca-Mg cation involvement (Boulard et al. 2012).

It has been established for a long time that the crystallographic symmetry of dolomite ($R\bar{3}$) is lower than that of calcite and magnesite ($R\bar{3}c$) due to alternating layers of Ca and Mg in dolomite. As a consequence, a weak additional peak lattice mode at $\sim 335\text{ cm}^{-1}$ is observed in dolomite (Bischoff et al. 1985). In most dolomite Raman spectra listed in the online Ruff database (<http://ruff.info/Dolomite>), as in Figure 1a, this peak is close to the T mode band and can be easily overlooked. Various authors (Couture 1947; Schauble et al. 2006; Valenzano et al. 2007) also noted that two Raman-active A_g modes in dolomite (at 231 and 876 cm^{-1}) are related to inactive A_{2g} modes in calcite and magnesite. These peaks should be observed in dolomite and not in calcite or magnesite. However, according to Schauble et al. (2006) these peaks would be too weak to be distinguished from experimental background noise. This observation is verified for the 231 cm^{-1} peak that has not been observed in any published Raman spectra (to our knowledge). On another hand, our measurements on the OCN dolomite show the presence of a sharp peak at 881 cm^{-1} well above background noise. This peak is also observed in six dolomites referenced in the Ruff database, in particular those from Bay Mag mine (British Columbia, Canada) and Oberdorf (Austria). Below, particular attention will be paid to this ν_2 mode at $\sim 880\text{ cm}^{-1}$, which can be taken as an indicator of dolomite-like ordering in Mg calcites. The structural difference between calcite/magnesite on one side, and dolomite on the other side, led Bischoff et al. (1985) to consider that calcite and magnesite were the actual end-members of the Mg calcite solid solution, and thus that the spectral properties of Mg calcites should plot between calcite and magnesite (the calcite-magnesite line) and not between calcite-dolomite. This is an important conclusion that has to be verified.

Concerning the FWHM, Figure 1 and Table 2 indicate that the peak widths of the T and L lattice modes progressively decrease from calcite to magnesite (as Mg increases) while those of the internal ν_1 and ν_4 modes increase. The situation is more complex regarding ν_3 and $2\nu_2$ since their FWHM increase from calcite to dolomite, then decrease slightly (or stay constant) from dolomite to magnesite (Fig. 1 and Table 2). Our FWHM determinations for the T, L, ν_1 , and ν_4 modes are in agreement with those of Bischoff et al. (1985) within $\pm 1\text{ cm}^{-1}$, which is the instrument resolution. This is not the case for the ν_3 and $2\nu_2$ modes that show higher FWHM than those determined by Bischoff et al. (1985). These differences could be due to larger error margins associated with low peak intensities and background removal processing.

Synthetic Mg calcites

MEB and EMP characterization. High-pressure and high-temperature experimental products were extracted from the gold

capsule as friable gray to white blocks of Mg calcite crystals. The gray color of some run products comes from a small fraction of graphite. Some SEM images of the run products are shown in Figure 2. Crystals display polyhedral shapes and have sizes in the range $100\text{--}200\text{ }\mu\text{m}$ (Figs. 2c and 2d). Numerous grain triple junctions at 120° indicative of textural equilibrium are observed (Fig. 2b). In almost all experiments, small empty spaces are found between Mg calcite grains (Figs. 2c and 2d). These voids are interpreted as pores containing a low-density fluid phase. Traces of carbonate melt evidenced by quench crystals (usually against the gold capsule) are observed in most experiments. They are attributed to small amounts of adsorbed water in the starting material that lead to incipient melting at temperatures below the solidus for the dry system. In one experiment (MgCc_45) carried out at 1100°C and 1.5 GPa , the proportion of melt was important as about half of the capsule was occupied by $1\text{--}2\text{ mm}$ long quench crystals, well segregated from polyhedral crystals in the other half of the capsule. These features indicate that the solidus was overstepped in this experiment. This is in fairly good agreement with the phase diagrams published on the system $\text{CaCO}_3\text{--MgCO}_3$ (Goldsmith and Heard 1961; Irving and Wyllie 1975). For micro-Raman acquisitions, zoned quench crystals were avoided and analyses were carried out on polyhedral crystals. The Mg contents of magnesian calcites determined by EMP are plotted against nominal compositions in Figure 3. The measured compositions are systematically slightly lower than expected. The difference between nominal and measured values increases from low to high Mg contents, at least up to $35\text{ mol\% MgCO}_3$. This systematic composition shift can be attributed to limited decarbonation of magnesite taking place during the heating stage at the beginning of the experiment. This interpretation is consistent with the presence of pores between grains (these pores being probably filled with CO_2). At $35\text{ mol\% MgCO}_3$, two different crystal compositions coexist in the same capsule (28.3 ± 0.3 and $33.3 \pm 0.2\text{ mol\% MgCO}_3$). This situation is attributed to the presence of a solvus between calcite and dolomite (Byrnes and Wyllie 1981).

The quality of the synthetic crystals was determined by conventional X-ray diffraction. No CaCO_3 polymorph other than calcite (aragonite or vaterite) was detected. Powder XRD data obtained on a high-flux X-ray synchrotron beamline will be presented in a companion paper. In the present article dedicated to micro-Raman spectroscopy, two groups of experiments corresponding to the $0\text{--}30$ and $35\text{--}50\text{ mol\% MgCO}_3$ composition ranges will be distinguished. This partition is justified by different facts. (1) Most biominerals have Mg contents in the range $0\text{--}30\text{ mol\% MgCO}_3$. For this reason, particular emphasis was put on this compositional range with syntheses carried out at a $2\text{ mol\% MgCO}_3$ step interval. For more magnesian compositions of lower practical interest for biominerals, a $5\text{ mol\% MgCO}_3$ step interval was used to minimize the number of experiments. (2) Phase diagrams indicate that due to the presence of a miscibility gap between calcite and dolomite, higher P and T are required to synthesize Mg calcites in the range $35\text{--}50\text{ mol\% MgCO}_3$ (1.5 GPa , 1100°C instead of 1 GPa and 1000°C). Thus, different experimental conditions were used for the two sets of experiments. Furthermore, phase relationships are more complicated in the high-Mg field with possibility of unmixing and partial

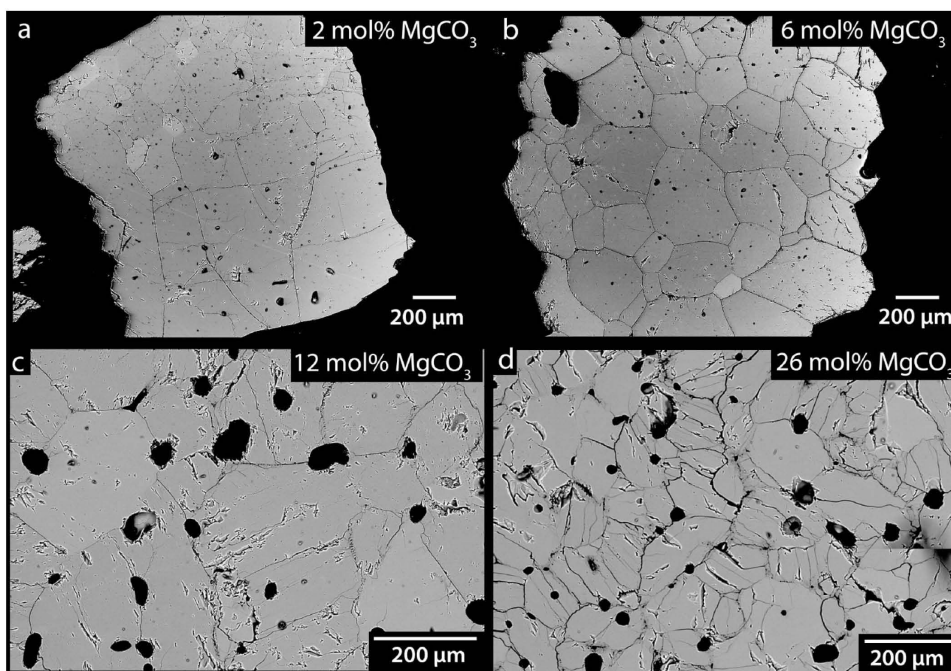


FIGURE 2. SEM-BSE images of synthetic magnesian calcites showing 100 to 200 μm polyhedral crystals. Homogeneous gray level in a given grain indicates homogeneous crystal composition; variations of gray level from one grain to another come from variations of lattice orientations. Note the presence of pores between the crystals.

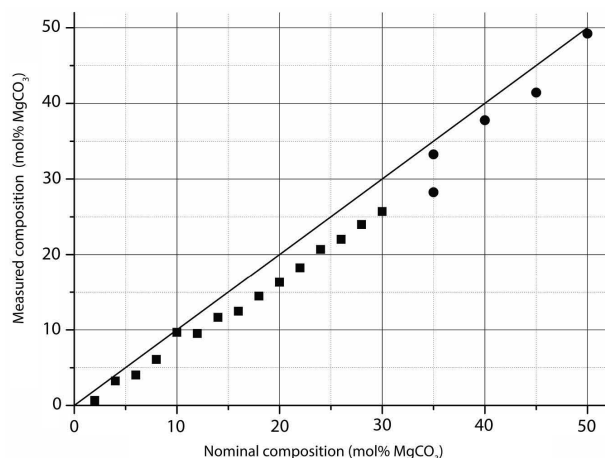


FIGURE 3. Compositions (mol% MgCO_3) of the synthetic Mg calcites determined by electron microprobe plotted against nominal compositions. (Error bars are smaller than symbols.)

melting (see Byrnes and Wyllie 1981 for a review). (3) Finally, the behavior of the solid solution above 30 mol% MgCO_3 is more complex than within the range 0–30 mol% MgCO_3 , and shows more dispersion in the analytical results.

The effect of Mg incorporation on synthetic Mg calcite Raman bands. The Raman spectra of synthetic calcites show decreasing intensities of the different modes as Mg increases as shown on three MgCO_3 compositions in Figure 4. This effect is important even at low-Mg contents: for instance, the T, L, and ν_1 intensities of the 3.2 mol% MgCO_3 calcite are about

half those of the OCN calcite crystal. As Mg increases, the six Raman carbonate bands show both progressive shifts toward high wavenumbers and peak enlargements. Normalized intensities after baseline extraction allow a precise analysis of the band shifts and enlargements. Table 3¹ summarizes the positions and FWHM of the Raman bands for all synthetic magnesian calcites. Figure 5 shows the position of the main active Raman modes as a function of magnesium contents between 2 and 30 mol% MgCO_3 . The ν_3 mode shows a large dispersion that cannot be attributed to instrumental error but to a strong decrease of peak intensity as Mg enters the structure. For all other modes, the wavenumbers as a function of magnesium content are well aligned and can be adjusted with third degree polynomial functions with excellent correlation coefficients ($R^2 > 0.98$) (see Table 3¹). A third-degree polynomial has been selected to have a better fit and also because the observed curvatures are considered experimentally meaningful. However, a simple linear function would also fit the data correctly (as we will see later when the complete composition range is considered). In most cases (T, L, and ν_1), the data are closer to the calcite-dolomite line than to calcite-magnesite. In addition, a significant negative deviation from the calcite-dolomite line is also observed at least up to 20 mol% MgCO_3 . The fact that the wavenumber of the $2\nu_2$ mode is closer to Cal-Mgs than Cal-Dol could be attributed to such a negative deviation from Cal-Dol and not to an alignment along Cal-Mgs. Table 4 summarizes the parameters and the correlation coefficients of the regression curves shown in Figure 5. To conclude, in the range 0–30 mol% MgCO_3 , the wavenumber of all modes except ν_3 are well aligned with slightly negative deviations with respect to the Cal-Dol line.

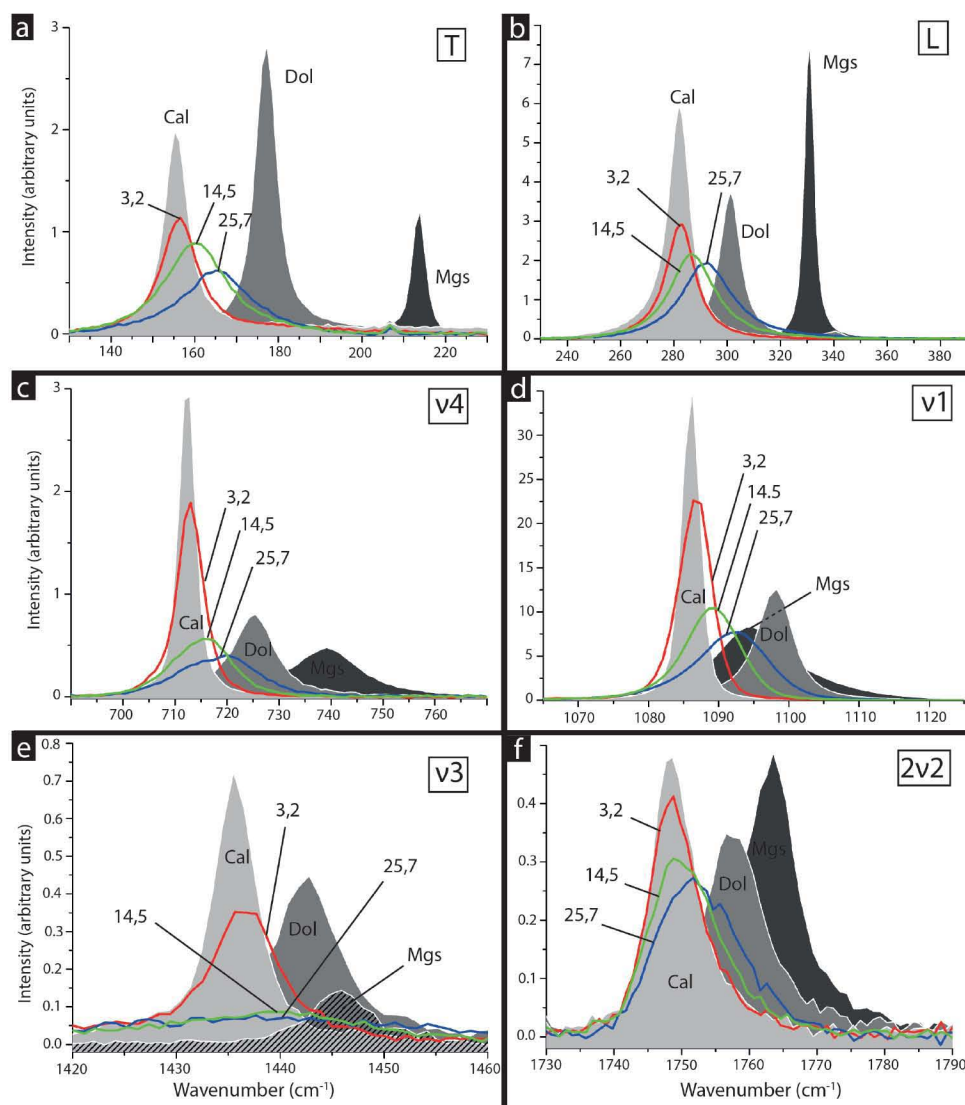


FIGURE 4. Raman spectra of some synthetic magnesian calcites. (a–b) T and L lattice modes; (c–f) ν_4 , ν_1 , ν_3 , and $2\nu_2$ internal modes. The spectra of OCN calcite, dolomite, and magnesite are reported for comparison. Abbreviations: Cal = calcite; Dol = dolomite; Mgs = magnesite. Laser 514.5 nm, accumulation of 5 scans.

Concerning the FWHM, Figure 6 emphasizes the systematic peak enlargement as Mg increases. However, the FWHM of the T mode reach a plateau at about 25 mol% MgCO_3 with an inversion of slope above this value. The normalized FWHM align along second-order polynomial curves. The regression curves of the L and ν_4 FWHM have correlation coefficients greater than 0.99. All parameters and correlation coefficients of the regression curves are listed in Table 4.

The 35–50 mol% MgCO_3 composition range

Figure 7 presents the positions of the vibration modes of Mg calcites synthesized between 35 and 50 mol% MgCO_3 . Data from the 0–30 mol% MgCO_3 range are also plotted for comparison. The position of the modes in the 35–50 mol% MgCO_3 range follows the trend defined earlier. However, the data dispersion is greater,

in particular for the L, ν_1 , and $2\nu_2$ modes. As observed within the 0–30 mol% MgCO_3 composition range, the shifts of the ν_3 mode do not show proper alignment due to very weak intensities. In all other modes and without ambiguity, even for the $2\nu_2$ overtone, the data are closer to the Cal-Dol line than to the Cal-Mgs line. Although the two data sets were obtained under different P and T conditions, the data generate linear regressions with high correlation coefficients (>0.98). These regressions are valid within the range 0–50 mol% MgCO_3 . The best correlation coefficients (>0.99) are obtained for the T, L, and ν_4 modes (Table 5).

The FWHM of the synthetic Mg calcites in the range 35–50 mol% MgCO_3 are shown in Figure 8. Again, data from the 0–30 mol% MgCO_3 composition range are plotted for comparison. These data confirm the incipient change of slope observed in Figure 6a for the T mode; they also show that a change of slope is observed

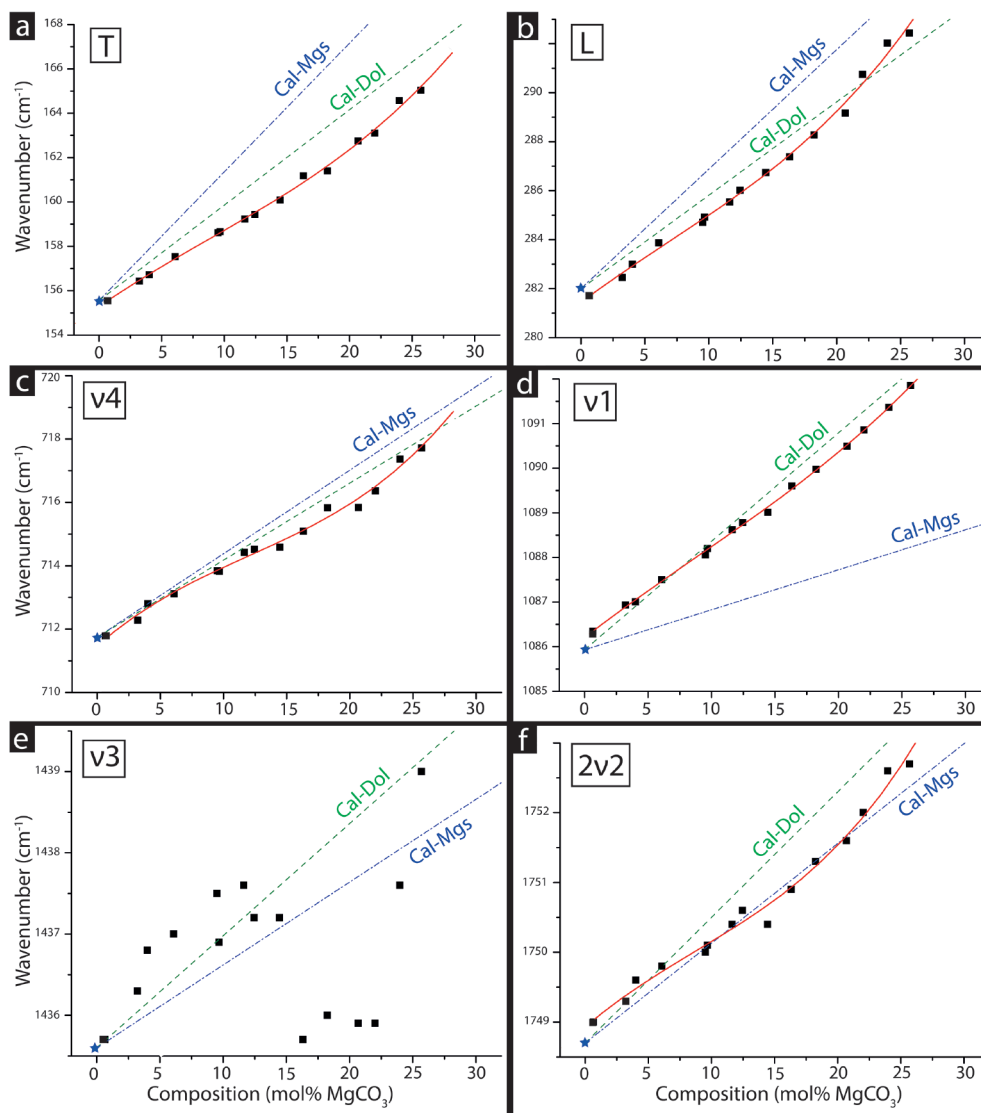


FIGURE 5. Wavenumber of the different Raman modes of synthetic Mg calcites as a function of composition in the range 0–30 mol% MgCO_3 . The straight lines joining calcite to dolomite (Cal-Dol) or to magnesite (Cal-Mgs) are shown for comparison. Fitting parameters of the third-order polynomials are given in Table 4

TABLE 4. Parameters and correlation coefficients of the fitting curves shown in red in Figures 5 and 6

	T	L	ν_4	ν_1	ν_3	$2\nu_2$
Wavenumber $f[\text{mol}\% \text{MgCO}_3]$	$155.28+0.39 X$ $-0.0078 X^2$ $+0.000293 X^3$	$281.44+0.4 X$ $-0.00743 X^2$ $+0.000359 X^3$	$711.48+0.35 X$ $-0.014 X^2$ $+0.000391 X^3$	$1086.2+0.22 X$ $-0.00276 X^2$ $+0.000106 X^3$	—	$1748.93+0.15 X$ $-0.00531 X^2$ $+0.000204 X^3$
R^2	0.997	0.995	0.991	0.999	—	0.988
FWHM $f[\text{mol}\% \text{MgCO}_3]$	$6.76+1.19 X$ $-0.0257 X^2$	$10.66+0.89 X$ $-0.0156 X^2$	$2.45+0.99 X$ $-0.0147 X^2$	$3.61+0.51 X$ $-0.00787 X^2$	$2.56+2.16 X$ $-0.026 X^2$	$7.67+0.38 X$ $-0.00448 X^2$
R^2	0.950	0.991	0.993	0.973	0.972	0.826

Notes: X expressed in mol% MgCO_3 . Valid in the range 0–26 mol% MgCO_3 .

for the L and ν_4 modes (and possibly ν_3 and $2\nu_2$). The data of the T, L, ν_4 , and $2\nu_2$ modes can be fit with a second-order polynomial function valid within the range 0–50 mol% MgCO_3 . The L and ν_4 modes present the best correlation coefficients ($R^2 > 0.98$).

Note that regressions for the entire 0–50 mol% MgCO_3 range are proposed to emphasize the consistency of the data. However, for applications in the 0–30 mol% MgCO_3 range, the regressions listed in Table 4 might be preferred. The maxima of the fitting parabola

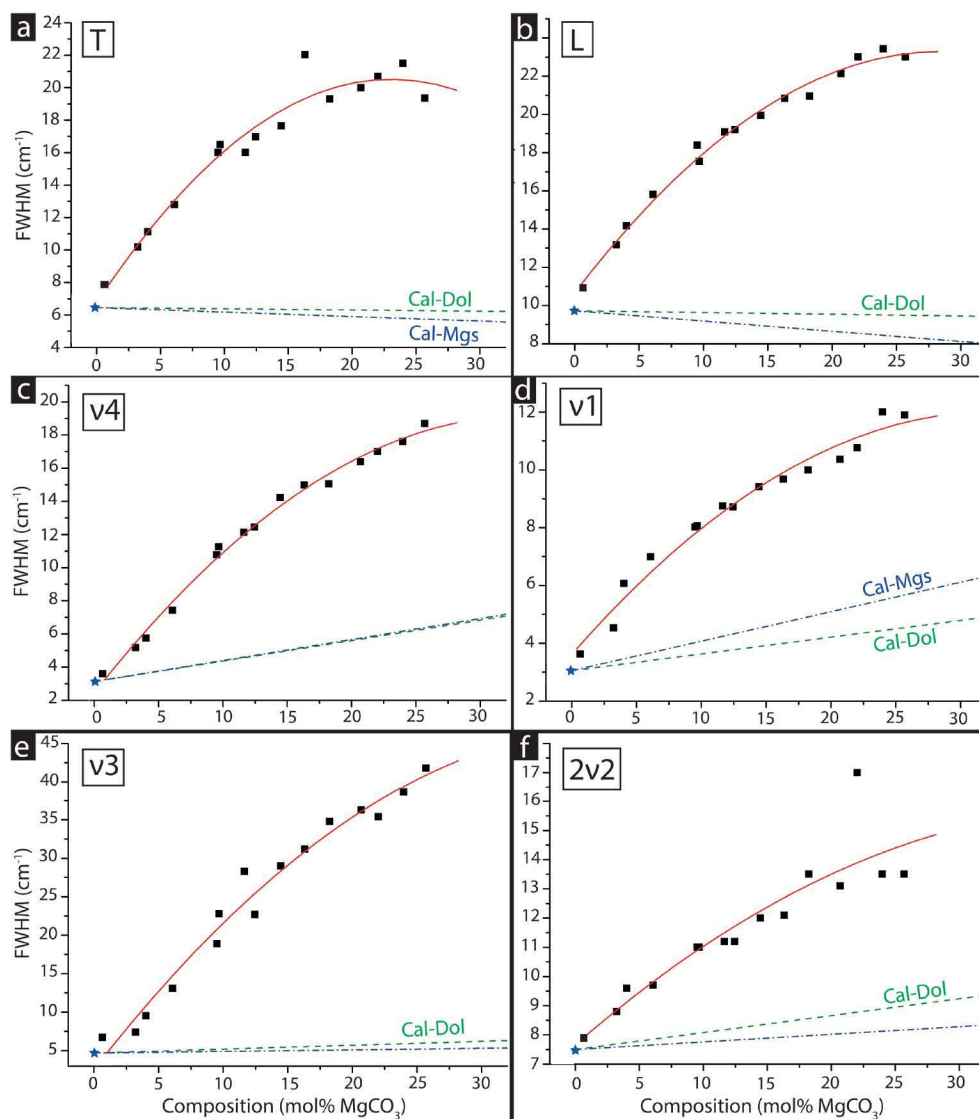


FIGURE 6. Full-width at half maximum (FWHM) of the Raman modes of synthetic Mg calcites as a function of composition in the range 0–30 mol% MgCO_3 . The Cal-Dol and Cal-Mgs lines (dashed and dash-dotted lines, respectively) are shown for comparison. The fitting parameters of the second-order polynomials are given in Table 4.

are reached for Mg contents of 25, 30, and 35 mol% MgCO_3 for the T, L, and v_4 modes, respectively. However, as a word of caution, it should be reminded that the two data sets plotted in Figure 8 were obtained from crystals synthesized under different temperatures, a critical parameter for crystal ordering, and thus FWHM. Nevertheless, the inversion of slope suspected in Figure 6 and confirmed in Figure 8 remains a robust observation that has to be considered to interpret the data. Concerning the v_3 mode, considering the poor alignment of the wavenumber as a function of Mg content (Fig. 7e), the FWHM displayed in Figure 8e are surprisingly well organized even if the data dispersion is greater above 30 mol% MgCO_3 ; here again, a change of slope can be suspected at about 30–35 mol% MgCO_3 . For the $2v_2$ mode, the change of slope is not observed at 30 mol% MgCO_3 , but could be present at 50 mol% MgCO_3 . Because of the large

data dispersion at high Mg contents and the lack of experiment above 50 mol% MgCO_3 , this conclusion has to be confirmed. The FWHM of the v_1 mode deserves further consideration since the data cannot be properly fit with a quadratic function (Fig. 8d). Indeed, the change of slope observed at about 30 mol% MgCO_3 (Fig. 8d) is due to peak doubling (Supplemental¹ Fig. EA1) that becomes obvious at 30 mol% MgCO_3 . Two different ways to fit the v_1 band with one and two peaks are presented and discussed in Supplemental¹ data EA1.

Above, the importance of two peaks that are specific to dolomite (at 340 and 880 cm^{-1}) has been emphasized. An important question is whether these peaks are observed in the synthetic Mg calcites. Not much can be said about the peak located at 340 cm^{-1} as the shift toward high wavenumbers and broadening of the adjacent L peak render the observation of this peak difficult.

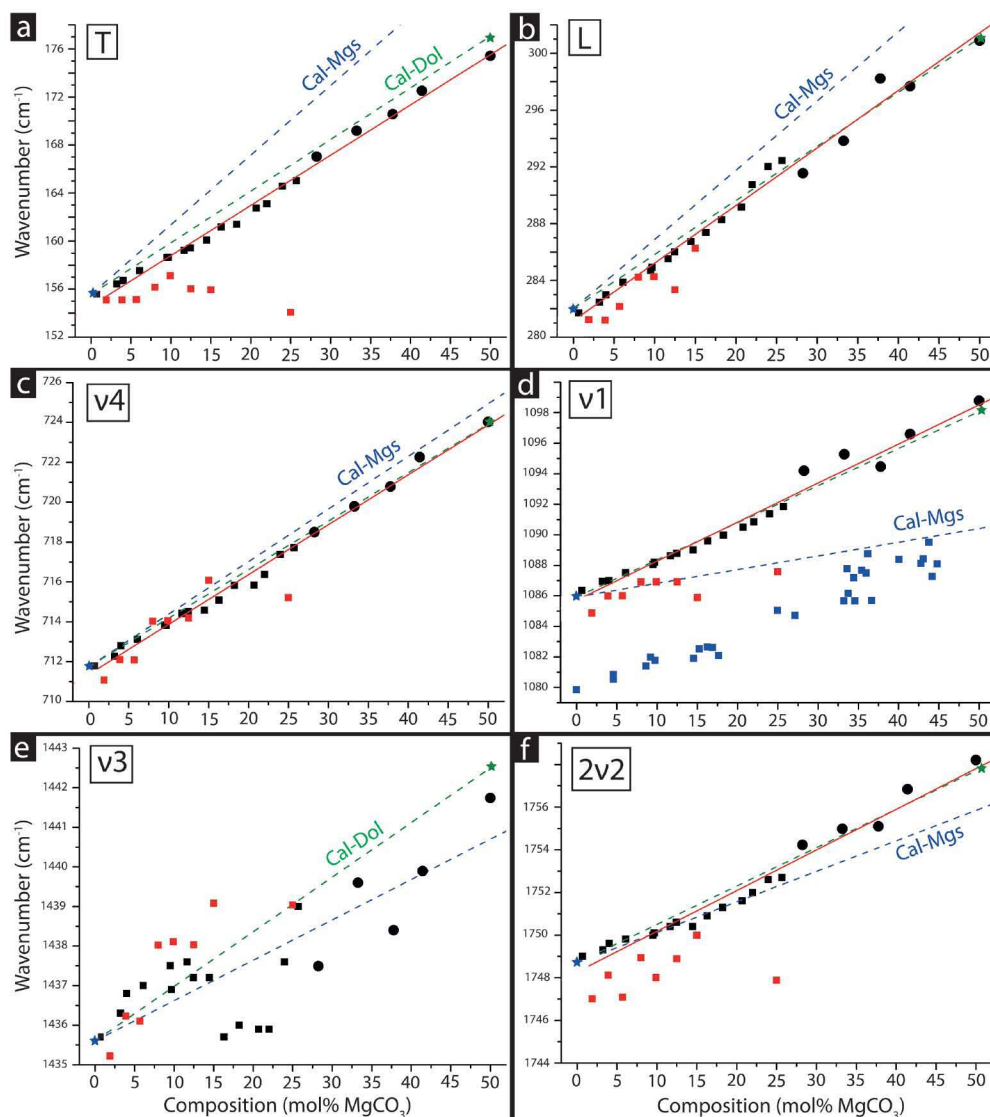


FIGURE 7. Wavenumber of the Raman modes of synthetic Mg calcites as a function of composition in the range 0–50 mol% MgCO_3 . The red squares are from Bischoff et al. (1985). Blue squares in **d** correspond to magnesian amorphous calcium carbonates from Wang et al. (2012). The Cal-Dol (green) and Cal-Mgs lines (blue) are also shown. The fitting parameters of the linear equations are listed in Table 5.

Nevertheless, a significant signal is detected in crystals with 49.2 mol% MgCO_3 . On another hand, ν_2 at $\sim 880\text{ cm}^{-1}$ should be easier to detect as it is not concealed by any neighbor. Figure 9 shows Raman spectra of all experimental products in the range $840\text{--}920\text{ cm}^{-1}$. It shows that the 880 cm^{-1} peak is absent at low Mg contents and progressively appears as Mg increases. In this series of measurements, the first experiment at which the peak can be identified with confidence is 18.2 mol% MgCO_3 . A second series of micro-Raman analyses of the magnesian calcites with MgCO_3 contents up to 14.5 mol% MgCO_3 was carried out in the restricted $650\text{--}950\text{ cm}^{-1}$ range, with longer exposure time to improve the signal/noise ratio. Results are presented in the inset of Figure 9. These data show that the 880 cm^{-1} peak can be identified down to 9.7 (and possibly 6.1) mol% MgCO_3 . A slight shift of this peak toward high wavenumbers is also observed as Mg increases.

DISCUSSION

Comparison with previous works

The shifts of vibration modes toward high wavenumbers as a function of Mg content can be compared to those of Bischoff et al. (1985) (Fig. 7). If the experiment at 25 mol% MgCO_3 of Bischoff et al. (1985) is discarded, the wavenumber shifts of the L and ν_4 modes are in good agreement in both studies, though the present data are less dispersed (Figs. 7b and 7c). For the T, ν_1 , and $2\nu_2$ modes, there is no agreement: Bischoff et al. (1985) observed a weak or no correlation of wavenumber positions with Mg content for these modes, while a strong Mg dependence with high coefficients of correlation is observed in our data set (Figs. 7a, 7d, and 7f). Finally, neither Bischoff et al. (1985) nor us observed a composition dependence on the ν_3 wavenumber (Fig. 7e).

TABLE 5. Parameters and correlation coefficients of the red fitting curves in Figures 7 and 8

	T	L	ν_4	ν_1	ν_3	$2\nu_2$
Wavenumber $f[\text{mol}\% \text{MgCO}_3]$	154.61	281.16	711.36	1085.71		1748.27
	$+0.418 X$	$+0.406 X$	$+0.25 X$	$+0.256 X$	–	$+0.191 X$
R^2	0.996	0.993	0.996	0.988	–	0.985
FWHM $f[\text{mol}\% \text{MgCO}_3]$	$8.23+0.923 X$	$11.07+0.806 X$	$2.7+0.952 X$	–	$1.78+2.98 X$	$7.69+0.376 X$
	$-0.0183 X^2$	$-0.013 X^2$	$-0.0138 X^2$		$-0.05 X^2$	$-0.00448 X^2$
R^2	0.950	0.983	0.990	–	0.84	0.836

Notes: X expressed in mol% MgCO_3 . Valid in the range 0–50 mol% MgCO_3 .

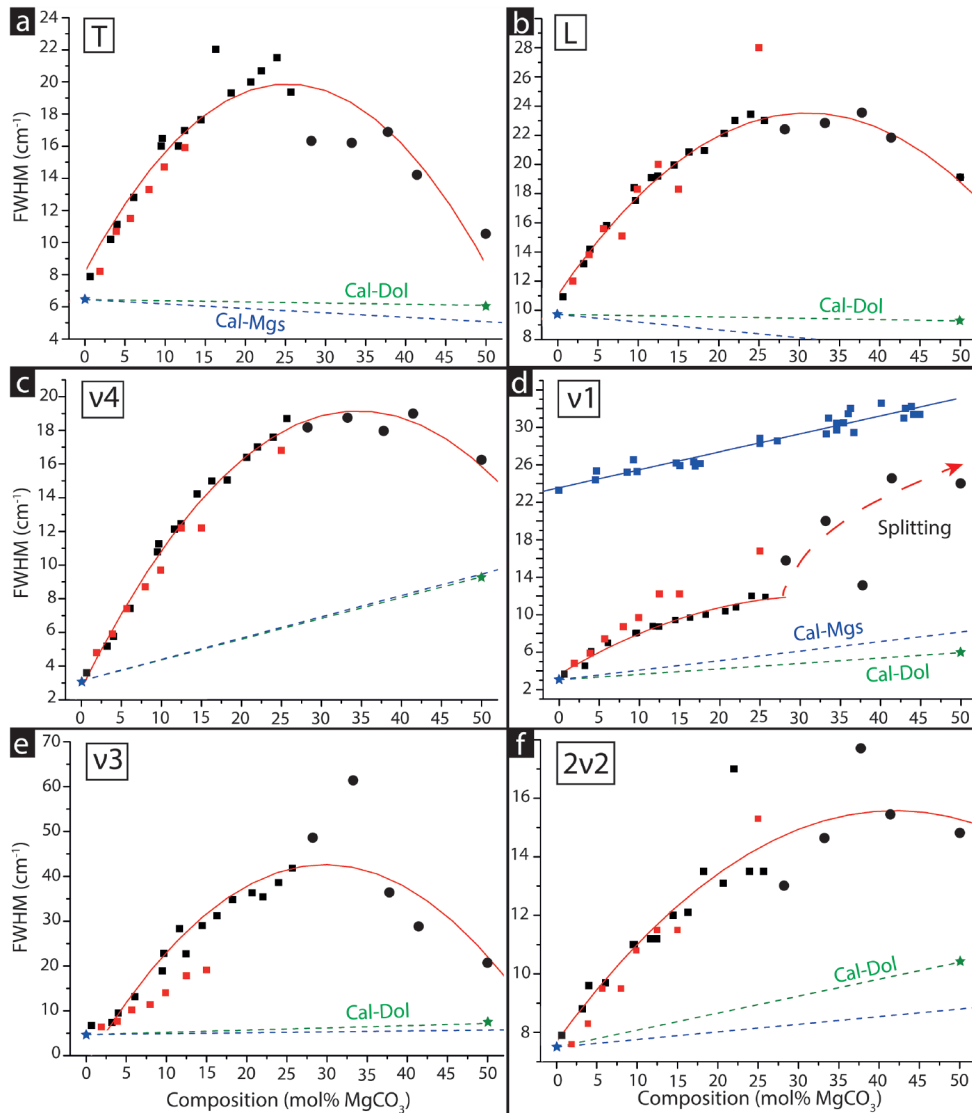


FIGURE 8. Full-width at half maximum of the Raman modes of synthetic Mg calcites as a function of composition in the range 0–50 mol% MgCO_3 . The red squares are from Bischoff et al. (1985). Blue squares in d correspond to magnesian amorphous calcium carbonates from Wang et al. (2012). The Cal-Dol (green) and Cal-Mgs lines (blue) are also shown. The fitting parameters of the linear equations are listed in Table 5.

Concerning the FWHM, Figure 8 indicates that the present results are in fairly good agreement with those of Bischoff et al. (1985) in the range 0–20 mol% MgCO_3 for all modes except ν_3 , even if the synthetic Mg calcite with 25 mol% MgCO_3 of

Bischoff et al. (1985) is not on the tendency for the L mode. The data for the ν_3 mode are well aligned in both our and Bischoff et al. (1985) data sets, but the slopes of the fitting curves differ (Fig. 8e). Finally, the wider range of compositions synthesized

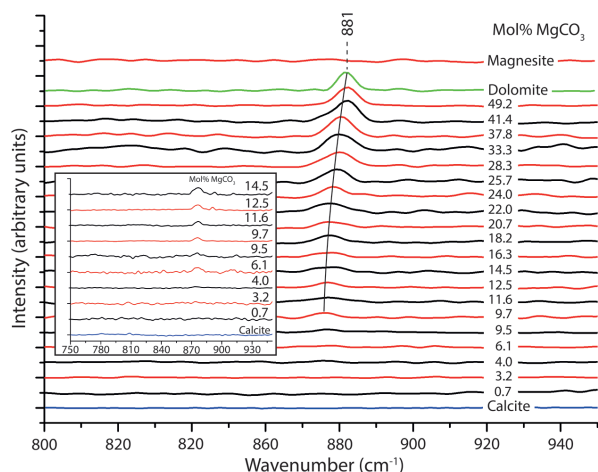


FIGURE 9. Raman spectra of calcite, dolomite, and magnesite OCN crystals, and synthetic Mg calcites in the range 840–920 cm^{-1} . Spectra were normalized to the ν_1 intensity; baselines were extracted following a similar process for all spectra. A second series of measurements with improved signal/noise ratio is shown in the inset. It indicates that the ν_2 peak could appear as soon as ~ 10 mol% MgCO_3 . In the inset, spectra were normalized to the ν_4 intensity.

in our study indicates that a curve and not a line is required to fit the data properly. The departure from linearity could not be detected by Bischoff et al. (1985) as it occurs above 25 mol% MgCO_3 , the highest Mg content studied by these authors.

STRUCTURAL INTERPRETATION

Raman shifts

The shift of Raman bands toward higher wavenumbers from calcite to magnesite OCN crystals (Fig. 1) can be attributed to the fact that the Mg^{2+} ion is smaller than Ca^{2+} ; the Ca/Mg substitution implies a decrease of interatomic metal-O distances (2.39 and 2.11 Å for the Ca-O and Mg-O bond, respectively (Politi et al. 2010, 2006), a variation of the cell volume and a subsequent increase of the vibrational frequencies of the carbonate ion (Krishnamurti 1956; White 1974a). In other words, the cation size is responsible for band displacements toward high wavenumbers as Mg increases (Rutt and Nicola 1974; White 1974a). It should be reminded that the shift toward high wavenumbers from calcite to dolomite and then magnesite is observed for all Raman modes except one, ν_1 (Fig. 1d, see also Bischoff et al. 1985, their Fig. 2) as discussed above.

Factor-group analysis predicts that Mg calcites should have Raman spectra similar to end-members but with a continual wavenumber shift between them (Bischoff et al. 1985; White 1974b). Thus the question of the nature of the end-members arises: should dolomite ($\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3$) or magnesite (MgCO_3) be considered the magnesian end-member of Mg calcites? From X-ray powder diffraction studies on their synthetic Mg calcites, Bischoff et al. (1983) concluded that there was no dolomite-like preferential atomic arrangement of magnesium in their synthetic Mg calcites and that the end-members of the Mg calcite solid solution should be calcite/magnesite, and not calcite/dolomite. This conclusion was in agreement with previous experimental

results. For instance, Goldsmith et al. (1961) stated that it is not correct to consider the region between calcite and dolomite as a simple solid solution because the dolomite structure ($R\bar{3}$) is ordered with respect to Ca and Mg, while the intermediate members of the solid solution have a disordered Ca-Mg array with the calcite space group $R\bar{3}c$. Mackenzie et al. (1983) moderated this conclusion and stated that the syntheses of Goldsmith et al. (1961) with concentrations greater than 42.5 mol% MgCO_3 always led to X-ray diffraction patterns showing evidence of dolomite-type cation ordering. Mackenzie et al. (1983) acknowledged the fact that there was no (101), (015), or (021) reflections in the XRD patterns of Bischoff et al.'s syntheses, probably excluding the possibility of dolomite-type cation ordering in Mg calcites. However, as a word of caution, Mackenzie et al. (1983) added that short-range ordering, not necessarily detected by XRD, could account for some of the negative excess volume observed in the synthetic Mg calcites (Bischoff et al. 1983). Nevertheless, at present, the generally accepted idea as summarized by Morse et al. (2007) is that magnesium substitutes for calcium in a completely random manner in magnesian calcites. On the contrary, different facts presented here lead to the idea of a progressive ordering of Ca and Mg atoms in the cation layers. (1) The trends observed in Figures 5 and 7 are closer to the Cal-Dol line than to the Cal-Mgs line. This is observed for the T, L, ν_4 , and ν_1 modes. (2) Peak asymmetry becomes more pronounced as peaks broaden with increasing Mg contents above 20 mol% MgCO_3 (valid for all the doubly degenerate modes but also the non-degenerate ν_1 and $2\nu_2$ modes); this could indicate that the peaks are a convolution of two discrete peaks. (3) Finally, an additional band at $\sim 880 \text{ cm}^{-1}$ corresponding to ν_2 vibration, only active in dolomite, appears in the synthetic Mg calcites at Mg contents of about 10 mol% MgCO_3 , and progressively grows with increasing Mg content (Fig. 9).

FWHM of Raman bands

Calcite, dolomite, and magnesite OCN crystals. The FWHM of Raman bands are function of temperature, analytical conditions (spectral resolution), sample crystallinity (crystalline defects, crystallite sizes), structural disorder, substitution of trace elements, and compositional variability of the crystallites. The cation size also plays a role in the FWHM of the various modes in rhombohedral carbonates (Bischoff et al. 1985). Raman data obtained on calcite and magnesite OCN crystals provide information on the parameters controlling the FWHM of the Raman bands. The differences of FWHM of lattice and internal modes of these two minerals are function of cation size associated with difference of strength of metal-oxygen bonds. In calcite and magnesite, the length of the C-O bond in the carbonate ion is almost similar [1.2878 Å in calcite vs. 1.2858 Å in magnesite (Valenzano et al. 2007)], but the Ca-O bond in calcite is longer (2.39 Å), and consequently weaker, than the Mg-O bond in magnesite (2.11 Å). A stronger Mg-O bond means a stronger coupling between cation and carbonate group and, less frequency, variation in the lattice modes (Bischoff et al. 1985). Thus, smaller FWHM of T and L modes in magnesite than in calcite are expected and observed. On the contrary, the FWHM of the internal modes ν_1 , $2\nu_2$, ν_3 and ν_4 of magnesite are larger than those of calcite (Fig. 8). Again, this could be due to stronger Mg-O bonds that might have more effect

on the internal vibrations of the carbonate than the weaker Ca-O bonds. Our experimental data on OCN crystals (Fig. 8, Table 2) are in agreement with this interpretation initially proposed by Bischoff et al. (1985). It will be noted that the ν_4 FWHM of dolomite is close to the calcite-magnesite line (Fig. 8): most other modes display slight to relatively large positive deviations with respect to the calcite-magnesite line, except ν_1 showing a singular behavior again, and a significant negative deviation.

Synthetic Mg calcites. The FWHM of the synthetic Mg calcites display radically different behaviors from those of the end-members as they diverge from both the calcite-dolomite and the calcite-magnesite lines (Fig. 8). The fitting curves are parabolas with maxima located between 25 and 35 mol% MgCO_3 . According to Bischoff et al. (1985), the random substitution of Ca and Mg would be accompanied by changes around the carbonate ion. The increase of FWHM as a function of magnesium content would be the result of increasing positional disorder of the carbonate ion and particularly of the rotation of these ions out of the basal plane, around the a axes. This disorder would prevail in the neighborhood of the Mg ions to accommodate shorter bonds. The hypothesis of carbonate positional disorder proposed by Bischoff et al. (1985) has been questioned by Falini et al. (1998), Zolotoyabko et al. (2010), and Wang et al. (2012). However, although the origin of Raman band enlargement due to the presence of magnesium is debated, there is a consensus on the fact that the random distribution of Mg in calcite increases the distribution of metal-O bond lengths in the crystal, which in turn increases the FWHM of the Raman bands (Wang et al. 2012). The idea that the number of metal-O configurations affects the FWHM of the Raman modes in synthetic calcites could explain the parabola shape of the FWHM as a function of composition. However, in case of random distribution, one would expect the maximum of different metal-O configurations to be located at ~50 mol% MgCO_3 . For instance, this is what is observed in the aragonite-strontianite solid solution (Alia et al. 1997), their Figure 4b. On the other hand, if the distribution of atoms is not random and some short-range dolomite-type ordering (alternating layers of Ca and Mg) appears, one would expect the maximum of metal-O configurations to be located between calcite and dolomite, and not calcite and magnesite. This situation would translate into FWHM maxima between calcite and dolomite as observed in our experiments. Thus, these new data can be interpreted in terms of progressive ordering or clustering of Ca and Mg in cation layers, starting at about 10 mol% MgCO_3 and evolving toward a generalized dolomite-like ordering.

Comparison with magnesian amorphous calcium carbonate

Wang et al. (2012) synthesized a series of ACC with magnesium contents in the range 0 to 43 mol% MgCO_3 . According to Wang et al. (2012), two internal modes are observed in ACC: the symmetric and antisymmetric C-O stretches (ν_1 and ν_3 , respectively). The results obtained by Wang et al. (2012) on the ν_1 mode are displayed in Figure 7d. Compared with Mg calcites, Mg ACC ν_1 wavenumbers are systematically shifted toward lower wavenumbers; in addition, they increase as Mg increases along a slope similar to the one of Mg calcites, but with lower intercept and greater data dispersion. It should also be noted that the dispersion of data increases above 30 mol%

MgCO_3 (Fig. 7d). The ν_1 FWHM of Mg ACC are higher than those of the magnesian calcites (greater than 22 cm^{-1}); they also depend on the Mg contents (Fig. 8d). The FWHM ACC data align along a straight line, while the ν_1 FWHM of the Mg calcites align along a curve up to 30 mol% MgCO_3 [Fig. 8d (see also the Supplemental¹ data Fig. EA2); the sudden change of slope of Mg calcites at about 27 mol% MgCO_3 has been discussed earlier and will not be reconsidered here].

Wang et al. (2012) explained the positional shift and the increase of the FWHM of the Mg ACC ν_1 mode as a function of Mg content by differences between Ca-O and Mg-O bonds. Interestingly, in a similar way to what is observed for the Mg calcite ν_1 band (Supplemental¹ Fig. EA1), these authors observed that the Mg ACC ν_1 peaks show some asymmetry that becomes more pronounced as the peak broadens with increasing Mg contents above 30 mol% MgCO_3 . The ACC peak asymmetry could also be fit with two discrete peaks. According to these authors that ν_1 peak could be a convolution of two (or more) discrete peaks, potentially invalidating a solid-solution model. It may suggest that high-Mg ACC could correspond to a heterogeneous mixture of both calcium and magnesium amorphous carbonate, rather than as a solid solution (Wang et al. 2012). Note that the authors underlined the fact that this conclusion remained hypothetical and required further investigation. In all cases, the analogy related to peak doubling between amorphous and crystalline carbonates is striking. Concerning the differences between the spectral properties of Mg ACC and Mg calcites, the systematic positional shift of the ν_1 mode toward lower wavenumbers and larger FWHM of Mg ACC can be attributed to the fact that Mg ACC are disordered solids, without order beyond 1.5 nm (Michel et al. 2008; Wang et al. 2012).

IMPLICATIONS

Raman properties and Mg contents of abiogenic and biogenic calcites

In addition to providing structural information, the Raman properties of Ca-Mg carbonates allow assessing the Mg contents of inorganic calcites with a good degree of confidence. In principle, these results could also be applied to biogenic calcites. However, Bischoff et al. (1985) noted singular Raman properties of biogenic calcites with respect to their inorganic counterparts. Thus, it is probable that features specific to biominerals such as small grain size, structural order, occluded organic matter, substitution of trace elements, and variability of composition may affect Raman spectra of biogenic calcites. Further work is required to characterize and understand the origin of the Raman singularities of biogenic Mg calcites.

Mg calcite vs. Mg ACC

Whether the results of Wang et al. (2012) on synthetic magnesian amorphous calcium carbonates can be applied to natural ACCs in biominerals is not yet determined as interactions with organic molecules may play a role just as in the case of biogenic calcites. Considering the difference of spectral properties between synthetic Mg calcites and Mg ACC, the determination of the crystalline or amorphous nature of an unknown carbonate is required prior to determining its Mg composition with Raman properties. Wavenumbers are not perfectly discriminant between

Mg ACCs and Mg calcites because of potential overlap in the range 1086–1090 cm^{-1} . On another hand, there is no overlap of FWHM between the two types of materials, which makes FWHM a good criterion to distinguish Mg ACCs from Mg calcites. Considering the range 0–30 mol% MgCO_3 particularly important for biominerals, ν_1 wavenumbers lower than 1086 cm^{-1} and ν_1 FWHM greater than 22 cm^{-1} are two adequate criteria to determine the amorphous nature of calcium carbonate in Raman spectra.

The nature of dolomite-like ordering in Mg calcites

As a general rule, intermediate compounds with superlattices may form in solid solutions if the radii of the involved cations differ by more than 15% (see Deelman 2003 for a review). In this respect, ordered dolomite is a superlattice of calcite or magnesite. Concerning the structural transition between calcite and ordered dolomite, we favor progressive dolomite like ordering rather than random substitution of Ca and Mg. This conclusion raises the question of the nature of this order. On the basis of enthalpy, entropy, and volume data of Mg calcites synthesized in the range 0–12.4 mol% MgCO_3 , Navrotsky and Capobianco (1987) cautiously proposed a structure with Ca layers randomly interspersed with Mg-rich layers. For example, for a magnesian calcite containing 10 mol% MgCO_3 , one layer in nine would be Mg-rich. These authors emphasized that such Mg-rich layers would occur at random in the stacking sequence and that the molar volumes would fall near the weighted average for calcite and dolomite. Instead of such a stacking of Ca or Mg layers, we prefer the idea of Mg clustering within a basal layer. This planar arrangement could be combined with ordering between successive basal planes so that a 3D short-range dolomite-like order would appear. The frequency and size of these 3D short-range dolomite-like clusters would increase with Mg content. This model is proposed as a working hypothesis considering that it is not yet sustained by direct observation or numerical simulation. Whatever the model selected [stacking of Mg layers (Navrotsky and Capobianco 1987), or cation ordering in successive cation basal layers (the present work)], both studies converge to conclude that Mg calcites show significant local order. Despite repeated efforts to find specific dolomite reflections in diffractograms of Mg calcites, such reflections have never been observed below 42.5 mol% MgCO_3 (Goldsmith et al. 1961; Mackenzie et al. 1983). And yet, the band at 880 cm^{-1} is observed in syntheses with Mg contents as low as ~10 mol% MgCO_3 . This could be ascribed to the fact that Raman spectroscopy is a more sensitive probe of local structural order than XRD, which is known to probe the overall average long-range order of crystalline materials (Doriguetto et al. 2004; Lekgoathi and Kock 2016). If the range of order probed by Raman and XRD differ (e.g., <5 nm and >10 nm, respectively) the fact that dolomite-like order is detected by Raman and not by powder XRD could provide an upper limit for the size of the dolomite-like clusters (i.e., less than 10 nm if the above numbers are accepted). It is often considered that physical and spectroscopic properties of carbonates vary linearly with cation radius or mass (Railsback 1999). The fact that it is not the case for the Raman properties of Mg calcites can be tentatively ascribed to the contribution of structural order to the Raman spectral properties of these carbonates.

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