# Raman characterization of synthetic magnesian calcites

# Revision_2

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**Abstract**

34

35 *Magnesian calcites are important components of sediments and biominerals. Although*
36 *Raman spectra of calcite, dolomite, and magnesite are well known, those of magnesian*
37 *calcites deserve further investigation. Nineteen syntheses of magnesian calcites covering the*
38 *range 0-50 mol% MgCO₃ have been carried out at high pressure and temperature (1-1.5*
39 *GPa, 1000-1100°C). The crystalline run products have been characterized by μ-Raman*
40 *spectroscopy.*
41     *For all lattice and internal modes (L, T, $v_1$, $v_4$, $2v_2$) but $v_3$, wavenumbers align closer*
42 *to the calcite–dolomite line than the calcite-magnesite line. The compositional dependence is*
43 *strong and regression curves with high correlation coefficients have been determined. Full*
44 *width at half maximum (FWHM) plot along parabolas that depart from the calcite–dolomite*
45 *or calcite–magnesite lines. The limited data dispersion of both shifts and FWHM allow using*
46 *Raman spectral properties of magnesian calcites to determine the Mg content of abiotic*
47 *calcites.*
48     *A comparison with Raman data from the literature obtained on synthetic magnesian*
49 *amorphous calcium carbonate (Mg ACC) shows that the wavenumber position of the ACC v1*
50 *mode is systematically shifted towards lower values, and that their FWHM are higher than*
51 *those of their crystalline counterparts. The FWHM parameters of crystalline and amorphous*
52 *materials do not overlap, which allows a clear-cut distinction between crystalline and*
53 *amorphous materials.*
54     *In synthetic magnesian calcites, the shift and FWHM of Raman bands as a function of*
55 *magnesium can be interpreted in terms of changes of metal-O bond lengths resulting from the*
56 *replacement of calcium by magnesium. The facts that the wavenumber of magnesian calcites*
57 *are close to the calcite–dolomite line (not calcite-magnesite), that the FWHM of the T, L, and*
58 *$v_4$ modes reach a maximum around $30\pm5$ mol% MgCO₃, and that a peak specific to dolomite*
59 *at $880$ $cm^{-1}$ is observed in high-magnesian calcites indicate that dolomite-like ordering is*
60 *present above ~10 mol% MgCO₃. Mg atom clustering in cation layers combined with*
61 *ordering in successive cation basal layers may account for the progressive ordering observed*
62 *in synthetic magnesian calcites.*

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## Introduction

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67    Calcite is the only $CaCO_3$ crystalline polymorph that can accommodate substantial amounts

68    of magnesium (Bischoff et al., 1983; Finch and Allison, 2007; Long et al., 2012; Mackenzie

69    et al., 1983; Morse et al., 2007; Wang et al., 2012). Magnesian calcites (Mg calcites) are

70    important components of modern and Pleistocene carbonate sediments (Bischoff et al., 1985;

71    Land, 1967). In the sediments, they are mostly found as remnants of skeletons of marines

72    invertebrates and as cement (Bathurst, 1975; Bischoff et al., 1985; Chave, 1954a; Chave,

73    1954b). Since Raman spectroscopy is sensitive to carbonate ion ($CO_3^{2-}$) vibrations, micro-

74    Raman spectroscopy is classically used to characterize small volumes of crystalline or

75    amorphous carbonate samples. Raman patterns of the different calcium carbonate polymorphs

76    (calcite, aragonite, vaterite, amorphous calcium carbonate) are well identified; however, the

77    Raman spectral modifications due to variations of chemical composition are less known. The

78    effect of magnesium incorporation in calcite has been thoroughly investigated by Bischoff et

79    al. (1985). These authors characterized the wavenumber shifts and enlargements of the

80    carbonate vibration modes in magnesian calcites as a function of their Mg contents. Carbonate

81    vibration modes of calcite (Cal: $CaCO_3$), dolomite (Dol: $Ca_{0.5}Mg_{0.5}CO_3$) and magnesite (Mgs:

82    $MgCO_3$) show a shift toward higher wavenumber and enlargement as a function of

83    magnesium content. Bischoff et al. (1985) also showed that magnesian calcites display

84    changes of spectral properties aligned along the calcite-magnesite line with slightly positive

85    or negative deviations from linearity for $v_3$ and the translational T modes. The full widths at

86    half maximum (FWHM) of the vibrational Raman bands progressively increase as a function

87    of magnesium contents. However, according to these authors, the shift and FWHM data

88    dispersions are too large to allow the determination of calcite Mg contents from their Raman

89    properties. In particular, the Raman shift of the 25 mol% $MgCO_3$ sample [i.e. the highest

90    magnesium content studied by Bischoff et al. (1985)] diverges from the general tendency.

91   Additional data are needed to clarify these points. In the present study, micro-Raman data

92   obtained on a new series of magnesian calcites synthesized at high pressure and temperature

93   are presented.

94      Amorphous calcium carbonates (ACC) are widespread in biomineralizing

95   environments, and the formation and transformation of this intermediate and reactive phase

96   are new centers of interest in the biomineralization community (Addadi et al., 2003; Beniash

97   et al., 1997; Benzerara et al., 2006; Politi et al., 2004; Politi et al., 2006; Tao et al., 2009;

98   Wang et al., 2009; Weiner et al., 2005; Weiss et al., 2002). A recent study dealing with the

99   experimental synthesis of ACC with variable magnesium contents (0 to 43 mol% $MgCO_3$)

100  showed that Raman spectroscopy can be used to determine magnesium contents of ACC

101  (Wang et al., 2012). Indeed, both the position and the FWHM of the fundamental band $v_1$ of

102  ACC are linear functions of magnesium content. Below, the data obtained on newly

103  synthesized magnesian calcites will be compared with the data obtained by Wang et al. (2012)

104  to better understand the changes of Raman properties of calcium carbonates as their Mg

105  contents and structure change.

## Materials and methods

### Experimental syntheses

108  Nineteen magnesian calcites have been synthesized in the range 2-50 mol% $MgCO_3$ at high

109  pressure and high temperature in a piston-cylinder apparatus. The starting material for our

110  synthesis experiments consists of pure synthetic calcite (Alfa Aesar) and natural magnesite

111  from Brumado (Bahia, Brazil). ICP-AES analyses of magnesite indicate trace amounts of Fe

112  (0.15 wt% $Fe_2O_3$) and Ca (0.22 wt% CaO). The magnesite was ground in a McCrone

113  micronizer agate mortar in ethanol for 30 min. Calcite and magnesite were mixed in

114  appropriate molar proportions and manually ground in an agate mortar with ethanol. After

115    desiccation in an oven at 110°C, about 60 mg of the mixture was put in a 7 mm high, 5 mm

116    outer diameter, gold capsule and welded shut. The gold capsule was placed in a salt-glass

117    assembly (Vielzeuf et al., 2007), pressurized and heated for ~96 h in a piston-cylinder

118    apparatus, at 1000°C and 1 GPa for compositions in the range 2-30 mol% $MgCO_3$, or 1100°C

119    and 1.5 GPa, for compositions in the range 35-50 mol% $MgCO_3$. Large thick-walled capsules

120    and long run durations were chosen to favor attainment of textural and thermodynamic

121    equilibrium and to yield sufficient quantity of crystalline material in a single experiment.

122    After the experiment, the run product was extracted from the capsule, part of it mounted in

123    epoxy and polished for electron microprobe and micro-Raman analyses, while the remaining

124    was ground and kept for X-ray diffraction (XRD) characterization.

125        Optically clear natural (OCN) calcite, dolomite and magnesite gem crystals have also

126    been analyzed to serve as references. OCN calcite comes from a perfect rhombohedron of

127    unknown origin. OCN dolomite and magnesite are from Azcárate Quarry, Eugui, Esteríbar

128    (Spain), and Brumado, Bahia (Brazil), respectively.

129                                    **Analytical methods**

130    *Electron microprobe (EMP) analyses* - Experimental magnesian calcites were mounted in

131    epoxy and analyzed with a SX100 Cameca electron microprobe (LMV, Clermont-Ferrand).

132    The following analytical conditions were used: 15 kV accelerating voltage, 8 to 20 nA beam

133    current, counting times of 20 s on the peak and 20 s on the background, and 20 μm spot size

134    to minimize crystal damage. All samples were polished with diamond paste down to 0.1 μm,

135    and coated with a ~20 nm thick carbon layer. The compositions in weight percent oxide were

136    measured as CaO and MgO, using synthetic periclase and natural calcite as standards. Since C

137    and O were not independently measured, $CO_2$ was calculated by stoichiometry from the

138    concentrations of CaO and MgO, considering that all Ca and Mg combine with $CO_3$. A sum

139    close to 100 was taken as an indication of a good analysis. Throughout this article, the

140    compositions of magnesian calcites are expressed in mol% $MgCO_3$.

141    *Micro-Raman spectroscopy* - Samples were analyzed on a Renishaw M-1000 Micro-Raman

142    spectrometer operating with a 514.5 nm argon ion laser, at a spectral resolution of 1 $cm^{-1}$. A

143    dual-wedge polarization scrambler inserted directly above the objective lens was used to

144    minimize polarization effects. A spot size of about 1 μm was used to respond to spatial

145    constraints associated with the size of the synthetic crystals (100-200 μm). Analytical

146    conditions were chosen to optimize signal to noise ratio: usually 10 scans per spectrum, 10 s

147    per wavelength on the detector, 100% power and a 20 μm slit. Spectral peak positions were

148    periodically calibrated against a silicon standard (at 520.5 $cm^{-1}$) and rarely varied more than 1

149    $cm^{-1}$. The additional measurements in the range 650-950 $cm^{-1}$ presented in the Fig. 9 (inset)

150    were carried out at LMV (Clermont-Ferrand – France) on a Renishaw InVia Micro Raman

151    spectrometer operating with a 532 nm argon ion laser. Analyses were carried out at a spectral

152    resolution of 1 $cm^{-1}$, in extended mode, with high confocality, 10% power, 10 scans per

153    spectrum, and 15 s exposure time. Spectral peak positions were also calibrated against a

154    silicon standard. All micro-Raman analyses were carried out on polished samples mounted in

155    epoxy. No additional sample preparation was needed for the Raman measurements. Whenever

156    possible, μ-Raman analyses were made on, or close to grains analyzed by electron microprobe

157    (EMP). Spot positioning was made using the 100× magnification lens on the microscope. The

158    Renishaw Wire software ([http://www.renishaw.fr/wire)](http://www.renishaw.fr/wire) was used for background removal and

159    wavenumber determination, while Winplotr (Roisnel and Rodríquez-Carvajal, 2001) was used

160    for peak FWHM determinations.

161

162 **Results**

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

164 Carbonates have six vibration modes composed of two external (or lattice) modes and four

165 internal modes (Couture, 1947; White, 1974a). Different notations are used in the literature to

166 refer to these vibration modes; they are listed in Table 1 with a brief description of their

167 physical significance. For clarity, the following notation initially used by Cabannes and

168 Aynard (1942), Couture (1947), Kastler and Rousset (1941) and also by Bischoff et al. (1985)

169 will be used throughout the text: translational (T) and librational (rotatory) (L) external

170 modes; $v_1$, $v_2$, $v_3$ et $v_4$ internal modes. The notation derived from factor group theory (see

171 Table 1) will be associated to the previous notation only when necessary. The internal

172 vibrations $v_1$, $v_2$, $v_3$ and $v_4$ involve bending or stretching of the C-O bonds in the carbonate

173 groups in and out of the plane in the *a* direction (Bhagavantam and Venkatarayudu, 1939;

174 Krishnan, 1945). Importantly, group theory shows that some silent Raman modes that cannot

175 be found in the first-order spectrum of a crystal can be observed in the second-order spectrum

176 (Dresselhaus et al., 2008). For instance, in calcite and magnesite, $v_2$ (at ~880 cm$^{-1}$) is Raman

177 silent while its overtone $2v_2$ (at ~1760 cm$^{-1}$) is observed (Couture, 1947). The external

178 vibrations (T and L) involve relative translations of the metal (e.g. Ca$^{2+}$ or Mg$^{2+}$) and CO$_3^{2-}$

179 ions and librations of CO$_3^{2-}$ ions (Couture, 1947). Band assignments of lattice modes (L or T)

180 are equivocal, probably as a consequence of mixing (Bischoff et al., 1985). Nevertheless, the

181 notation used by Bischoff et al. (1985) (T: [155-212 cm$^{-1}$]; L: [282-331 cm$^{-1}$]) will be used for

182 the sake of simplicity.

183     The positions of the six active Raman modes in calcite, dolomite and magnesite OCN

184 crystals are displayed in Fig. 1 and Table 2. The doubly degenerate lattice modes T and L and

185 the three internal modes $v_4$, $v_3$ and $2v_2$ show a shift toward high wavenumbers from calcite to

186 magnesite, i.e. as Mg increases (Fig. 1). However, this systematic effect is not observed in the

187   non-degenerated $\nu_1$ internal mode, which is less shifted in magnesite than in dolomite. These

188   observations are in agreement with the previous measurements of Bischoff et al. (1985) and,

189   at least qualitatively with the calculated values of Schauble et al. (2006) using density

190   functional perturbation theory. The singular behavior of $\nu_1$ could be due to the fact that this

191   mode is related to a $CO_3^{2-}$ in-plane vibration (stretch) with little Ca-Mg cation involvement

192   (Boulard et al., 2012).

193       It has been established for a long time that the crystallographic symmetry of dolomite (R-

194   3) is lower than that of calcite and magnesite (R-3c) due to alternating layers of Ca and Mg in

195   dolomite. As a consequence, a weak additional peak lattice mode at ~335 cm$^{-1}$ is observed in

196   dolomite (Bischoff et al., 1985). In most dolomite Raman spectra listed in the online Rruff

197   database (http://rruff.info/Dolomite), as in Fig. 1 (inset a), this peak is close to the T mode

198   band and can be easily overlooked. Various authors (Couture, 1947; Schauble et al., 2006;

199   Valenzano et al., 2007) also noted that two Raman-active $A_g$ modes in dolomite (at 231 and

200   876 cm$^{-1}$) are related to inactive $A_{2g}$ modes in calcite and magnesite. These peaks should be

201   observed in dolomite and not in calcite or magnesite. However, according to Schauble et al.

202   (2006) these peaks would be too weak to be distinguished from experimental background

203   noise. This observation is verified for the 231 cm$^{-1}$ peak that has not been observed in any

204   published Raman spectra (to our knowledge). On another hand, our measurements on the

205   OCN dolomite show the presence of a sharp peak at 881 cm$^{-1}$ well above background noise.

206   This peak is also observed in six dolomites referenced in the Rruff database, in particular

207   those from Bay Mag mine (British Columbia, Canada) and Oberdorf (Austria). Below,

208   particular attention will be paid to this $\nu_2$ mode at ~880 cm$^{-1}$ which can be taken as an

209   indicator of dolomite-like ordering in Mg calcites. The structural difference between

210   calcite/magnesite on one side, and dolomite on the other side, led Bischoff et al. (1985) to

211   consider that calcite and magnesite were the actual end members of the Mg calcite solid

212   solution, and thus that the spectral properties of Mg calcites should plot between calcite and

213   magnesite (the calcite-magnesite line) and not between calcite-dolomite. This is an important

214   conclusion that has to be verified.

215       Concerning the FWHM, Fig. 1 and Table 2 indicate that the peak widths of the T and L

216   lattice modes progressively decrease from calcite to magnesite (as Mg increases) while those

217   of the internal $v_1$ and $v_4$ modes increase. The situation is more complex regarding $v_3$ and $2v_2$

218   since their FWHM increase from calcite to dolomite, then decrease slightly (or stay constant)

219   from dolomite to magnesite (Fig. 1 and Table 2). Our FWHM determinations for the T, L, $v_1$

220   and $v_4$ modes are in agreement with those of Bischoff et al. (1985), within $\pm$ 1 cm$^{-1}$ which is

221   the instrument resolution. This is not the case for the $v_3$ and $2v_2$ modes that show higher

222   FWHM than those determined by Bischoff et al. (1985). These differences could be due to

223   larger error margins associated with low peak intensities and background removal processing.

224                           **Synthetic Mg calcites**

225                           **MEB and EMP characterization**

226   High pressure and high temperature experimental products were extracted from the gold

227   capsule as friable grey to white blocks of Mg calcite crystals. The grey color of some run

228   products comes from a small fraction of graphite. Some SEM images of the run products are

229   shown in Fig 2. Crystals display polyhedral shapes and have sizes in the range 100-200 μm

230   (Fig. 2c, d). Numerous grain triple junctions at 120° indicative of textural equilibrium are

231   observed (Fig. 2b). In almost all experiments, small empty spaces are found between Mg

232   calcite grains (Fig. 2c, d). These voids are interpreted as pores containing a low density fluid

233   phase. Traces of carbonate melt evidenced by quench crystals (usually against the gold

234   capsule) are observed in most experiments. They are attributed to small amounts of adsorbed

235   water in the starting material that lead to incipient melting at temperatures below the solidus

236   for the dry system. In one experiment (MgCc_45) carried out at 1100°C and 1.5 GPa, the

237  proportion of melt was important as about half of the capsule was occupied by 1-2 mm long

238  quench crystals, well segregated from polyhedral crystals in the other half of the capsule.

239  These features indicate that the solidus was overstepped in this experiment. This is in fairly

240  good agreement with the phase diagrams published on the system $CaCO_3$-$MgCO_3$ (Goldsmith

241  and Heard, 1961; Irving and Wyllie, 1975). For micro-Raman acquisitions, zoned quench

242  crystals were avoided and analyses were carried out on polyhedral crystals. The Mg contents

243  of magnesian calcites determined by EMP are plotted against nominal compositions in Fig. 3.

244  The measured compositions are systematically slightly lower than expected. The difference

245  between nominal and measured values increases from low to high Mg contents, at least up to

246  35 mol% $MgCO_3$. This systematic composition shift can be attributed to limited

247  decarbonation of magnesite taking place during the heating stage at the beginning of the

248  experiment. This interpretation is consistent with the presence of pores between grains (these

249  pores being probably filled with $CO_2$). At 35 mol% $MgCO_3$, two different crystal

250  compositions coexist in the same capsule ($28.3 \pm 0.3$ and $33.3 \pm 0.2$ mol% $MgCO_3$). This

251  situation is attributed to the presence of a solvus between calcite and dolomite (Byrnes and

252  Wyllie, 1981).

253      The quality of the synthetic crystals was determined by conventional X-ray diffraction.

254  No $CaCO_3$ polymorph other than calcite (aragonite or vaterite) was detected. Powder XRD

255  data obtained on a high flux X-ray synchrotron beamline will be presented in a companion

256  paper. In the present article dedicated to micro-Raman spectroscopy, two groups of

257  experiments corresponding to the 0-30 and 35-50 mol% $MgCO_3$ composition ranges will be

258  distinguished. This partition is justified by different facts: (1) most biominerals have Mg

259  contents in the range 0-30 mol% $MgCO_3$. For this reason, particular emphasis was put on this

260  compositional range with syntheses carried out at a 2 mol% $MgCO_3$ step interval. For more

261  magnesian compositions of lower practical interest for biominerals, a 5 mol% $MgCO_3$ step

262    interval was used to minimize the number of experiments. (2) Phase diagrams indicate that

263    due to the presence of a miscibility gap between calcite and dolomite, higher P and T are

264    required to synthesize Mg calcites in the range 35-50 mol% $MgCO_3$ (1.5 GPa, 1100°C instead

265    of 1 GPa and 1000°C). Thus, different experimental conditions were used for the two sets of

266    experiments. Furthermore, phase relationships are more complicated in the high Mg field with

267    possibility of unmixing and partial melting (see Byrnes and Wyllie, 1981 for a review). (3)

268    Finally, the behavior of the solid solution above 30 mol% $MgCO_3$ is more complex than

269    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 0-30 mol% $MgCO_3$ composition range

272    The Raman spectra of synthetic calcites show decreasing intensities of the different modes as

273    Mg increases as shown on three $MgCO_3$ compositions in Fig. 4. This effect is important even

274    at low Mg contents: for instance, the T, L and $\nu_1$ intensities of the 3.2 mol% $MgCO_3$ calcite

275    are about half those of the OCN calcite crystal. As Mg increases, the six Raman carbonate

276    bands show both progressive shifts towards high wavenumbers, and peak enlargements.

277    Normalized intensities after baseline extraction allow a precise analysis of the band shifts and

278    enlargements. Table 3 summarizes the positions and FWHM of the Raman bands for all

279    synthetic magnesian calcites. Figure 5 shows the position of the main active Raman modes as

280    a function of magnesium contents between 2 and 30 mol% $MgCO_3$. The $\nu_3$ mode shows a

281    large dispersion that cannot be attributed to instrumental error but to a strong decrease of peak

282    intensity as Mg enters the structure. For all other modes, the wavenumbers as a function of

283    magnesium content are well aligned and can be adjusted with third degree polynomial

284    functions with excellent correlation coefficients ($R^2$ >0.98) (see Table 3). A third degree

285    polynomial has been selected to have a better fit and also because the observed curvatures are

286    considered experimentally meaningful. However, a simple linear function would also fit the

287    data correctly (as we will see later when the complete composition range is considered). In

288    most cases (T, L and $v_1$), the data are closer to the calcite-dolomite line than to calcite-

289    magnesite. In addition, a significant negative deviation from the calcite-dolomite line is also

290    observed at least up to 20 mol% $MgCO_3$. The fact that the wavenumber of the $2v_2$ mode is

291    closer to Cal-Mgs than Cal-Dol could be attributed to such a negative deviation from Cal-Dol

292    and not to an alignment along Cal-Mgs. Table 4 summarizes the parameters and the

293    correlation coefficients of the regression curves shown in Fig. 5. To summarize, in the range

294    0-30 mol% $MgCO_3$, the wavenumber of all modes except $v_3$ are well aligned with slightly

295    negative deviations with respect to the Cal-Dol line.

296         Concerning the FWHM, Fig. 6 emphasizes the systematic peak enlargement as Mg

297    increases. However, the FWHM of the T mode reach a plateau at about 25 mol% $MgCO_3$ with

298    an inversion of slope above this value. The normalized FWHM align along $2^{nd}$ order

299    polynomial curves. The regression curves of the L and $v_4$ FWHM have correlation

300    coefficients greater than 0.99. All parameters and correlation coefficients of the regression

301    curves are listed in Table 4.

302                          **The 35-50 mol% $MgCO_3$ composition range**

303    Figure 7 presents the positions of the vibration modes of Mg calcites synthesized between 35

304    and 50 mol% $MgCO_3$. Data from the 0-30 mol% $MgCO_3$ range are also plotted for

305    comparison. The position of the modes in the 35-50 mol% $MgCO_3$ range follows the trend

306    defined earlier. However, the data dispersion is greater, in particular for the L, $v_1$ and $2v_2$

307    modes. As observed within the 0-30 mol% $MgCO_3$ composition range, the shifts of the $v_3$

308    mode do not show proper alignment due to very weak intensities. In all other modes and

309    without ambiguity, even for the $2v_2$ overtone, the data are closer to the Cal-Dol line than to

310    the Cal-Mgs line. Although the two datasets were obtained under different P and T conditions,

311    the data generate linear regressions with high correlation coefficients (>0.98). These

312    regressions are valid within the range 0-50 mol% $MgCO_3$. The best correlation coefficients

313    (>0.99) are obtained for the T, L and $v_4$ modes (Table 5).

314        The FWHM of the synthetic Mg calcites in the range 35-50 mol% $MgCO_3$ are shown

315    in Fig. 8. Again, data from the 0-30 mol% $MgCO_3$ composition range are plotted for

316    comparison. These data confirm the incipient change of slope observed in Fig. 6a for the T

317    mode; they also show that a change of slope is observed for the L and $v_4$ modes (and possibly

318    $v_3$ and $2v_2$). The data of the T, L, $v_4$ and $2v_2$ modes can be fit with a $2^{nd}$ order polynomial

319    function valid within the range 0-50 mol% $MgCO_3$. The L and $v_4$ modes present the best

320    correlation coefficients ($R^2$ >0.98). Note that regressions for the entire 0-50 mol% $MgCO_3$

321    range are proposed to emphasize the consistency of the data. However, for applications in the

322    0-30 mol% $MgCO_3$ range, the regressions listed in Table 4 should be preferred. The maxima

323    of the fitting parabola are reached for Mg contents of 25, 30, and 35 mol% $MgCO_3$ for the T,

324    L, and $v_4$ modes, respectively. However, as a word of caution, it should be reminded that the

325    two datasets plotted in Fig. 8 were obtained from crystals synthesized under different

326    temperatures, a critical parameter for crystal ordering, and thus FWHM. Nevertheless, the

327    inversion of slope suspected in Fig. 6 and confirmed in Fig. 8 remains a robust observation

328    that has to be considered to interpret the data. Concerning the v3 mode, considering the poor

329    alignment of the wavenumber as a function of Mg content (Fig. 7e), the FWHM displayed in

330    Fig.8e are rather well organized even if the data dispersion is greater above 30 mol% $MgCO_3$;

331    here again, a change of slope can be suspected at about 30-35 mol% $MgCO_3$. For the $2v_2$

332    mode, the change of slope is not observed at 30 mol% $MgCO_3$, but could be present at 50

333    mol% $MgCO_3$. Because of the large data dispersion at high Mg contents and the lack of

334    experiment above 50 mol% $MgCO_3$, this conclusion has to be confirmed. The FWHM of the

335    $v_1$ mode deserves further consideration since the data cannot be properly fit with a quadratic

336    function (Fig. 8d). Indeed, the change of slope observed at about 30 mol% $MgCO_3$ (Fig. 8d) is

337    due to peak doubling (Fig. EA1) that becomes obvious at 30 mol% $MgCO_3$. Two different

338    ways to fit the $v_1$ band with one and two peaks are presented and discussed in supplementary

339    data EA1.

340        In paragraph 3.1, the importance of two peaks that are specific to dolomite (at 340 and

341    880 $cm^{-1}$) has been emphasized. An important question is whether these peaks are observed in

342    the synthetic Mg calcites. Not much can be said about the peak located at 340 $cm^{-1}$ as the shift

343    towards high wavenumbers and broadening of the adjacent L peak render the observation of

344    this peak difficult. Nevertheless, a significant signal is detected in crystals with 49.2 mol%

345    $MgCO_3$. On another hand, $v_2$ at ~880 $cm^{-1}$ should be easier to detect as it is not concealed by

346    any neighbor. Figure 9 shows Raman spectra of all experimental products in the range 840-

347    920 $cm^{-1}$. It shows that the 880 $cm^{-1}$ peak is absent at low Mg contents and progressively

348    appears as Mg increases. In this series of measurements, the first experiment at which the

349    peak can be identified with confidence is 18.2 mol% $MgCO_3$. A second series of micro-

350    Raman analyses of the magnesian calcites with $MgCO_3$ contents up to 14.5 mol% $MgCO_3$ was

351    carried out in the restricted 650-950 $cm^{-1}$ range, with longer exposure time to improve the

352    signal/noise ratio. Results are presented in the inset of Fig. 9. These data show that the 880

353    $cm^{-1}$ peak can be identified down to 9.7 (and possibly 6.1) mol% $MgCO_3$. A slight shift of this

354    peak towards high wavenumbers is also observed as Mg increases.

355                                    **Discussion**

356                            **Comparison with previous works**

357    The shifts of vibration modes toward high wavenumbers as a function of Mg content can be

358    compared to those of Bischoff et al. (1985) (Fig. 7). If the experiment at 25 mol% $MgCO_3$ of

359    Bischoff et al. (1985) is discarded, the wavenumber shifts of the L and $v_4$ modes are in good

360    agreement in both studies, though the present data are less dispersed (Fig. 7b, c). For the T, $v_1$,

361    and $2v_2$ modes, there is no agreement: Bischoff et al. (1985) observed a weak or no

362    correlation of wavenumber positions with Mg content for these modes, while a strong Mg

363    dependence with high coefficients of correlation is observed in our dataset (Fig. 7a, d, f).

364    Finally, neither Bischoff et al. (1985) nor us observed a composition dependence on the $v_3$

365    wavenumber (Fig. 7e).

366        Concerning the FWHM, Fig. 8 indicates that the present results are in fairly good

367    agreement with those of Bischoff et al. (1985) in the range 0-20 mol% $MgCO_3$ for all modes

368    except $v_3$, even if the synthetic Mg calcite with 25 mol% $MgCO_3$ of Bischoff et al. (1985) is

369    not on the tendency for the L mode. The data for the $v_3$ mode are well aligned in both our and

370    Bischoff et al. (1985) datasets but the slopes of the fitting curves differ (Fig. 8e). Finally, the

371    wider range of compositions synthesized in our study indicates that a curve and not a line is

372    required to fit the data properly. The departure from linearity could not be detected by

373    Bischoff et al. (1985) as it occurs above 25 mol% $MgCO_3$, the highest Mg content studied by

374    these authors.

375                                **Structural interpretation**

376                                    **Raman shifts**

377    The shift of Raman bands toward higher wavenumbers from calcite to magnesite OCN

378    crystals (Fig. 1) can be attributed to the fact that the $Mg^{2+}$ ion is smaller than $Ca^{2+}$; the Ca/Mg

379    substitution implies a decrease of interatomic metal-O distances (2.39 Å, and 2.11 Å for the

380    Ca-O and Mg-O bond, respectively (Politi et al., 2010; Politi et al., 2006), a variation of the

381    cell volume and a subsequent increase of the vibrational frequencies of the carbonate ion

382    (Krishnamurti, 1956; White, 1974a). In other words, the cation size is responsible for band

383    displacements toward high wavenumbers as Mg increases (Rutt and Nicola, 1974; White,

384    1974a). It should be reminded that the shift towards high wavenumbers from calcite to

385    dolomite and then magnesite is observed for all Raman modes except one, $v_1$ (Fig. 1d, see also

386    Bischoff et al 1985, their Fig. 2) as discussed above.

387   Factor group analysis predicts that Mg calcites should have Raman spectra similar to

388 end members but with a continual wavenumber shift between them (Bischoff et al., 1985;

389 White, 1974b). Thus the question of the nature of the end members arises: should dolomite

390 $(Ca_{0.5}Mg_{0.5}CO_3)$ or magnesite $(MgCO_3)$ be considered the magnesian end member of Mg

391 calcites? From X-ray powder diffraction studies on their synthetic Mg calcites, Bischoff et al.

392 (1983) concluded that there was no dolomite-like preferential atomic arrangement of

393 magnesium in their synthetic Mg calcites and that the end members of the Mg calcite solid

394 solution should be calcite/magnesite, and not calcite/dolomite. This conclusion was in

395 agreement with previous experimental results. For instance, Goldsmith et al. (1961) stated that

396 it is not correct to consider the region between calcite and dolomite as a simple solid solution

397 because the dolomite structure (R-3) is ordered with respect to Ca and Mg, while the

398 intermediate members of the solid solution have a disordered Ca-Mg array with the calcite

399 space group R-3c. Mackenzie et al. (1983) moderated this conclusion and stated that the

400 syntheses of Goldsmith et al. (1961) with concentrations greater than 42.5 mol% $MgCO_3$

401 always led to X-ray diffraction patterns showing evidence of dolomite-type cation ordering.

402 Mackenzie et al. (1983) acknowledged the fact that there was no (101), (015) or (021)

403 reflections in the XRD patterns of Bischoff et al.'s syntheses, probably excluding the

404 possibility of dolomite-type cation ordering in Mg calcites. However, as a word of caution,

405 Mackenzie et al. (1983) added that short range ordering, not necessarily detected by XRD,

406 could account for some of the negative excess volume observed in the synthetic Mg calcites

407 (Bischoff et al., 1983). Nevertheless, at present, the generally accepted idea as summarized by

408 Morse et al. (2007) is that magnesium substitutes for calcium in a completely random manner

409 in magnesian calcites. On the contrary, different facts presented here lead to the idea of a

410 progressive ordering of Ca and Mg atoms in the cation layers: (1) the trends observed in Figs.

411 5 and 7 are closer to the Cal-Dol line than to the Cal-Mgs line. This is observed for the T, L,

412    $v_4$, and $v_1$ modes. (2) Peak asymmetry becomes more pronounced as peaks broaden with

413    increasing Mg contents above 20 mol% $MgCO_3$ (valid for all the doubly degenerate modes

414    but also the non-degenerate $v_1$ and $2v_2$ modes); this could indicate that the peaks are a

415    convolution of two discrete peaks. (3) Finally, an additional band at ~880 cm$^{-1}$ corresponding

416    to $v_2$ vibration, only active in dolomite, appears in the synthetic Mg calcites at Mg contents of

417    about 10 mol% $MgCO_3$, and progressively grows with increasing Mg content (Fig. 9).

<div align="center">**FWHM of Raman bands**</div>

<div align="center">**Calcite, dolomite, magnesite OCN crystals**</div>

420    The FWHM of Raman bands are function of temperature, analytical conditions (spectral

421    resolution), sample crystallinity (crystalline defects, crystallite sizes), structural disorder,

422    substitution of trace elements, and compositional variability of the crystallites. The cation size

423    also plays a role in the FWHM of the various modes in rhombohedral carbonates (Bischoff et

424    al., 1985). Raman data obtained on calcite and magnesite OCN crystals provide information

425    on the parameters controlling the FWHM of the Raman bands. The differences of FWHM of

426    lattice and internal modes of these two minerals are function of cation size associated with

427    difference of strength of metal-oxygen bonds. In calcite and magnesite, the length of the C-O

428    bond in the carbonate ion is almost similar [1.2878 Å in calcite vs 1.2858 Å in magnesite

429    (Valenzano et al., 2007)], but the Ca-O bond in calcite is longer (2.39 Å), and consequently

430    weaker, than the Mg-O bond in magnesite (2.11 Å). A stronger Mg-O bond means a stronger

431    coupling between cation and carbonate group, and less frequency variation in the lattice

432    modes (Bischoff et al., 1985). Thus, smaller FWHM of T and L modes in magnesite than in

433    calcite are expected and observed. On the contrary, the FWHM of the internal modes $v_1$, $2v_2$,

434    $v_3$ and $v_4$ of magnesite are larger than those of calcite (Fig. 8). Again, this could be due to

435    stronger Mg-O bonds that might have more effect on the internal vibrations of the carbonate

436    than the weaker Ca-O bonds. Our experimental data on OCN crystals (Fig. 8, Table 2) are in

437    agreement with this interpretation initially proposed by Bischoff et al. (1985). It will be noted

438    that the $v_4$ FWHM of dolomite is close to the calcite-magnesite line (Fig. 8): most other

439    modes display slight to relatively large positive deviations with respect to the calcite-

440    magnesite line, except $v_1$ showing a singular behavior again, and a significant negative

441    deviation.

**Synthetic Mg calcites**

443    The FWHM of the synthetic Mg calcites display radically different behaviors from those of

444    the end members as they diverge from both the calcite-dolomite and the calcite-magnesite

445    lines (Fig. 8). The fitting curves are parabolas with maxima located between 25 and 35 mol%

446    $MgCO_3$. According to Bischoff et al. (1985), the random substitution of Ca and Mg would be

447    accompanied by changes around the carbonate ion. The increase of FWHM as a function of

448    magnesium content would be the result of increasing positional disorder of the carbonate ion

449    and particularly of the rotation of these ions out of the basal plane, around the $a$ axes. This

450    disorder would prevail in the neighborhood of the Mg ions to accommodate shorter bonds.

451    The hypothesis of carbonate positional disorder proposed by Bischoff et al. (1985) has been

452    questioned by Falini et al. (1998), Zolotoyabko et al. (2010) and Wang et al. (2012).

453    However, although the origin of Raman band enlargement due to the presence of magnesium

454    is debated, there is a consensus on the fact that the random distribution of Mg in calcite

455    increases the distribution of metal-O bond lengths in the crystal, which in turn increases the

456    FWHM of the Raman bands (Wang et al., 2012). The idea that the number of metal-O

457    configurations affects the FWHM of the Raman modes in synthetic calcites could explain the

458    parabola shape of the FWHM as a function of composition. However, in case of random

459    distribution, one would expect the maximum of different metal-O configurations to be located

460    at ~50 mol% $MgCO_3$. For instance, this is what is observed in the aragonite-strontianite solid

461    solution (Alia et al., 1997), their Fig. 4b. On the other hand, if the distribution of atoms is not

462    random and some short range dolomite-type ordering (alternating layers of Ca and Mg)

463    appears, one would expect the maximum of metal-O configurations to be located between

464    calcite and dolomite, and not calcite and magnesite. This situation would translate into

465    FWHM maxima between calcite and dolomite as observed in our experiments. Thus, these

466    new data can be interpreted in terms of progressive ordering or clustering of Ca and Mg in

467    cation layers, starting at about 10 mol% $MgCO_3$ and evolving towards a generalized

468    dolomite-like ordering.

469    **Comparison with magnesian amorphous calcium carbonate**

470    Wang et al. (2012) synthesized a series of ACC with magnesium contents in the range 0 to 43

471    mol% $MgCO_3$. According to Wang et al. (2012), two internal modes are observed in ACC:

472    the symmetric and antisymmetric C-O stretches ($v_1$ and $v_3$, respectively). The results obtained

473    by Wang et al. (2012) on the $v_1$ mode are displayed in Fig. 7d. Compared with Mg calcites,

474    Mg-ACC $v_1$ wavenumbers are systematically shifted towards lower wavenumbers; in

475    addition, they increase as Mg increases along a slope similar to the one of Mg calcites, but

476    with lower intercept and greater data dispersion. It should also be noted that the dispersion of

477    data increases above 30 mol% $MgCO_3$ (Fig. 7d). The $v_1$ FWHM of Mg-ACC are higher than

478    those of the magnesian calcites (greater than 22 cm$^{-1}$); they also depend on the Mg contents

479    (Fig. 8d). The FWHM ACC data align along a straight line, while the $v_1$ FWHM of the Mg

480    calcites align along a curve up to 30 mol% $MgCO_3$ [Fig. 8d (see also the supplementary data

481    Fig. EA2); the sudden change of slope of Mg calcites at about 27 mol% $MgCO_3$ has been

482    discussed earlier and will not be reconsidered here].

483    Wang et al. (2012) explained the positional shift and the increase of the FWHM of the

484    Mg-ACC $v_1$ mode as a function of Mg content by differences between Ca-O and Mg-O bonds.

485    Interestingly, in a similar way to what is observed for the Mg calcite $v_1$ band (Fig. EA1), these

486    authors observed that the Mg-ACC $v_1$ peaks show some asymmetry that becomes more

487    pronounced as the peak broadens with increasing Mg contents above 30 mol % $MgCO_3$. The

488    ACC peak asymmetry could also be fit with two discrete peaks. According to these authors

489    that $v_1$ peak could be a convolution of two (or more) discrete peaks, potentially invalidating a

490    solid solution model. It may suggest that high-Mg-ACC could correspond to a heterogeneous

491    mixture of both calcium and magnesium amorphous carbonate, rather than as a solid solution

492    (Wang et al., 2012). Note that the authors underlined the fact that this conclusion remained

493    hypothetical and required further investigation. In all cases, the analogy related to peak

494    doubling between amorphous and crystalline carbonates is striking. Concerning the

495    differences between the spectral properties of Mg-ACC and Mg calcites, the systematic

496    positional shift of the $v_1$ mode toward lower wavenumbers and larger FWHM of Mg-ACC can

497    be attributed to the fact that Mg-ACC are disordered solids, without order beyond 1.5 nm

498    (Michel et al., 2008; Wang et al., 2012).

499                               **Implications**

500

501    *Raman properties and Mg contents of abiotic and biogenic calcites* - In addition to providing

502    structural information, the Raman properties of Ca-Mg carbonates allow assessing the Mg

503    contents of inorganic calcites with a good degree of confidence. In principle, these results

504    could also be applied to biogenic calcites. However, Bischoff et al. (1985) noted singular

505    Raman properties of biogenic calcites with respect to their inorganic counterparts. Thus, it is

506    probable that features specific to biominerals such as small grain size, structural order,

507    occluded organic matter, substitution of trace elements, and variability of composition may

508    affect Raman spectra of biogenic calcites. Further work is required to characterize and

509    understand the origin of the Raman singularities of biogenic Mg calcites.

510    *Mg calcite versus Mg ACC* – Whether the results of Wang et al. (2012) on synthetic

511    magnesian amorphous calcium carbonates can be applied to natural ACCs in biominerals is

512    not yet determined as interactions with organic molecules may play a role just as in the case

513    of biogenic calcites. Considering the difference of spectral properties between synthetic Mg

514    calcites and Mg-ACC, the determination of the crystalline or amorphous nature of an

515    unknown carbonate is required prior to determining its Mg composition with Raman

516    properties. Wavenumbers are not perfectly discriminant between Mg ACCs and Mg calcites

517    because of potential overlap in the range 1086-1090 $cm^{-1}$. On another hand, there is no

518    overlap of FWHM between the two types of materials, which makes FWHM a good criterion

519    to distinguish Mg ACCs from Mg calcites. Considering the range 0-30 mol% $MgCO_3$

520    particularly important for biominerals, $v_1$ wavenumbers lower than 1086 $cm^{-1}$ and $v_1$ FWHM

521    greater than 22 $cm^{-1}$ are two adequate criteria to determine the amorphous nature of calcium

522    carbonate in Raman spectra.

523    *The nature of dolomite-like ordering in Mg calcites* – As a general rule, intermediate

524    compounds with superlattices may form in solid solutions if the radii of the involved cations

525    differ by more than 15% (see Deelman (2003) for a review). In this respect, ordered dolomite

526    is a superlattice of calcite or magnesite. Concerning the structural transition between calcite

527    and ordered dolomite, we favor progressive dolomite like ordering rather than random

528    substitution of Ca and Mg. This conclusion raises the question of the nature of this order. On

529    the basis of enthalpy, entropy and volume data of Mg calcites synthesized in the range 0-12.4

530    mol% $MgCO_3$, Navrotsky and Capobianco (1987) cautiously proposed a structure with Ca

531    layers randomly interspersed with Mg-rich layers. For example, for a magnesian calcite

532    containing 10 mol% $MgCO_3$, one layer in nine would be Mg-rich. These authors emphasized

533    that such Mg-rich layers would occur at random in the stacking sequence and that the molar

534    volumes would fall near the weighted average for calcite and dolomite. Instead of such a

535    stacking of Ca or Mg layers, we prefer the idea of Mg clustering within a basal layer. This

536    planar arrangement could be combined with ordering between successive basal planes so that

537    a 3D short-range dolomite-like order would appear. The frequency and size of these 3D short-

538    range dolomite-like clusters would increase with Mg content. This model is proposed as a

539    working hypothesis considering that it is not yet sustained by direct observation or numerical

540    simulation. Whatever the model selected [stacking of Mg layers (Navrotsky and Capobianco,

541    1987), or cation ordering in successive cation basal layers (the present work)], both studies

542    converge to conclude that Mg calcites show significant local order. Despite repeated efforts to

543    find specific dolomite reflections in diffractograms of Mg calcites, such reflections have never

544    been observed below 42.5 mol% $MgCO_3$ (Goldsmith et al., 1961; Mackenzie et al., 1983).

545    And yet, the band at 880 $cm^{-1}$ is observed in syntheses with Mg contents as low as ~10 mol%

546    $MgCO_3$. This could be ascribed to the fact that Raman spectroscopy is a more sensitive probe

547    of local structural order than XRD which is known to probe the overall average long range

548    order of crystalline materials (Doriguetto et al., 2004; Lekgoathi and Kock, 2016). If the range

549    of order probed by Raman and XRD differ (e.g. <5 nm and >10 nm, respectively) the fact that

550    dolomite-like order is detected by Raman and not by powder XRD could provide an upper

551    limit for the size of the dolomite-like clusters (i.e. less than 10 nm if the above numbers are

552    accepted). It is often considered that physical and spectroscopic properties of carbonates vary

553    linearly with cation radius or mass (Railsback, 1999). The fact that it is not the case for the

554    Raman properties of Mg calcites can be tentatively ascribed to the contribution of structural

555    order to the Raman spectral properties of these carbonates.

556                                         **Acknowledgments**

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710

711

712

# Figure captions:

713

714 **Figure 1:** *Raman spectra of calcite, dolomite and magnesite optically clear natural (OCN)*

715 *crystals. (a-b) T and L lattice modes, (c-f) $v_4$, $v_1$ $v_3$ and $2v_2$ internal modes.*

716

717 **Figure 2:** *SEM-BSE images of synthetic magnesian calcites showing 100 to 200 μm*

718 *polyhedral crystals. Homogeneous grey level in a given grain indicates homogeneous crystal*

719 *composition; variation of grey level from one grain to another result from variations of lattice*

720 *orientations. Note the presence of pores between the crystals.*

721

722 **Figure 3:** *Compositions (mol% $MgCO_3$) of the synthetic Mg calcites determined by electron*

723 *microprobe plotted against nominal compositions. (Error bars are smaller than symbols).*

724

725 **Figure 4:** *Raman spectra of some synthetic magnesian calcites. (a-b) T and L lattice modes;*

726 *(c-f) $v_4$, $v_1$, $v_3$ and $2v_2$ internal modes. The spectra of OCN calcite, dolomite and magnesite are*

727 *reported for comparison. Abbreviations: Cal: calcite; Dol: dolomite; Mgs: magnesite. Laser*

728 *514.5 nm, accumulation of 5 scans.*

729

730 **Figure 5:** *Wavenumber of the different Raman modes of synthetic Mg calcites as a function of*

731 *composition in the range 0-30 mol% $MgCO_3$. The straight lines joining the calcite spectral*

732 *data to the dolomite data (Cal-Dol) or to the magnesite data (Cal-Mgs) are shown for*

733 *comparison. Fitting parameters of the $3^{rd}$ order polynomials are given in Table 3 (valid*

734 *within the range 0-30 mol% $MgCO_3$).*

735

736 **Figure 6:** *Full width at half maximum (FWHM) of the Raman modes of synthetic Mg calcites*

737 *as a function of composition in the range 0-30 mol% MgCO$_3$. The Cal-Dol and Cal-Mgs lines*

738 *(dashed and dash-dotted lines, respectively) are shown for comparison. The fitting*

739 *parameters of the 2$^{nd}$ order polynomials are given in Table 3.*

740

741 **Figure 7:** *Wavenumber of the Raman modes of synthetic Mg calcites as a function of*

742 *composition in the range 0-50 mol% MgCO$_3$. The red squares are from Bischoff et al.,*

743 *(1985). Blue squares in Fig. 7d correspond to magnesian amorphous calcium carbonates*

744 *from Wang et al., (2012). The Cal-Dol (green) and Cal-Mgs lines (blue) are also shown. The*

745 *fitting parameters of the linear equations are listed in Table 4.*

746

747 **Figure 8:** *Full width at half maximum of the Raman modes of synthetic Mg calcites as a*

748 *function of composition in the range 0-50 mol% MgCO$_3$. The red squares are from Bischoff et*

749 *al., (1985). Blue squares in Fig. 8d correspond to magnesian amorphous calcium carbonates*

750 *from Wang et al., (2012). The Cal-Dol (green) and Cal-Mgs lines (blue) are also shown. The*

751 *fitting parameters of the linear equations are listed in Table 4.*

752

753 **Figure 9:** *Raman spectra of calcite, dolomite and magnesite gem crystals, and synthetic Mg*

754 *calcites in the range 840-920 cm$^{-1}$. Spectra were normalized to the $v_1$ intensity; baselines*

755 *were extracted following a similar process for all spectra. A second series of measurements*

756 *with improved signal/noise ratio in shown in the inset. It indicates that the $v_2$ peak could*

757 *appear as soon as ~10 mol% MgCO$_3$. In the inset, spectra were normalized to the $v_4$ intensity.*

758

759    **Figure EA-1:** *Simple (a, c) and double (b, d) peak fitting for Mg calcite syntheses with 14.5*

760    *and 37.8 mol% MgCO₃.*

761

762    **Figure EA-2:** *(a) Wavenumber of the $v_1$ Raman mode of synthetic Mg calcites as a function of*

763    *composition in the range 0-50 mol% MgCO₃. Results of simple and double peak fittings are*

764    *shown in red and black, respectively. Cal-Dol and Cal-Mgs lines are shown for comparison.*

765    *(b) FWHM of the $v_1$ Raman mode of synthetic Mg calcites as a function of composition in the*

766    *range 0-30 and 0-50 mol% MgCO₃ for the simple (red) and double (black) peak fitting,*

767    *respectively.*

768

**Supplementary materials:**

770    EA1 – $\nu_1$ Peak doubling

771        Figure EA1 shows the $\nu_1$ mode of Mg calcites containing 14.5 and 37.8 mol% $MgCO_3$.

772    The peak becomes asymmetric to the left as Mg increases, and increasingly difficult to fit

773    with a single peak. This simple fact explains the features observed in Fig. 8d with a marked

774    change of trend above 30 mol% $MgCO_3$. The one- and two-peak fits are shown in Fig. EA1.

775    For the two-peak fit, the constraint of FWHM similarity for the two peaks had to be

776    introduced to minimize the number of potential solutions. Figure EA2a shows the peak

777    wavenumbers as a function of Mg content. The position of the major peak is close to that

778    determined with a single peak. The position of the second peak departs significantly from the

779    one of the first peak, with higher data dispersion. However, the slopes of the two datasets are

780    similar. As far as FWHM is concerned (Fig. EA2b), the data alignment is better than in the

781    one-peak fit and does no longer show divergence at 30 mol% $MgCO_3$. As in the case of $2\nu_2$, a

782    maximum seems to be reached at about 50 mol% $MgCO_3$. However, this conclusion is

783    difficult to ascertain as no data were collected above 50 mol% $MgCO_3$. Note that for the

784    double peak fitting, a single set of FWHM is reported on this figure as the constraint of

785    similarity of FWHM for the two peaks was introduced in the model.

786        The main purpose of these supplementary materials is to explain the particular

787    behavior of the $\nu_1$ FWHM above ~30 mol% $MgCO_3$ (Fig. 8d). They indicate that the Raman

788    spectra of the Ca-Mg carbonate solid-solution may show more complicated features than

789    expected. The origin of peak doubling as Mg increases in the solid-solution is not yet fully

790    understood, though a tentative explanation is provided in the main text.

791

**Table 1:** *Raman modes for Ca-Mg carbonates. Wavenumber ranges come from the present study. For complete reviews of carbonate modes see Schauble et al. (2006), Valenzano et al. (2007) and Gillet et al. (1993).*

| Main notation | Space group notation | Schematic of vibration | Type of vibration | Geometry of vibration | Wavenumber range ($cm^{-1}$) | Comments | Vibration type attribution |
|---|---|---|---|---|---|---|---|
| T | $(E_g)$ | | External | In Plane Translation | 155-212 | Doubly degenerate | (Kastler and Rousset, 1941), (Cabannes and Aynard, 1942), (Couture, 1947) |
| 235 $cm^{-1}$ | $(A_g)$ | | External | Vertical Translation | 230-240 | **Only active in dolomite** | (Valenzano et al., 2007) |
| L | $(E_g)$ | | External | Libration | 282-331 | Doubly degenerate | (Kastler and Rousset, 1941), (Cabannes and Aynard, 1942) |
| 335 $cm^{-1}$ | $(A_g)$ | | External | Vertical Translation | 330-340 | **Only active in dolomite** | $(A_{2g})$ mode in magnesite (Valenzano et al., 2007) |
| $v_4$ | $(E_g)$ | | Internal | In Plane Bending | 711-740 | Doubly degenerate | (Kastler and Rousset, 1941), (Cabannes and Aynard, 1942), (Couture, 1947) |
| $v_2$ | $(A_g)$ | | Internal | Out of Plane Bending | 872-881 | **Only active in dolomite** | $(A_{2g})$ mode in calcite and magnesite (Schauble et al., 2006) |
| $v_1$ | $(A_{1g})$ | | Internal | Symmetric Strech | 1086-1095 | Active as $(A_g)$ mode in dolomite | (Kastler and Rousset, 1941), (Cabannes and Aynard, 1942), (Couture, 1947) |
| $v_3$ | $(E_g)$ | | Internal | Anti-Symmectric Strech | 1435-1446 | Doubly degenerate | (Kastler and Rousset, 1941), (Cabannes and Aynard, 1942), (Couture, 1947) |
| 2 $v_2$ | $(A_{2g})$ | | Internal | Out of Plane Bending | 1748-1763 | Overtone of the silent υ2 mode in most Ca-Mg carbonate | (Kastler and Rousset, 1941), (Cabannes and Aynard, 1942), (Couture, 1947) |
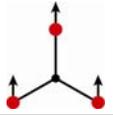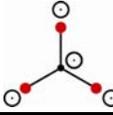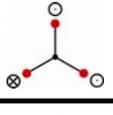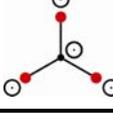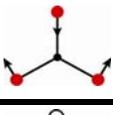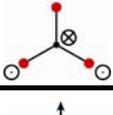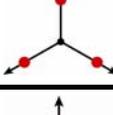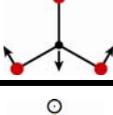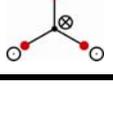
1    **Table 2:** *Wavenumbers and FWHM (in italics) of all Raman modes of calcite, dolomite and magnesite OCN crystals and other reference crystals*
2    *from the literature (units in cm$^{-1}$).*

| | 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 *6.5* | Inactive | 282 *9.7* | Inactive | 711.8 *3.1* | Inactive | 1086 *3.1* | 1435.6 *4.7* | 1748.7 *7.5* |
| **Calcite** (Bischoff et al., 1985) | 154 *6.2* | Inactive | 281 *10.1* | Inactive | 711 *3.6* | Inactive | 1085 *2.5* | 1434 *2.0* | 1748 *3.6* |
| **Calcite** (theoretical) (Schauble et al., 2006) | 155.5 | Inactive | 273 | 310.4 (A$_{2g}$) | 711 | 872.5 (A$_{2g}$) | 1094.3 | 1437.6 | ø |
| **Dolomite** Azcárate OCN crystal | 177.1 *6.1* | | 301.1 *9.3* | 340 | 723.9 *9.3* | 881 | 1098.1 *6* | 1442.5 *7.2* | 1757.7 *10.4* |
| **Dolomite** (Bischoff et al., 1985) | 175 *5.5* | | 299 *9.8* | 335 | 724 *9.0* | Not observed | 1097 *6.1* | 1441 *3.8* | 1756 *4.3* |
| **Dolomite** (theoretical) (Schauble et al., 2006) | 176.2 | 231.2 | 295.8 | 338.3 (A$_g$) | 724.7 | 876.5 | 1104.4 | 1446.6 | ø |
| **Magnesite** Brumado OCN crystal | 213.6 *3.7* | Inactive | 331 *4.4* | Inactive | 738.1 *15.8* | Inactive | 1094.9 *13.2* | 1445.8 *6.7* | 1763 *10.1* |
| **Magnesite** (Bischoff et al., 1985) | 213 *4.0* | Inactive | 329 *4.9* | Inactive | 738 *12.2* | Inactive | 1093 *12.5* | 1444 *3.1* | 1762 *4.8* |
| **Magnesite** (theoretical) (Schauble et al., 2006) | 208.4 | Inactive | 324.4 | 361.7 (A$_{2g}$) | 737.7 | 875.9 (A$_{2g}$) | 1103.3 | 1452.6 | ø |

**Table 3:** *Wavenumbers and FWHM (in italics) of the six Raman modes of synthetic Mg calcites (units in cm⁻¹). Experiments were named after the nominal composition of the starting material; the composition measured with the electron microprobe is given below each name (e.g. MgCc_8 stands for a starting material with 8 mol% MgCO₃ – the measured composition is 6.1 mol% MgCO₃). Experiments MgCc_2 to MgCc_30 were carried out at 1 GPa, 1000°C, others at 1.5 GPa and 1100°C.*

| | T | L | $v_4$ | $v_1$ | $v_3$ | $2 v_2$ |
|---|---|---|---|---|---|---|
| MgCc_2 | 155.55 | 281.71 | 711.78 | 1086.34 | 1435.7 | 1749 |
| 0.7 mol% MgCO₃ | *7.87* | *10.92* | *3.60* | *3.62* | *6.7* | *7.9* |
| MgCc_4 | 156.43 | 282.46 | 712.28 | 1086.94 | 1436.3 | 1749.3 |
| 3.2 mol% MgCO₃ | *10.20* | *13.18* | *5.17* | *4.53* | *7.4* | *8.8* |
| MgCc_6 | 156.72 | 282.99 | 712.8 | 1087.00 | 1436.8 | 1749.6 |
| 4 mol% MgCO₃ | *11.11* | *14.18* | *5.75* | *6.07* | *9.5* | *9.6* |
| MgCc_8 | 157.53 | 283.87 | 713.11 | 1087.5 | 1437 | 1749.8 |
| 6.1 mol% MgCO₃ | *12.81* | *15.81* | *7.43* | *6.90* | *13.1* | *9.7* |
| MgCc_10 | 158.65 | 284.92 | 713.82 | 1088.2 | 1436.9 | 1750.1 |
| 9.7 mol% MgCO₃ | *16.47* | *17.53* | *11.26* | *8.06* | *22.8* | *11* |
| MgCc_12 | 158.61 | 284.70 | 713.84 | 1088.06 | 1437.5 | 1750 |
| 9.5 mol% MgCO₃ | *16.00* | *18.39* | *10.77* | *8.03* | *18.9* | *11* |
| MgCc_14 | 159.23 | 285.54 | 714.42 | 1088.78 | 1437.6 | 1750.4 |
| 11.6 mol% MgCO₃ | *12.5* | *19.10* | *12.13* | *8.75* | *28.3* | *11.2* |
| MgCc_16 | 159.43 | 286.01 | 714.52 | 1088.78 | 1437.2 | 1750.6 |
| 12.5 mol% MgCO₃ | *16.98* | *19.20* | *12.46* | *8.72* | *22.7* | *11.2* |
| MgCc_18 | 160.10 | 286.73 | 714.58 | 1089.01 | 1437.2 | 1750.4 |
| 14.5 mol% MgCO₃ | *17.64* | *19.95* | *14.22* | *9.41* | *29* | *12* |
| MgCc_20 | 161.18 | 287.37 | 715.09 | 1089.6 | 1435.7 | 1750.9 |
| 16.3 mol% MgCO₃ | *22.03* | *20.85* | *14.98* | *9.67* | *31.2* | *12.1* |
| MgCc_22 | 161.39 | 288.27 | 715.82 | 1089.97 | 1436 | 1751.3 |
| 18.2 mol% MgCO₃ | *19.31* | *20.96* | *15.05* | *9.99* | *34.8* | *13.5* |
| MgCc_24 | 162.75 | 289.17 | 715.84 | 1090.49 | 1435.9 | 1751.6 |
| 20.7 mol% MgCO₃ | *20.00* | *22.13* | *16.39* | *10.36* | *36.3* | *13.1* |
| MgCc_26 | 163.10 | 290.75 | 716.37 | 1090.86 | 1435.9 | 1752 |
| 22 mol% MgCO₃ | *20.68* | *23.00* | *17.01* | *10.76* | *35.4* | *17* |
| MgCc_28 | 164.56 | 292.02 | 717.37 | 1091.36 | 1437.6 | 1752.6 |
| 24 mol% MgCO₃ | *21.51* | *23.44* | *17.60* | *12.01* | *38.6* | *13.5* |
| MgCc_30 | 165.03 | 292.44 | 717.72 | 1091.85 | 1439 | 1752.7 |
| 25.7 mol% MgCO₃ | *19.36* | *23.01* | *18.70* | *11.90* | *41.8* | *13.5* |
| MgCc_35-1* | 167.03 | 291.56 | 718.49 | 1094.19 | 1437.49 | 1754.23 |
| 28.3 mol% MgCO₃ | *16.33* | *22.39* | *18.18* | *15.77* | *48.69* | *13.01* |
| MgCc_35-2* | 169.19 | 293.83 | 719.79 | 1095.28 | 1439.6 | 1754.98 |
| 33.3 mol% MgCO₃ | *16.22* | *22.83* | *18.76* | *19.96* | *61.38* | *14.64* |
| MgCc_40 | 170.57 | 298.22 | 720.78 | 1094.47 | 1438.4 | 1755.1 |
| 37.8 mol% MgCO₃ | *16.88* | *23.51* | *17.95* | *13.13* | *36.4* | *17.7* |
| MgCc_45 | 172.51 | 297.68 | 722.26 | 1096.59 | 1439.89 | 1756.83 |
| 41.4 mol% MgCO₃ | *14.23* | *21.83* | *19.00* | *24.52* | *28.77* | *15.46* |
| MgCc_50 | 175.41 | 300.89 | 724.02 | 1098.78 | 1441 | 1758.21 |
| 49.2 mol% MgCO₃ | *10.54* | *19.10* | *16.24* | *23.96* | *20.72* | *14.81* |

*A single experiment with two compositions

**Table 4:** *Equation coefficients to estimate the magnesium content (mol% MgCO₃) of inorganic calcites from their Raman wavenumbers and FWHM in the range 0-30 mol% MgCO₃ (cf. Figs 5 and 6). Parameter X is either the wavenumber or the FWHM of the T, L, $v_4$, $v_1$, $v_3$ and $2v_2$ modes (in cm⁻¹).*

| | **T** | **L** | $v_4$ | $v_1$ | $v_3$ | $2v_2$ |
|---|---|---|---|---|---|---|
| mol% MgCO₃ $f$[Wavenuber] | $155.28+0.39$ X $-0.0078$ X² $+0.000293$ X³ | $281.44+0.4$ X $-0.00743$ X² $+0.000359$ X³ | $711.48+0.35$ X $-0.014$ X² $+0.000391$ X³ | $1086.2+0.22$ X $-0.00276$ X² $+0.000106$ X3 | - | $1748.93+0.15$ X $-0.00531$ X² $+0.000204$ X³ |
| R² | 0.997 | 0.995 | 0.991 | 0.999 | - | 0.98 |
| mol% MgCO₃ $f$[FWHM] | $6.76+1.19$ X $-0.0287$ X² | $10.66+0.89$ X $-0.0156$ X² | $2.45+0.99$ X $-0.0147$ X² | $3.61+0.51$ X $-0.00787$ X² | $2.56+2.16$ X $-0.026$ X² | $7.67+0.38$ X $-0.00448$ X² |
| R² | 0.950 | 0.990 | 0.993 | 0.973 | 0.972 | 0.826 |

*Valid in the range 0-30 mol% MgCO₃*

**Table 5:** *Equation coefficients to estimate the magnesium content (mol% $MgCO_3$) of inorganic calcites from their Raman wavenumbers (WN) and FWHM in the range 0-50 mol% $MgCO_3$ (see Fig. 7 and 8). Parameter X is either the wavenumber or the FWHM of the T, L, $v_4$, $v_1$, $v_3$ and $2v_2$ modes (in $cm^{-1}$).*

| | **T** | **L** | $v_4$ | $v_1$ | $v_3$ | $2v_2$ |
|---|---|---|---|---|---|---|
| mol% $MgCO_3$ f[Wavenumber] | 154.61 +0.418 X | 281.16 +0.406 X | 711.36 +0.25 X | 1085.71 +0.256 X | - | 1748.27 +0.191 X |
| R² | 0.996 | 0.993 | 0.996 | 0.988 | - | 0.985 |
| mol% $MgCO_3$ f[FWHM] | 8.23+0.923 X -0.0183 X² | 11.07+0.806 X -0.013 X² | 2.7+0.952 X -0.0138 X² | - | 1.78+2.98 X -0.05 X² | 7.69+0.376 X -0.00448 X² |
| R² | 0.950 | 0.983 | 0.990 | - | 0.84 | 0.836 |

*Valid in the range 0-50 mol% $MgCO_3$ except for $v_1$ (0-30 mol% $MgCO_3$). Note that for applications in the range 0-30 mol% $MgCO_3$, equations presented in Table 4 should be preferred.*

Figure 1
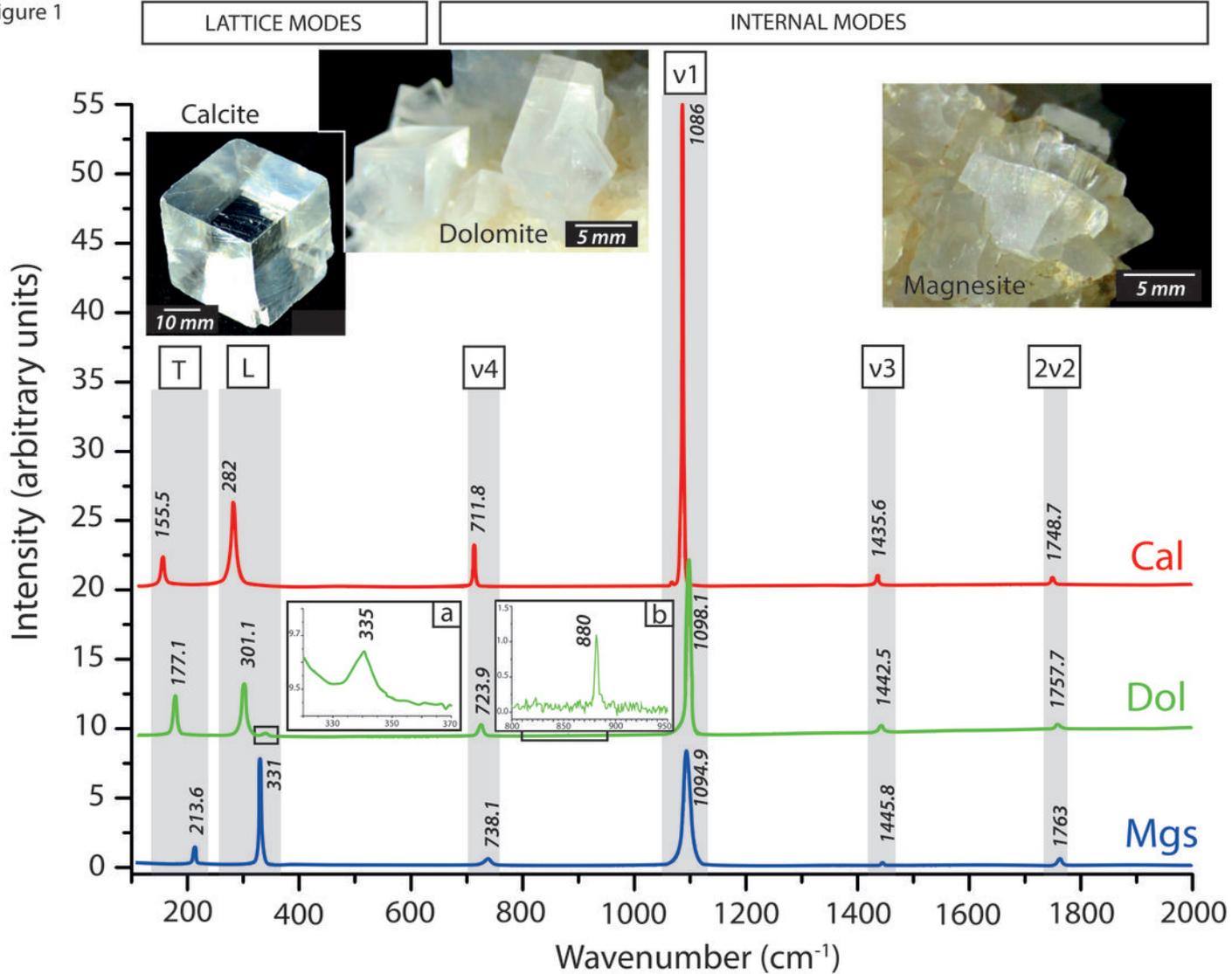
Figure 2
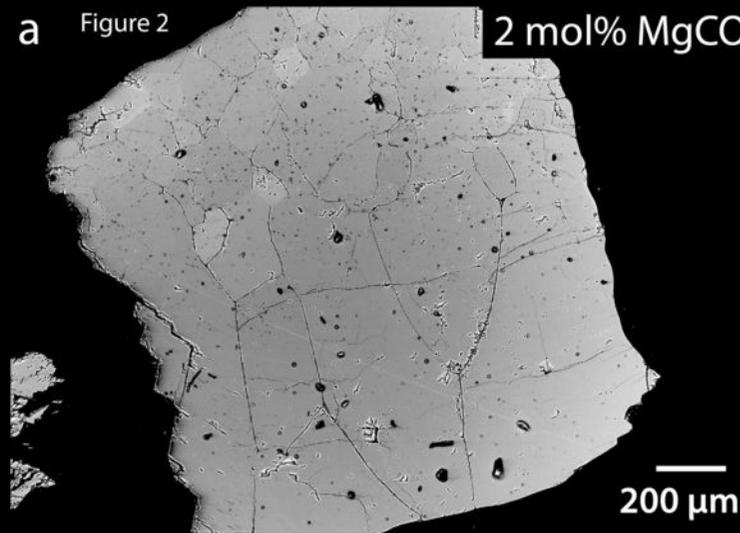
a  2 mol% MgCO$_3$

b  6 mol% MgCO$_3$
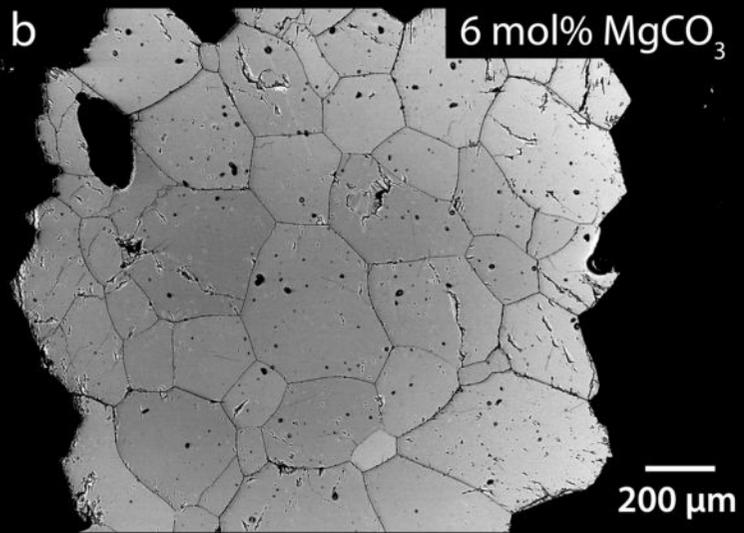
c  12 mol% MgCO$_3$

d  26 mol% MgCO$_3$

200 μm

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure EA1

Figure EA2