1   **Revision 2**

2   **Raman modes of carbonate minerals as pressure and temperature gauges up to 6 GPa and**

3   **500°C**

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9

10   **Abstract**

11   Diamond anvil cell (DAC) experiments focusing on the solubility of carbonates and aqueous

12   carbon speciation at subduction zones require pressure monitoring with sensitive, chemically

13   inert sensors. Commonly used pressure indicators are either too insensitive or prone to

14   contaminate pressure-transmitting media due to their increased solubility at high pressure and/or

15   temperature (P/T). Here, the P- and T-induced frequency shifts of the Raman vibrational modes

16   of natural crystalline carbonate minerals aragonite, calcite, dolomite, magnesite, rhodochrosite,

17   and siderite have been calibrated for application as Raman spectroscopic P and T sensors in

18   DACs up to 500°C and 6 GPa. The shifts of all modes are quasi-constant over the observed P

19   and T ranges and are generally less prominent for internal modes than for external modes. Our

20   method provides a sensitive and robust alternative to traditional pressure calibrants, and has three

21   principal advantages: (1) higher sensitivity (for particular Raman vibrational modes), (2)

22   monitoring P/T-induced shifts of several modes allows even more accurate P/T determination,

23   and (3) no contamination of pressure-transmitting media by foreign materials can occur.

24   Additionally, the isobaric and isothermal equivalent of the Grüneisen parameter and the

25   anharmonic parameter for each of the traced modes have been determined.

28

Introduction

29

30 Carbonate minerals are the dominant carbon-bearing phases within Earth's crust and lithospheric

31 mantle, representing the most stable carbon-bearing phases down to depths of at least 200 km,

32 corresponding to pressures of up to ~6 GPa (e.g. Redfern 2000; Dasgupta et al. 2004; Dasgupta

33 and Hirschmann 2006, 2010; Rohrbach and Schmidt 2011; Oganov et al. 2013). They are the

34 primary carriers of carbon into the deeper Earth at subduction zones and their behavior in the

35 high P/T environments of the lithosphere determines how much, and on what timescales, carbon

36 gets recycled to the atmosphere and hence oceans, or is retained in the mantle (e.g. Ague and

37 Nicolescu 2014; Manning 2014; Kelemen and Manning 2015). Because of the important role

38 carbonate minerals play in the key geological processes (such as subduction, arc volcanism, and

39 dissolution in aqueous fluids) of the Earth's deep carbon cycle, the accurate determination of

40 their physical and chemical properties under high P and T conditions is of great importance. The

41 interest in the topic is reflected by a significant and increasing number of experimental studies

42 based on the coupling of Raman spectroscopy with DAC techniques to understand the properties

43 of carbonate minerals at conditions corresponding to planetary interiors (Liu and Mernagh 1990;

44 Kraft et al. 1991; Williams et al. 1992; Gillet et al. 1993; Lin and Liu 1997; Minch et al. 2010a,

45 2010b, Farfan et al. 2012, 2013; Spivak et al. 2014; Facq et al. 2014, 2016; Cerantola et al. 2015;

46 Chaney et al. 2015; Pippinger et al. 2015; Xu et al. 2015; Liu et al. 2016; Müller et al. 2016;

47 Koch-Müller et al. 2016; Maruyama et al. 2017; Chariton et al. 2017).

48 Monitoring, recording, and reproducing extensive thermodynamic variables such as

49 pressure and temperature is crucial in any high P/T study, and is a particular requirement in DAC

50 experiments. Pressure is typically measured in such experiments based on the Raman or

51 fluorescence frequency shifts of a calibrant inside the compression chamber (e.g. ruby or

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52   diamond). The principal limitations of traditionally used optical pressure sensors of this type are

53   discussed here. Ruby, a Cr^{3+}-doped α-Al_2O_3, is the most extensively-used pressure sensor

54   (Barnett et al. 1973; Datchi et al. 2007). Broadening the ruby R_1 and R_2 fluorescence peaks and

55   the decreasing signal-to-background ratio at high temperatures and the large uncertainty on the

56   pressure and temperature cross derivative of the frequency, all significantly reduce the accuracy

57   of pressure determination (Ragan et al. 1992; Goncharov et al. 2005; Datchi et al. 2007). A

58   further complication is the chemical dissolution of ruby into water (the pressure medium), due to

59   its increased solubility at high P/T conditions (Tropper and Manning 2007; Andreani et al. 2013).

60   This may become particularly significant in DAC experiments that aim to determine the

61   solubility of carbonates and aqueous carbon speciation via carbonate–water equilibria, since

62   these experiments assume no chemical interaction between the pressure-transmitting medium

63   and the pressure sensor. For this reason, it is imperative that the use of pressure sensors made of

64   materials soluble in the fluid phase in the DAC at high P/T is avoided. Other pressure sensors,

65   including SrB_4O_7:Sm^{2+}, quartz, α-SiO_2, and berlinite, $AlPO_4$, also exhibit increased solubility at

66   high T, making them unusable in solubility and aqueous speciation experiments (Manning 1994;

67   Datchi et al. 2000; Watenphul and Schmidt 2012). The use of zircon, $ZrSiO_4$, which is only

68   soluble at the ppm level in high P/T fluids (Bernini et al. 2013), should also be avoided, as even

69   low concentrations of contaminants can affect the solubility of phases and corresponding

70   aqueous speciation. Although stable over a large P/T range, and chemically inert, ^{12}C and [13]C

71   diamond, and cubic boron nitride show relatively low pressure-sensitivity (2.83, 2.83, and 3.27

72   cm^{-1}/GPa, respectively), which has a deleterious effect on the precision of pressure determination

73   (Schiferl et al. 1997; Grasset et al. 2005; Datchi et al. 2007). Furthermore, below 13 GPa the

74   Raman signal from ^{12}C diamond is hidden by the strong signal produced by the diamond anvils,

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75   while ^{13}C diamond, which could be used in this P range, is not readily available (Datchi et al.

76   2007).

77   Instead of introducing foreign material to the compression chamber to measure P and/or

78   T, here we propose the use of frequency shifts of the Raman vibrational modes of the crystalline

79   carbonates themselves (cross-calibrated against the ruby R_1 fluorescence peak) as P/T sensors.

80   Indeed, most of the Raman vibrational modes of carbonates are particularly sensitive to subtle

81   P/T changes. The simultaneous monitoring of the behavior of multiple modes of varying

82   sensitivity provides an additional route for an even more accurate determination of P/T

83   conditions. Moreover, by avoiding the introduction of foreign material into the DAC, the

84   possibility of its interaction with aqueous media is ruled out. This alternative method has been

85   recently employed in carbon aqueous speciation experiments of aqueous fluids in equilibrium

86   with aragonite at subduction zone environmental conditions (Facq et al. 2014, 2016).

87   Here, we report P- and T-induced frequency shifts of the Raman vibrational modes of

88   natural aragonite ($CaCO_3$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), magnesite ($MgCO_3$),

89   rhodochrosite ($MnCO_3$), and siderite ($FeCO_3$) up to 6-6.5 GPa and 400-500 °C, respectively.

90   From these data, the isobaric and isothermal equivalent of the Grüneisen parameter and the

91   anharmonic parameter for the corresponding vibrational modes were calculated to provide a

92   robust method for combined P/T measurement in the DAC.

Experimental methods

94   High-purity naturally-occurring carbonate minerals were used in all experiments, including

95   aragonite from Landes, France; calcite from Miskolctapolca, Hungary; dolomite from

96   Campolongo, Italy; magnesite from Hnúšťa, Slovakia; rhodochrosite from Colorado, USA; and

97   siderite from Tincroft Mine, Cornwall, UK. All carbonate minerals were characterized by X-ray

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98   diffraction (XRD), electron probe microanalysis, and Raman spectroscopy prior to investigation.

99   The unit cell parameters and measured chemical formulae are reported in Table 1.

100   The high-*P* experiments were conducted at room *T* in a membrane-type diamond anvil

101   cell (Letoullec et al. 1988) equipped with IIa diamond anvils with culet diameters of 500 μm. A

102   pressure-transmitting medium and some natural carbonate single crystals were loaded in a pre-

103   indented (initially 240 μm and after indentation 100 μm) thick steel gasket, drilled with a 200 μm

104   diameter hole. The pressure-transmitting medium comprised a 4:1 methanol-ethanol fluid

105   mixture, which is hydrostatic over the full pressure range of our experiments (Klotz et al. 2009).

106   The pressure inside the compression chamber was increased from ~0 to ~6 GPa in pressure

107   increments of ~0.5 GPa using a PDS 200 pneumatic drive system (BETSA). Pressure was

108   calculated from the calibrated shift of the ruby R_1 fluorescence line (Mao et al. 1986) after at

109   least 30 minutes of response time required for the ruby fluorescence peak to reach its equilibrium

110   value (Picard et al. 2006).

111   The high-*T* experiments were conducted at room *P* using a DSC600 heating stage

112   (Linkam Scientific Instruments) with the sample held within an aluminum sample pan. The

113   temperature was gradually increased from 25 ˚C to 425 °C for rhodochrosite and siderite and to

114   500 °C for the other carbonates in temperature increments of 25 °C using a TMS94 temperature

115   controller (Linkam Scientific Instruments).

116   Raman spectra were collected in the 100–1800 cm^{-1} spectral range using a confocal

117   LabRAM 300 (Horiba Jobin Yvon) Raman spectrometer of 300 mm focal length. A holographic

118   grating of 1800 gr.mm^{-1} coupled to a Peltier front illuminated CCD detector (1024 × 256 pixel in

119   size) enabled a spectral resolution of ~1 cm^{-1}. The excitation line at 532.05 nm was produced by

120   a Ventus 532 laser source (Laser Quantum) focused on the sample using an Olympus LMPLFLN

121   50× long working distance objective.

122   All Raman spectra were treated by PeakFit™ software. For each Raman spectrum, the

123   baseline was subtracted and peak features were determined by least squares fitting to Voigt

124   profiles for the Raman bands. Peak positions were calibrated against the measured excitation of a

125   Ne light reference spectrum (Saloman and Sansonetti 2004).

126   **Results and Discussion**

127   **Raman-active modes**

128   Aragonite crystallizes in space group *Pmcn*. Its orthorhombic cell contains 20 atoms per lattice

129   point and its 57 vibrational modes can be classified as

130    $$\Gamma = 9A_g + 6A_u + 6B_{1g} + 8B_{1u} + 9B_{2g} + 5B_{2u} + 6B_{3g} + 8B_{3u}$$

131   of which the gerade A_g, B_{1g}, B_{2g}, and B_{3g} modes are Raman-active (De La Pierre et al. 2014). Of

132   these 30, 20 modes were observed in the Raman spectrum taken at 25 °C (Figure 1). The

133   vibrational modes located in the low frequency range at 115, 125, 145, 155, 164, 182, 192, 208,

134   216, 250, 263, 274, and 285 cm^{-1} represent external or lattice modes, resulting from the

135   interactions between Ca^{2+} and CO_3^{2-} ions. The high frequency vibrational modes ν_4 at 701, 705,

136   and 716 cm^{-1}, ν_2 at 853 cm^{-1}, ν_1 at 1085 cm^{-1}, and ν_3 at 1463 and 1576 cm^{-1} represent internal

137   modes of the CO_3^{2-} group (Gillet et al. 1993). Of these, 14 could be traced across the entire

138   pressure range of investigation and 11 could be traced up to temperatures of the aragonite-calcite

139   phase transition.

140   Calcite, magnesite, rhodochrosite, and siderite all crystallize in space group $R\overline{3}c$. Their

141   rhombohedral primitive cell contains ten atoms per lattice point and their 27 vibrational modes

142   can be classified as

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143
$$\Gamma = A_{1g} + 2A_{1u} + 3A_{2g} + 3A_{2u} + 4E_{g} + 5E_{u}$$

144 of which the gerade A_{1g} and E_{g} modes are Raman-active (Rutt and Nicola 1974; Valenzano et al.

145 2007; De La Pierre et al. 2014). All of these, apart from the ν_3 mode in siderite, were observed in

146 the Raman spectrum taken at 25 °C (Figure 1). The lack of the ν_3 mode in siderite is in

147 agreement with Rutt and Nicola (1974). The low-frequency vibrational modes (158 and 284 cm^{-1}

148 in calcite, and 330 cm^{-1} in magnesite, 185 and 290 cm^{-1} in rhodochrosite, and 183 and 284 cm^{-1}

149 in siderite) represent external modes, resulting from the interactions between M^{2+} and CO_3^{2-} ions,

150 M being Ca, Mg, Mn, and Fe, respectively. The high-frequency vibrational modes, ν_4 (713 cm^{-1}

151 in calcite, 738 cm^{-1} in magnesite, 718 cm^{-1} in rhodochrosite, and 731 cm^{-1} in siderite), ν_1 (1088

152 cm^{-1} in calcite, 1094 cm^{-1} in magnesite, 1086 cm^{-1} in rhodochrosite, and 1085 cm^{-1} in siderite),

153 and ν_3 (1438 cm^{-1} in calcite, 1446 cm^{-1} in magnesite, and 1415 cm^{-1} in rhodochrosite) represent

154 internal modes of the CO_3^{2-} group. Silent mode ν_2 was absent and ν_3 (corresponding to the

155 asymmetric CO_3 stretching with E_g symmetry) was not traced due to its highly asymmetric

156 nature, which results from the existence of weak satellite excitations at the lower-frequency side

157 of the main ν_3 Raman-active mode (Krishnamurti 1957). The high-frequency mode at 1751 cm^{-1}

158 in calcite, 1763 cm^{-1} in magnesite, 1727 cm^{-1} in rhodochrosite, and 1724 cm^{-1} in siderite

159 represents the $2\nu_2$ overtone mode of the silent, IR-active ν_2 mode (Couture 1947). An additional

160 broad, low-intensity feature at 507 cm^{-1} was observed and traced in siderite, which is caused by

161 an Fe^{2+} electronic excitation (Popkov et al. 1972).

162 Dolomite crystallizes in space group $R\bar{3}$. It has ten atoms per lattice point and its 27

163 vibrational modes can be classified as

164
$$\Gamma = 4E_{g} + 4A_{g} + 5E_{u} + 5A_{u}$$

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165   of which the gerade A_g and E_g modes are Raman-active (Valenzano et al. 2007) and were

166   observed in the Raman spectrum taken at 25 °C (Figure 1). The modes at lower frequencies (178,

167   229, 301, and 340 cm^{-1}) represent external modes, resulting from the interactions between M^{2+}

168   and CO_3^{2-} ions, M being both Ca and Mg. The higher-frequency modes v_4 at 724 cm^{-1}, v_2 at 881

169   cm^{-1}, v_1 at 1098 cm^{-1}, and v_3 at 1442 cm^{-1} represent internal modes of the CO_3^{2-} group. The 229

170   cm^{-1} frequency external mode and v_3 (corresponding to the asymmetric CO_3 stretching with E_g

171   symmetry) was not analyzed due to the low intensity and highly asymmetric nature of peak,

172   respectively. The high-frequency mode at 1759 cm^{-1} represents the $2v_2$ overtone mode of the v_2

173   mode (Couture 1947).

174   **High-pressure experiments**

175   The frequency-evolution of carbonate modes as a function of pressure is reported in Figure 2 and

176   the relative changes in frequency $\delta v_i/\delta P$ along with literature values in Table 2. The values of

177    $\delta v_i/\delta P$ for all modes are quasi-constant over the observed pressure range. Pressure-induced shifts

178   of internal modes are generally less prominent than those of the external modes due to the greater

179   incompressibility of the CO_3 units (Ross and Reeder 1992; Gillet et al. 1993).

180   In aragonite, the frequencies of all traced modes, except the 145 cm^{-1} external mode,

181   increase monotonously with pressure. Most $\delta v_i/\delta P$ values are in good agreement with previous

182   experimental data from Gillet et al. (1993), except for the 182 and 274 cm^{-1} external modes. For

183   these Raman bands, Gillet et al. (1993) may have reported the evolution of multiple vibrational

184   modes, as this could explain the difference between our values and theirs. A similar trend is

185   observed for the frequencies of all traced modes in calcite, except the 1751 cm^{-1} overtone mode,

186   which exhibits a frequency decrease with pressure. The abrupt changes observed between ~1.6

187   and ~2.1 GPa are attributed to the well-known structural transitions of calcite I to calcite II,

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188 which is a reversible first-order ferroelastic transition (Archer et al. 2003), and calcite II to

189 calcite III, which occur at 1.4 and 1.7 GPa, respectively (Bridgman 1938). Above these transition

190 pressures, due to the large number of low intensity low frequency peaks (Pippinger et al. 2015),

191 only data for the most intense peaks resulting from the splitting of the 1088 cm^{-1} peak are

192 presented. These four peaks observed at 1079, 1086, 1098, and 1102 cm^{-1} (at 2.3 GPa) change

193 frequency with a $\delta v_i/\delta P$ of 3.15(6), 3.21(6), 3.5(2), and 3.0(1) cm^{-1}/GPa, respectively. A detailed

194 account of the evolution of other calcite modes is given by Pippinger et al. (2015). In dolomite,

195 magnesite, rhodochrosite, and siderite, all traced modes increase in frequency with pressure,

196 except the 881 cm^{-1} internal mode and 1759 cm^{-1} overtone mode in dolomite, the 1727 cm^{-1}

197 overtone mode in rhodochrosite, and the 507 cm^{-1} Fe^{2+} electronic excitation mode and the 1724

198 cm^{-1} overtone mode in siderite.

199 **High-temperature experiments**

200 The frequency evolution of carbonate modes as a function of temperature is reported in Figure 3

201 and the relative changes in frequency $\delta v_i/\delta T$ along with literature values in Table 2. The values of

202 $\delta v_i/\delta T$ of all modes are quasi constant over the observed temperature range. Temperature-induced

203 shifts of internal modes are generally less prominent than those of the external modes due to the

204 rigidity of C−O bonds in the CO$_3$ units (Markgraf and Reeder 1985; Reeder and Markgraf 1986;

205 Gillet et al. 1993).

206 In aragonite, all traced modes except the 701 and 705 cm^{-1} internal modes decrease in

207 frequency with temperature. Above 250 °C these two modes merge and were treated as one and

208 the neighboring 716 cm^{-1} internal mode no longer appears in spectra. The 164 cm^{-1} external

209 mode is present as a shoulder of the 155 cm^{-1} external mode and could only be traced up to 225

210 °C. The 216, 250, 263, and 274 cm^{-1} external modes could only be traced up to 200 °C, above

211 which temperature they merge into one broad peak and become indistinguishable from one

212 another. The spectral modifications observed between 425 and 450 °C in Figure 2 are attributed

213 to the aragonite-calcite structural phase transition, which is thermally activated and has been

214 reported to occur at 385 °C (Parker et al. 2010) and 468 °C (Antao and Hassan 2010). In calcite,

215 all traced Raman bands decrease in frequency with temperature. The values of $\delta v_i/\delta T$ for all

216 modes in calcite, which has not undergone transformation are lower than those measured from

217 calcite that has formed upon the aragonite-calcite transition. These values are reported in Table 3

218 along with the corresponding isobaric equivalents of Grüneisen parameter. In dolomite,

219 magnesite, rhodochrosite, and siderite, all traced modes decrease in frequency with temperature,

220 except the 718 cm^{-1} internal mode in rhodochrosite, and the 183 cm^{-1} external mode and the 507

221 cm^{-1} Fe^{2+} electronic excitation mode in siderite. Thermal decomposition of rhodochrosite was

222 observed between 400 and 425 °C, marked by the sudden disappearance of all its Raman bands.

223 This result is consistent with an XRD study carried out by Kissinger et al. (1956). The 507 cm^{-1}

224 frequency feature in siderite is relatively weak and has the largest $\delta v_i/\delta T$ value, but could only be

225 traced up to 250 °C, at which point no longer appears clearly above the background. Popkov et

226 al. (1972) managed to trace this mode from 4.2 K, at which temperature it occurs at 438 cm^{-1} and

227 Langille and O'Shea (1977) from 6 K to room temperature and found that above the Néel

228 temperature its $\delta v_i/\delta T$ is linear. Thermal decomposition of siderite was observed between 375

229 and 400 °C, above which temperature its vibrational modes can no longer be detected. These

230 temperature values are in good agreement with those found in earlier XRD experiments

231 (Kissinger et al. 1956).

232 **Grüneisen and anharmonic parameters**

233   The mode Grüneisen parameter, γ_i, is a dimensionless quantity that links the change in frequency

234   of mode i, v_i (measured at 25 °C), to the change in volume V (Born and Huang 1954):

235
$$\gamma_i = -\frac{d \ln v_i}{d \ln V} = -\frac{V dv_i}{v_i dV}$$

236   Its isobaric equivalent, γ_{iP} (Gillet et al. 1989) can be expressed as:

237
$$\gamma_{iP} = -\frac{d \ln v_i}{d \ln V\ (T)} = -\frac{dv_i}{\alpha v_i dT}$$

238   where α is the thermal expansion coefficient. Its isothermal equivalent, γ_{iT} (Gillet et al. 1989;

239   Wagner 2000) can be expressed as:

240
$$\gamma_{iT} = -\frac{d \ln v_i}{d \ln V\ (P)} = \frac{K_T dv_i}{v_i dP}$$

241   where K_T is the isothermal bulk modulus.

242   From γ_{iT} and γ_{iP}, the intrinsic anharmonic parameter, a_i, can be calculated for each mode (Gillet

243   et al. 1989):

244
$$a_i = \alpha(\gamma_{iT} - \gamma_{iP})$$

245   The isobaric and isothermal equivalents of the Grüneisen parameter and the anharmonic

246   parameter have been calculated for each studied mode and are presented in Table 2.

247   There is noticeable variation in published v_i, $\delta v_i/\delta P$, $\delta v_i/\delta T$, and, consequently, γ_{iT}, γ_{iP}, and

248   a_i values corresponding to the same Raman-active modes of any particular carbonate mineral.

249   The primary reason for this variation is probably trace element content. Owing to the difference

250   in ion size (Mg^{2+}, Mn^{2+}, and Fe^{2+} are significantly smaller than Ca^{2+}), substitution with a smaller

251   ion will decrease the average inter-atomic distances and increase the frequency of external

252   modes (Krishnamurti 1956; Rutt and Nicola 1974). As CaO_6 octahedra are slightly more

253   compressible than MgO_6 and FeO_6 octahedra (Ross and Reeder 1992), trace element content will

254   also affect $\delta v_i/\delta P$ values. Due to the variable and more complex effects of temperature on the

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255 structure of carbonates with different ions (e.g. Markgraf and Reeder 1985; Reeder and Markgraf

256 1986), non-end-member compositions will exhibit a range of $\delta v_i/\delta T$ values too.

257 **Development of a Pressure/Temperature Calibrant**

258 The Raman data presented above allow us to develop a *P/T* calibrant for each of the carbonate

259 phases on the basis of the measured frequencies of each of their Raman-active modes. The

260 separate impacts of pressure and temperature on each of the modes, and their subtle differences,

261 provide a robust route to identifying the temperature and pressure conditions within the DAC

262 assembly, based on the set of measured Raman peaks for each sample.

263   As the pressure and temperature cross derivative of the frequency is negligible (Matas et

264 al. 2000), the frequency v_{PTi} of mode *i* at any *P/T* condition (in the experimental range) can be

265 expressed as

266
$$v_{PTi} = v_{0i} + P\frac{dv_i}{dP} + T\frac{dv_i}{dT}$$

267 where v_{0i} is the extrapolated frequency of mode *i* at ambient pressure and zero temperature.

268   In an experiment carried out at known temperature, *T* (e.g. measured by a thermocouple),

269 pressure can be determined based on a measured v_{PTi} of a single mode. If v_{PTi} of multiple modes

270 are measured, pressure can be most accurately determined by the simple linear regression

271 method. We have tested our method by determining pressure and temperature for a cell loaded

272 with rhodochrosite and employing the frequencies of the 185, 290, 1086, and 1415 cm^{-1} modes

273 of rhodochrosite. The cell was held at 300 ˚C as set temperature and experiments were conducted

274 at two separate pressures. In our experiment, this method gave 1.2(1) and 1.4(3) GPa for two

275 determinations at pressure 1 and 4.7(1) and 4.9(1) GPa for two at pressure 2, while *T* was fixed

276 to the value determined by thermocouple, measured to be 300 ˚C. In an experiment carried out at

277 unknown pressure *P* and temperature *T*, these variables can be determined based on measured

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278   v_{PTi} of two or more modes. If v_{PTi} of more than two modes are measured, pressure and

279   temperature can be determined by a multiple linear regression method. In our experiment, using

280   rhodochrosite as pressure and temperature sensor, this method gave 1.2(1) and 1.4(4) GPa at

281   pressure 1 and 4.6(1) and 4.8(2) GPa at pressure 2 with the temperature also determined by fit to

282   the P/T dependence of all modes and calculated as 293(8) ˚C, which is equal to the value

283   determined by thermocouple to within the stated error.

284   In general, the most suitable modes are those with high peak intensity, high sensitivity to

285   pressure and temperature changes, with an anharmonic parameter close to 0 and with γ_{iT} and γ_{iP}

286   similar to each other. The latter two features are indicative of quasi-harmonic behavior, where

287   pressure and temperature affect the vibration frequencies only through the volume changes and

288   not by modifications of the electronic structure of the chemical bond involved (Gillet et al.

289   1989). As mentioned above, trace element content could affect v_i, $\delta v_i/\delta P$, and $\delta v_i/\delta T$ for

290   carbonate modes, particularly those of external modes. This important factor should also be

291   taken into consideration when choosing the most suitable modes for P/T determination. To

292   overcome the uncertainty arising from carbonate composition, it is safest to carry out

293   independent P/T calibration against ruby or other pressure sensor, when dealing with impure

294   samples.

295   In aragonite, the internal v_1 mode is most suitable for P/T determination (Facq et al. 2014,

296   2016), followed by the external modes, in decreasing order of priority: 155, 208, 182, 192, 216,

297   145, 250, 263, 274, and 285 cm^{-1}. In calcite, dolomite, magnesite, rhodochrosite, and siderite the

298   preferred use of the internal v_1 mode is recommended, followed by the external modes and the

299   overtone mode. The external modes, in decreasing order of priority should be used as follows. In

300   calcite: 284 and 158 cm^{-1}, in dolomite: 301, 178, and 340 cm^{-1}, in magnesite: 330 and 214 cm^{-1},

301   in rhodochrosite: 290 and 185 cm^{-1}, and in siderite: 284 and 183 cm^{-1}.

302   It is worth noting that the widths of Raman peaks have previously been proposed as a

303   proxy for temperature (Gillet et al. 1993). The reported errors in temperature for this approach

304   are generally larger than those for temperatures obtained from peak positions. Additionally,

305   instrumental peak broadening makes this method dependent (to a greater extent than peak

306   positions) on the experimental set up in the laboratory within which analyses are conducted.

307   Furthermore, the influence of combined pressure and temperature on peak widths is significantly

308   more complicated than their impact on peak positions alone. For these reasons we have chosen

309   not to make use of any additional information encoded into the peak widths of our measured

310   carbonate Raman-active modes.

311   Our P/T determination method has limited use in calcite high P/T experiments. In case of

312   calcite II and calcite III $CaCO_3$ polymorphs, $\delta v_i/\delta T$ is not measurable at ambient pressure

313   because of the location of stability fields of these phases. For this reason, simultaneous P/T

314   determination is not possible based on the Raman-active modes of these phases and our method

315   is limited to pressure determination at known (measured) temperature.

316   **Implications**

317   From our results, it can be seen that pressure- and temperature-induced frequency shifts in

318   aragonite, calcite, dolomite, magnesite, rhodochrosite, and siderite all provide a sensitive and

319   robust alternative to traditional pressure calibrants (e.g. ruby, diamond) in DAC experiments, and

320   this is especially useful when any such external traditional calibrant might contaminate the

321   pressure transmitting media due to their increased solubility at high P/T conditions (Manning

322   1994; Datchi et al. 2000; Tropper and Manning 2007; Watenphul and Schmidt 2012; Andreani et

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323   al. 2013). As they do not interfere with the primary measurement, our carbonate calibrants

324   represent an alternative for *P/T* measurement in a wide range of DAC experiments addressing

325   carbonate solubility and/or aqueous speciation at high *P/T* conditions relevant to the Earth's crust

326   and mantle in order to better constrain the Earth's deep carbon cycle. The measured pressure-

327   and temperature-induced frequency shifts have been used to calculate the isobaric and isothermal

328   equivalents of the Grüneisen parameter and the anharmonic parameter. This could be used for

329   the anharmonic correction of specific heat capacity at constant volume, which is responsible for

330   the departure from the Dulong-Petit limit at high temperature (Gillet et al. 1989). The

331   anharmonic correction also helps to refine thermodynamic properties and phase equilibriums at

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528   Figure 1. Raman spectra of carbonate minerals collected at ambient pressure (1 bar) and

529   temperature (25 °C).

530   Figure 2. Frequency evolution of the traced vibrational modes of carbonates as a function of

531   pressure. The experimental uncertainty lies within the size of the symbol. In the calcite

532   experiment, no data points in the calcite II stability field (situated between calcite I and calcite III

533   stability fields) have been collected.

534   Figure 3. Frequency evolution of the traced vibrational modes of carbonates as a function of

535   temperature. The experimental uncertainty lies within the size of the symbol.

536

Sample	Ideal formula	Calculated formula	Space Group	Unit cell parameters (Å)		
				a	b	c
Aragonite	$CaCO_3$	$Ca_{1.00}CO_3$	*Pmcn*	4.9612(5)	7.9701(9)	5.7420(4)
Calcite	$CaCO_3$	$Ca_{1.00}CO_3$	$R\bar{3}c$	4.9864(2)		17.0491(8)
Dolomite	$CaMg(CO_3)_2$	$Ca_{0.50}Mg_{0.50}CO_3$	$R\bar{3}$	4.8069(4)		16.012(2)
Magnesite	$MgCO_3$	$Mg_{0.96}Ca_{0.01}Fe_{0.03}CO_3$	$R\bar{3}c$	4.6371(2)		15.0365(5)
Rhodochrosite	$MnCO_3$	$Mn_{0.99}Fe_{0.01}CO_3$	$R\bar{3}c$	4.7756(7)		15.669(2)
Siderite	$FeCO_3$	$Fe_{0.98}Mg_{0.01}Mn_{0.01}CO_3$	$R\bar{3}c$	4.6910(4)		15.379(2)

537   Table 1. Compositions and unit cell parameters of carbonate minerals used.

538

Observed mode, Symmetry*	ν_i (cm^{-1})	$\delta\nu_i/\delta P$ (cm^{-1}/GPa)	$\delta\nu_i/\delta T$ (cm^{-1}/K)	γ_{iT}**	γ_{iP}***	a_i (10^{-5} K^{-1})	Reference
			Aragonite				
External, B$_{1g}$	115	?	$-3.1(1)\times10^{-2}$	?	4.10	?	This work
External, B$_{3g}$	125	?	?	?	?	?	This work
External, A$_g$	145	-0.40(3)	$-9(2)\times10^{-3}$	-0.19	0.94	-7.30	This work
External, B$_{1g}$	155	3.23(3)	$-1.9(1)\times10^{-2}$	1.44	1.93	-3.21	This work
	152	2.7(2)					Kraft et al. 1991
	155	$3.0(3)-5(2)\times10^{-4}$	$-2.7(3)\times10^{-2}$	1.2	2.7	-7.2	Gillet et al. 1993
External, A$_g$	164	?	$-3.9(3)\times10^{-2}$	?	3.65	?	This work
External, B$_{2g}$	182	4.04(7)	$-1.9(2)\times10^{-2}$	1.53	1.58	-0.29	This work
	180	3.4(6)					Kraft et al. 1991
	180	$7.2(3)-4.7(4)\times10^{-3}$	$-2.4(3)\times10^{-2}$	2.6	2.1	3.4	Gillet et al. 1993
External, B$_{3g}$	192	6.47(5)	$-1.5(1)\times10^{-2}$	2.32	1.23	7.11	This work
External, B$_{2g}$	208	5.30(3)	$-3.49(6)\times10^{-2}$	1.75	2.58	-5.35	This work
	206	3.3(5)					Kraft et al. 1991
	209	4.0(4)	$-4.1(4)\times10^{-2}$	1.2	3.0	-11.6	Gillet et al. 1993
External, A$_g$	216	6.94(9)	$-2.5(2)\times10^{-2}$	2.21	1.77	2.88	This work
	217	$6.6(4)-3.3(3)\times10^{-3}$					Gillet et al. 1993
External, B$_{2g}$	250	4.03(6)	$-2.7(2)\times10^{-2}$	1.11	1.66	-3.57	This work
	254	?	$-2.0(3)\times10^{-2}$				Gillet et al. 1993
External, B$_{2g}$	263	4.79(6)	$-4.5(2)\times10^{-2}$	1.27	2.64	-8.90	This work
External, B$_{3g}$	274	6.02(5)	$-3.40(6)\times10^{-2}$	1.51	1.91	-2.56	This work
	275	3.4(3)					Gillet et al. 1993
External, A$_g$	285	7.0(1)	$-2.9(1)\times10^{-2}$	1.68	1.57	0.76	This work
Internal ν_4, B$_{3g}$	701	1.69(3)	$5.3(6)\times10^{-3}$	0.17	-0.12	1.84	This work
	704	1.5(1)					Kraft et al. 1991
	702	1.6(3)	0	0.14	0.0	0.9	Gillet et al. 1993
Internal ν_4, A$_g$	705	2.25(3)	$2.6(6)\times10^{-3}$	0.22	-0.06	1.80	This work
	710	2.0(3)	$-1.5(3)\times10^{-2}$	0.20	0.3	-0.9	Gillet et al. 1993
Internal, ν_4 B$_{2g}$	716	2.85(5)	$-4(2)\times10^{-3}$	0.27	0.09	1.17	This work
Internal ν_2, A$_g$	853	?	$-2.4(7)\times10^{-3}$	?	0.04	?	This work
Internal ν_1, A$_g$	1085	3.07(2)	$-1.32(7)\times10^{-2}$	0.20	0.19	0.06	This work
	1086	2.3(1)					Kraft et al. 1991
	1084	2.7(3)	$-1.5(2)\times10^{-2}$	0.16	0.21	-0.2	Gillet et al. 1993
Internal ν_3, B$_{1g}$	1463	?	$-2.6(1)\times10^{-2}$	?	0.27	?	This work
	1463	?	$-2.2(3)\times10^{-2}$				Gillet et al. 1993
Internal ν_3, B$_{2g}$	1576	?	$-3.3(3)\times10^{-2}$	?	0.32	?	This work
	1575	?	$-3.1(3)\times10^{-2}$				Gillet et al. 1993
			Calcite				
External, E$_g$	158	2.42(4)	$-2.65(2)\times10^{-2}$	1.16	18.61	-15.71	This work
	156	2.47		1.18(6)			Liu and Mernagh 1990
	156	2.3(3)	$-2.8(3)\times10^{-2}$	1.2	19.9	-16.9	Gillet et al. 1993
	156	2.52(8)		1.14(4)			Liu et al. 2016
External, E$_g$	284	6.2(1)	$-4.30(4)\times10^{-2}$	1.65	16.85	-13.68	This work
	283	5.27		1.38(8)			Liu and Mernagh 1990
	281	6.0(5)	$-4.0(3)\times10^{-2}$	1.4	15.8	-13.0	Gillet et al. 1993
	282	5.19(17)		1.33(6)			Liu et al. 2016
Internal ν_4, E$_g$	713	2.2(1)	$-5.0(2)\times10^{-3}$	0.23	0.77	-0.48	This work
	713	2.22		0.24			Liu and Mernagh 1990
	711	1.7(3)	$-4(1)\times10^{-3}$	0.23	0.62	-0.3	Gillet et al. 1993
	713	2.35(7)		0.23(1)			Liu et al. 2016
Internal ν_1, A$_{1g}$	1088	4.1(2)	$-9.7(3)\times10^{-3}$	0.29	0.99	-0.63	This work
	1085	5.87		0.41(1)			Liu and Mernagh 1990
	1085	3.0(3)	$-4.0(2)\times10^{-3}-1.40(5)\times10^{-5}$	0.40	0.51	-0.1	Gillet et al. 1993
	1086	5.96(15)		0.39(2)			Liu et al. 2016
Internal ν_3, E$_g$	1438	?	?	?	?	?	This work
	1434	9.0		0.47(3)			Liu and Mernagh 1990
	1434	7.5(5)	$-2.5(3)\times10^{-2}+2.9(3)\times10^{-5}$	0.46	1.94	-1.3	Gillet et al. 1993
Overtone	1751	-0.7(5)	$-1.36(6)\times10^{-2}$	-0.03	0.86	-0.80	This work
	1748	-1.0(4)	$-5.3(5)\times10^{-3}-2.3(2)\times10^{-5}$	-0.04	0.34	-0.34	Gillet et al. 1993

539

Observed mode, Symmetry*	ν_i (cm^{-1})	$\delta\nu_i/\delta P$ (cm^{-1}/GPa)	$\delta\nu_i/\delta T$ (cm^{-1}/K)	γ_{iT}**	γ_{iP}***	a_i (10^{-5} K^{-1})	Reference
			Dolomite				
External, E$_g$	178	2.83(3)	$-1.65(8)\times10^{-2}$	1.50	3.84	-5.65	This work
	177	1.4(2)					Kraft et al. 1991
	178	1.8(2)	$-1.9(2)\times10^{-2}-3.5(3)\times10^{-6}$	0.9	4.4	-8.4	Gillet et al. 1993
External, A$_g$	229	?	?	?	?	?	This work
External, E$_g$	301	5.53(5)	$-3.60(9)\times10^{-2}$	1.73	4.95	-7.78	This work
	301	4.4(3)					Kraft et al. 1991
	300	4.4(3)	$-3.2(3)\times10^{-2}-1.96(5)\times10^{-5}$	1.4	4.4	-7.3	Gillet et al. 1993
External, A$_g$	340	6.11(7)	$-4.7(3)\times10^{-2}$	1.69	5.73	-9.73	This work
	335	2.9(2)	$-1.9(2)\times10^{-2}-7.8(5)\times10^{-5}$	0.8	2.3	-3.7	Gillet et al. 1993
Internal ν_4, E$_g$	724	1.9(1)	$-2.8(9)\times10^{-3}$	0.25	0.16	0.21	This work
	725	1.1(2)					Kraft et al. 1991
	724	1.6(3)	$-2.1(5)\times10^{-3}-1.7(3)\times10^{-5}$	0.2	0.12	0.2	Gillet et al. 1993
Internal ν_2, A$_g$	881	-0.10(4)	$-4.2(9)\times10^{-3}$	-0.01	0.20	-0.50	This work
	880	?	0				Gillet et al. 1993
Internal ν_1, A$_g$	1098	2.9(1)	$-6(1)\times10^{-3}$	0.25	0.24	0.03	This work
	1101	3.5(3)					Kraft et al. 1991
	1097	2.9(3)	$-6.4(4)\times10^{-3}-1.6(3)\times10^{-5}$	0.25	0.24	0.0	Gillet et al. 1993
Internal ν_3, E$_g$	1442	?	?	?	?	?	This work
	1439	3.5(3)	$-3.5(3)\times10^{-2}+4.1(2)\times10^{-5}$	0.23	1.01	-1.9	Gillet et al. 1993
Overtone	1759	-0.15(6)	$-1.5(1)\times10^{-2}$	-0.01	0.35	-0.87	This work
	1750	-0.79(5)	$-1.3(2)\times10^{-3}-1.60(4)\times10^{-5}$	-0.02	0.03	-0.1	Gillet et al. 1993
			Magnesite				
External, E$_g$	214	3.52(3)	$-2.05(5)\times10^{-2}$	1.76	4.95	-6.16	This work
	216	2.6(2)		1.4(1)			Williams et al. 1992
	213	$4.6(4)-4.4(3)\times10^{-3}$	$-9(2)\times10^{-3}-2.6(2)\times10^{-5}$	2.6	2.4	0.3	Gillet et al. 1993
External, E$_g$	330	4.89(3)	$-3.01(5)\times10^{-2}$	1.59	4.73	-6.07	This work
	329	4.7(1)		1.67(4)			Williams et al. 1992
	329	4.5(3)	$-1.9(3)\times10^{-2}-2.5\times10^{-5}$	1.7	3.0	-2.5	Gillet et al. 1993
Internal ν_4, E$_g$	738	1.52(4)	$-2.0(8)\times10^{-3}$	0.22	0.14	0.16	This work
	735	1.5(2)		0.24(3)			Williams et al. 1992
	738	1.4(2)	0	0.23	0.00	0.44	Gillet et al. 1993
Internal ν_1, A$_{1g}$	1094	2.87(4)	$-1.4(7)\times10^{-3}$	0.28	0.07	0.41	This work
	1095	2.3(1)		0.24(2)			Williams et al. 1992
	1094	2.5(3)	$-3.5(3)\times10^{-3}-3.1(2)\times10^{-5}$	0.28	0.17	0.21	Gillet et al. 1993
Internal ν_3, E$_g$	1446	?	?	?	?	?	This work
	1444	4.0(4)	$-3.0(3)\times10^{-2}+5.5(2)\times10^{-5}$	0.34	1.08	-1.42	Gillet et al. 1993
Overtone	1763	0.21(3)	$-1.63(8)\times10^{-2}$	0.01	0.48	-0.90	This work
	1762	-0.42(4)	$-2.6(3)\times10^{-2}$	-0.03	0.76	-1.52	Gillet et al. 1993
			Rhodochrosite				
External, E$_g$	185	3.38(6)	$-1.98(6)\times10^{-2}$	2.09	4.63	-5.81	This work
	201	2.685					Farfan et al. 2013
	184	2.91(5)		2.37(7)			Liu et al. 2016
External, E$_g$	290	4.83(8)	$-2.93(6)\times10^{-2}$	1.90	4.43	-5.76	This work
	302	4.147					Farfan et al. 2013
	290	3.68(9)		1.99(8)			Liu et al. 2016
Internal ν_4, E$_g$	718	2.03(4)	$1.4(8)\times10^{-3}$	0.32	-0.09	0.95	This work
	723	0.946					Farfan et al. 2013
	719	1.28(6)		0.33(3)			Liu et al. 2016
Internal ν_1, A$_{1g}$	1086	3.34(5)	$-5.8(7)\times10^{-3}$	0.35	0.22	0.29	This work
	1100	1.906					Farfan et al. 2013
	1086	2.17(7)		0.38(3)			Liu et al. 2016
Internal ν_3, E$_g$	1415	?	?	?	?	?	This work
Overtone	1727	-0.92(7)	$-1.3(1)\times10^{-2}$	-0.06	0.31	-0.85	This work
			Siderite				
External, E$_g$	183	3.98(9)	$1(1)\times10^{-3}$	2.54	-0.17	7.29	This work
External, E$_g$	284	4.52(5)	$-1.0(1)\times10^{-2}$	1.86	1.31	1.49	This work
	299	3.74					Farfan et al. 2012
Fe^{2+} electronic excitation	507	-2.2(1)	0.130(4)	-0.51	-9.55	24.32	This work
Internal ν_4, E$_g$	731	2.4(2)	$-1.35(9)\times10^{-2}$	0.38	0.68	-0.81	This work
Internal ν_1, A$_{1g}$	1085	2.60(7)	$-3(1)\times10^{-3}$	0.28	0.10	0.48	This work
	1088	2.20					Farfan et al. 2012
Overtone	1724	-0.8(1)	$-1.6(1)\times10^{-2}$	-0.06	0.35	-1.10	This work

540 Table 2. Pressure and temperature induced shifts, isobaric and isothermal equivalents of the

541 Grüneisen parameter and anharmonic parameters of carbonate minerals. The values of v_i were

542 measured at ambient pressure and temperature (in this work, 1 bar and 25˚C).

543 *Symmetry of the modes are from: aragonite (De La Pierre et al. 2014), dolomite (Valenzano et

544 al. 2007), calcite, magnesite, rhodochrosite, and siderite (Rutt and Nicola 1974).

545 **The isothermal equivalent of the Grüneisen parameter was calculated with the following bulk

546 moduli: aragonite 68.9 GPa (Liu et al. 2005), calcite 76.1 GPa (Chen et al. 2001), dolomite 94

547 GPa (Ross and Reeder 1992), magnesite 107 GPa (Zhang and Reeder 1999), rhodochrosite 114.3

548 GPa (Chen et al. 2001), and siderite 117 GPa (Zhang and Reeder 1999).

549 ***The isobaric equivalent of the Grüneisen parameter was calculated with the following

550 thermal expansion coefficients: aragonite 6.5×10^{-5} K^{-1} (Ye et al. 2012), calcite 0.9×10^{-5} K^{-1}

551 (Markgraf and Reeder 1985), dolomite 2.41×10^{-5} K^{-1} (Reeder and Markgraf 1986), magnesite

552 1.93×10^{-5} K^{-1} (Markgraf and Reeder 1985), rhodochrosite 2.28×10^{-5} K^{-1} (Krishna Rao and

553 Satyanaryana Murthy 1970), and siderite 2.69×10^{-5} K^{-1} (Pfaff cited in Mellor 1935).

Observed mode, Symmetry	ν_i (cm^{-1})	$\delta\nu_i/\delta T$ (cm^{-1}/K)	$\delta\nu_i/\delta T$ (cm^{-1}/K)	γ_{iP}*	γ_{iP}*
		Calcite	**Calcite after Aragonite**	**Calcite**	**Calcite after Aragonite**
External, E_g	158	-2.65(2)×10^{-2}	-3.4(2)×10^{-2}	18.61	23.60
External, E_g	284	-4.30(4)×10^{-2}	-6.1(7)×10^{-2}	16.85	24.02
Internal ν_4, E_g	713	-5.0(2)×10^{-3}	-1.1(4)×10^{-2}	0.77	1.67
Internal ν_1, A_{1g}	1088	-9.7(3)×10^{-3}	-2.40(2)×10^{-2}	0.99	2.45
Overtone	1751	-1.36(6)×10^{-2}	-3.3(9)×10^{-2}	0.86	2.10

554 Table 3. Temperature induced shifts and isobaric equivalents of the Grüneisen parameter of

555 calcite and calcite after aragonite-calcite transition.

556 *The isobaric equivalent of the Grüneisen parameter was calculated with a calcite thermal

557 expansion coefficient of 0.9×10^{-5} K^{-1} (Markgraf and Reeder 1985).