1   **Revision 1**

2   **Trona at extreme conditions: A pollutant-sequestering material at high pressures and low**

3   **temperatures**

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9   **Abstract**

10   Single crystal X-ray diffraction of trona, $Na_3CO_3HCO_3 \cdot 2H_2O$, was measured between

11   100 and 340 K at ambient pressures, and the infrared and Raman spectra of this material

12   characterized to ~25 GPa. The thermal expansion of trona is greatest in the *b* direction, which is

13   due to a particularly large expansion of the long $Na_2\text{-}O_1$ and the short $Na_2\text{-}O_4$ bonds within the

14   sodium septahedron in the trona structure. This crystallographic direction is associated with the

15   distance between neighboring carbonate groups and neighboring water molecules within the

16   structure. The dimensions of the carbonate group undergo no systematic changes over this

17   temperature range, and the disordered hydrogen atom within the structure does not order at

18   temperatures down to 100 K. Thus, detailed changes in the geometry of the sodium polyhedra

19   primarily modulate the response of trona to decreases in temperature. The infrared and Raman

20   spectra undergo discontinuous and reversible changes at ~7 GPa and ~14.5 GPa: the former of

21   these phase transitions is likely associated with a shift primarily in the sodium-oxygen polyhedra,

22   while the latter also involves shifts in bonding of the carbonate groups. New assignments are

23   suggested for portions of the vibrational spectrum based on the high-pressure results. Resonance

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24   effects between different vibrational modes are observed, including the observation of a

25   transmission maximum associated with a resonant interaction between the carbonate symmetric

26   stretching vibration and a broad mode at similar frequencies. The behavior of trona under

27   extreme conditions is useful for understanding CO_2-vapor-saturated alkali-rich systems, and late-

28   stage peralkaline magmatic processes and, in its usage as both a sorbent and scrubber of SO_2 and

29   CO_2 in flue gasses and lignite coals.

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31   Keyword: trona, high pressure, low temperature, single crystal diffraction, vibrational

32   spectroscopy

Introduction

34   Trona, $Na_3CO_3HCO_3 \cdot 2H_2O$, is a non-marine evaporite mineral that, from the perspective

35   of its chemical formula, contains the unusual combination of both a carbonate and bicarbonate

36   anion. It has environmental importance as a product of carbon sequestration of flue gasses (Yoo

37   et al. 2013; Ficicilar and Dogu 2006) and in its utilization in sulfur removal from both flue gasses

38   and lignite coals (Kong and Wood 2010; Su et al. 2011; Sutcu and Eker 2013). Additional uses

39   of trona include as a food additive (Nielsen, 1999; Ekosse, 2010), and as a common source of

40   soda ash, which is a significant economic commodity because of its applications in

41   manufacturing glass, chemicals, paper, detergents, and textiles. Trona is also observed as a phase

42   within deteriorating concrete (Figg et al. 1976). Hence, the properties of trona at differing

43   conditions of pressure and temperature can provide insights into the interplay between the

44   structure and stability of this phase. From a crystal chemical viewpoint, trona is of interest as a

45   carbonated phase that contains both water and hydroxyl units, and hence may provide insights

46   into how water and carbonate ions interact within a single phase: indeed, its response to pressure

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47   may provide insight into the structural changes undergone by salt-bearing carbon-rich aqueous

48   fluids and/or hydrated carbonatitic magmas under compression.

49   Trona has also been found in magmatic environments: Markl and Baumgartner (2002)

50   show that trona can be formed by autometasomatic reactions of late-magmatic fluids or melts (or

51   supercritical fluid-melt mixtures), with earlier crystallized rocks within the same plutonic

52   complex, or by large-scale vapor unmixing in the very final stages of magmatism. Furthermore,

53   Liu and Fleet (2009) have found that trona's thermal stability is markedly enhanced by pressures

54   of only a few tenths of a GPa: at ambient pressure, trona begins to decompose at ~340 K, but Liu

55   and Fleet (2009) observed it to be stable up to 848 K at 0.21 GPa in equilibrium with CO_2-rich

56   vapor. Thus, understanding the behavior of trona under extreme conditions is useful for

57   understanding late-stage peralkaline magmatic processes, and CO_2-vapor-saturated alkali-rich

58   systems.

59   Brown et al. (1949) first determined the crystal structure of trona using single crystal x-

60   ray diffraction. Bacon and Curry (1956) refined the structure with two-dimensional single-crystal

61   neutron diffraction, and suggested that the H atom in the symmetric $(HC_2O_6)^{3-}$ anion is

62   disordered. This disordering of the hydrogen generates a sharing of the hydrogen atom between

63   the carbonate units, and hence produces the mixed carbonate/bicarbonate character of these

64   anion groups. Candlin (1956) refined the structure at both low (103 K) and room temperature

65   using two-dimensional X-ray diffraction, which confined the data to thermal changes within the

66   (010) plane of the trona structure. The results suggested that six of the twelve Na-O nearest

67   neighbor distances measured at 103 K were larger than at ambient conditions, implying that the

68   thermal response of the Na-O polyhedra may be complex. The environment of the disordered H

69   atom was later investigated by Choi and Mighell (1982) at 300 K with three-dimensional single-

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70   crystal neutron diffraction: they concluded that the H atom is dynamically disordered between

71   two equivalent sites, separated from one another by 0.211(9) Å. The dynamically disordered H-

72   atom was later reinvestigated by Pertlik (1986) with single crystal x-ray diffraction and

73   determined it to be separated by 0.95(4) Å to 0.77(3) Å.

74   From a spectroscopic viewpoint, trona has attracted interest as an example of a phase

75   with weak- to medium strength hydrogen bonds, which displays a variety of resonance-related

76   phenomena, including having an anomalous sharp transmission *maximum* within its infrared

77   spectrum (Novak et al. 1963; Bertoluzza et al. 1981). Additionally, its far-infrared spectrum has

78   recently been characterized as an example of a hydrated acid carbonate (Brusentsova et al. 2010).

79   The response, and stability, of carbonates under pressure utilizing vibrational spectroscopy has

80   been a topic of widespread interest (e.g., Kraft et al. 1991; Biellman et al. 1993; Catalli and

81   Williams 2005; Lin et al. 2012; Palaich et al. 2013). In the instance of trona, we examine the

82   effect of a markedly different chemical environment on the stability of the carbonate unit under

83   pressure: a phase that incorporates the bicarbonate ion and abundant water, and hence is a

84   crystallographic representative of the well-known carbonate-bicarbonate equilibrium.

85   Hence, because of its interest as both an industrial material and its novel crystal

86   chemistry, we have examined trona at temperatures spanning most of its ambient pressure

87   stability range (100 K-340 K), and at high pressures. Trona was reinvestigated with single crystal

88   x-ray diffraction techniques at low and ambient temperature to: (1) improve our understanding of

89   the thermal response of this material at a range of temperatures below the onset of its

90   decomposition at ~340 K (e.g., Cho et al. 2008); and (2) to assess the results of Candlin (1956) in

91   which she calculated that some Na-O bonds anomalously contract with increasing temperature.

92   Correspondingly, we have measured the infrared and Raman spectrum of this phase at high

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93   pressures, extending up to ~25 GPa to: (1) examine whether pressure-induced polymorphism

94   occurs in this phase; (2) probe how the bonding of this carbonate/bicarbonate/water-bearing

95   phase shifts as a function of compression and particularly how the hydrogen bonding in this

96   phase changes; (3) investigate the behavior of resonant interactions within this phase under

97   compression; and (4) to constrain how the sodium polyhedra (which comprise both octahedral

98   and septahedral sites) might respond to compression. Our net goals are to gain insights into the

99   underlying cause of trona's low-pressure, modest temperature decomposition, and its stability or

100   metastability under high-pressure conditions.

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Experimental methods

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102   **Single-crystal structural refinement**

103   The specimen studied is from the Green River Basin in Wyoming and contained

104   columnar, optical quality crystals of trona. The sample identity was confirmed by x-ray

105   diffraction, and both Raman and infrared spectroscopy (Figure 1). Indeed, our spectroscopic

106   results are in excellent accord with prior results on synthetic samples (Novak et al. 1963;

107   Bertoluzza et al. 1981).

108   For low- and ambient-temperature measurements, a single crystal was prepared with

109   approximate dimensions of 0.02 x 0.02 x 0.03 mm, which was mounted in oil (Infineum V8512)

110   on a MiTeGen MicroMount. Data were collected at 100 K, 200 K, and 300 K on a Bruker

111   diffractometer equipped with a Cu-Kα IμS source and MX optic with an APEX-II CCD detector.

112   The sample was placed in a cooled liquid nitrogen stream provided by an Oxford Cryosystems

113   Cryostream 700 liquid nitrogen-cooling device, with a temperature accuracy of ±2 K. An

114   approximate half sphere of data to $2\theta_{max}=135.9°$ was collected using 0.5° ω and Φ scans.

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115   The higher temperature single-crystal data were collected at 320 K, 330 K, and 340 K.

116   The sample was placed into a warmed nitrogen stream provided by an Oxford Cryosystems

117   Cryostream 700 Plus low/high temperature apparatus, again with an accuracy of ±2 K. A Bruker

118   D8 diffractometer equipped with an ApexII CCD detector on beamline 11.3.1 at the Advanced

119   Light Source in Berkeley, CA was used. Diffraction data were collected using monochromatic

120   synchrotron radiation at a wavelength of 0.61990(1) Å. An approximate full sphere of data to 2θ

121      $_{max}$=64° was collected using 0.3° ω scans.

122   The data were integrated using the program SAINT v8.27B. A multi-scan correction for

123   absorption was applied using the program SADABS-2012/1 and TWINABS-2012/1, for high

124   temperatures and low temperatures, respectively. The structure was solved by the charge flipping

125   methods of OLEX 2 (Dolomanov et al., 2009) and refined by full-matrix least-squares on F^2

126   SHELXL-2013 (Sheldrick, 2008).

127   **High pressure techniques**

128   High static pressures were generated by a Merrill-Basset type diamond anvil cell (DAC)

129   equipped with type Ia diamonds with 500 μm 16-sided culets. An inconel gasket with a 200 μm

130   hole was used as the sample compartment. Three to five ruby chips were loaded with each

131   sample to measure the pressure using the standard ruby fluorescence method (Mao et al., 1986).

132   All experiments were conducted at room temperature.

133   **Raman Spectroscopy**

134   Raman spectra were collected with a Horiba LabRAM HR Evolution Raman

135   spectrometer with a spectrometer focal length of 800 mm. Spectra were collected to a pressure of

136   25 GPa at 300 K. An excitation wavelength of 633 nm was used to collect spectra from 50-350

137   cm^{-1}, while 532 nm excitation was used to collect from 500-1200 cm^{-1}. An Olympus BXFM-

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138   ILHS microscope with a 50x long working distance objective (18 mm working distance and 3.6

139   mm focal distance) was used to focus the laser beam onto the sample. An 1800 lines/mm grating

140   with a corresponding spectral resolution of ~1 cm^{-1} was utilized. A single crystal of trona was

141   loaded with spectroscopic-grade KBr as the pressure medium: since KBr has no first-order

142   Raman spectrum, no spectral contamination of the trona spectrum is generated, and there is no

143   interaction between the pressure medium and the trona sample. Spectra were collected from a

144   laser spot size of ~2 μm, so we do not anticipate that pressure gradients will notably adversely

145   affect our spectra. Multiple samples were run with the trona loaded into the cell in different

146   orientations, so the amplitudes of peaks shift between different runs, due to the orientation-

147   dependence of the Raman modes of trona. Raman spectra were fit using a combination of

148   Gaussian and Lorentzian functions with Horiba Labspec6 software.

149   **Infrared spectroscopy**

150   Mid-infrared absorbance spectra were collected from 0 to 24 GPa using a Bruker Vertex

151   70v evacuated Fourier transform infrared spectrometer (FTIR) equipped with a globar source,

152   KBr-beamsplitter and a liquid-N$_2$ cooled mercury-cadmium-telluride (MCT) detector. All

153   infrared spectra were collected with a resolution of 4 cm^{-1}. Trona was ground into a powder and

154   mixed with spectroscopic-grade KBr in a ratio of 90% KBr: 10% sample by weight, with KBr

155   serving as both an infrared window and the pressure medium. Infrared spectra were fit using a

156   combination of Gaussian and Lorentzian functions with Bruker OPUS6.5 software.

157   **Single-Crystal Diffraction Results**

158   Trona crystallizes in the monoclinic C2/c crystal system in the range between 100-340 K

159   (Figure 2). The architecture of the structure is comprised of units of 3 edge-sharing sodium

160   polyhedra (a central octahedron flanked by septahedra), cross-linked by carbonate groups and

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161   hydrogen bonds. The unit cell dimensions as a function of temperature are given in Table 1, and

162   the volume as a function of temperature in Figure 3. The high temperature data are somewhat

163   scattered, and we do not preclude that this scatter may be associated with behavior precursory to

164   trona decomposition, which has been observed to initiate, with a substantial kinetic impediment,

165   at temperatures as low as 330 K (Cho et al. 2008). Indeed, our sample lost its single crystal

166   character on heating to 350 K. The average thermal expansion is 7.81 ($\pm$ 0.52) x 10^{-5}/K over this

167   temperature range. This is at the lower end of the range of other water-bearing molecular

168   minerals with comparatively low decomposition temperatures, such as gypsum (8.2 x 10^{-5}/K:

169   Ballirano and Melis 2009), mirabilite (~11 x 10^{-5}/K at 300 K: Brand et al. 2009) and ikaite (~12

170   x 10^{-5}/K: Lennie et al. 2004). The modulated structure of γ-Na_2CO_3 has, for comparison, an

171   anomalously high thermal expansion over this temperature range of ~14.6 x 10^{-5}/K (Arakcheeva

172   et al. 2010). Yet, the thermal expansion of trona is dramatically greater than that of non-alkali,

173   and non-water-bearing phases such as, for example, calcite at 300 K (3.8 x 10^{-6}/K: Markgraf and

174   Reeder 1985).

175   The normalized *a* and *c* axes have similar linear thermal expansion values with increasing

176   temperature, whereas the *b* axis linear thermal expansion is higher by a factor of three (Figure 4).

177   For each temperature the fractional atomic coordinates are listed in Table 2, the bond lengths and

178   the thermal expansion values listed in Table 3, and the corresponding bond angles are listed in

179   Table 4. The underpinning structural rationale for this anisotropy in thermal expansion is

180   straightforward: the carbonate unit lies within the *a-c* plane, and the structural rigidity of this unit

181   likely limits the thermal expansion in both the *a*- and *c*-directions. In contrast, bonding within the

182   *b*-direction is predominantly associated with Na-O bonds, and to a lesser extent hydrogen

183   bonding (Figure 2).

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184   Indeed, the carbonate group undergoes no resolvable changes in geometry over the

185   temperature range of this study, with no systematic changes in either bond length or bond angle.

186   It is slightly distorted from ideal three-fold symmetry: only the O_2-C_1-O_3 angle is close to 120°,

187   with the other two angles being near $116°$ and $124°$. The carbonate group is also nearly planar,

188   with deviations from the plane being less than 0.005 Å.

189   The Na-O bonds in the structure all expand with increasing temperature (Figure 5), in

190   contrast to the prior results of Candlin (1956). The volume of the Na_1 octahedron increases

191   systematically with increasing temperature, and does not become more distorted with increasing

192   temperature, as measured by its quadratic elongation (Robinson et al. 1971). The Na_1-O_2 bonds

193   expand by 0.0188(18) Å while the Na_1-O_3 bonds expand by 0.0107(18) and 0.0103(18) Å over

194   the 240 K interval of these measurements. The volume of the Na_2 septahedron increases with

195   increasing temperature and becomes more elongated in the *b*-direction with an increase in

196   temperature. The longer of the two Na_2-O_1 bonds and the shorter of the two Na_2-O_4 bonds

197   expand substantially more than the other bonds in the septahedron, by 0.0322(19) Å and

198   0.0238(19) Å, respectively, while the other Na_2-O bonds of the septahedron expand by notably

199   smaller amounts (ranging from 0.0101(18) Å to 0.0232(16) Å).

200   The Na_2-O_1 bond and the Na_2-O_4 bond that are particularly responsive to temperature are

201   oriented in such a way that their expansion is directly associated with the enhanced thermal

202   expansion of the *b*-direction (Figure 6). The *b*-direction reflects the interplanar separation

203   between the carbonate units and between the hydrogens of the water molecules: this unit cell

204   parameter increases from 3.4583(5) to 3.4922(5) Å from 100 to 340 K. This ~1% linear

205   expansion in the separation between carbonate groups and water molecules in the *b*-direction

206   may represent an indication of the manner in which trona ultimately decomposes, with

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207 progressively greater separations being accessed between water groups in the *b*-direction as

208 temperature is increased. The most parsimonious explanation for the means of water escape from

209 the structure during decomposition likely involves migration of the water molecules along the

210 structural channels between sodium polyhedra that are oriented along the *b*-axis of the structure.

211 It is likely that compaction of these channels produces the marked enhancement of the thermal

212 stability of trona that occurs under modest compression (Liu and Fleet 2009).

213 The refinements require that the H3 hydrogen atom remains disordered with 50%

214 occupancy between two O_2 sites at low temperatures, in accord with the 300 K structure derived

215 by Choi and Mighall (1982). Inclusion of the disordered H atom produced a substantial reduction

216 in the R-values of the final structure refinements. Thus, temperatures as low as 100 K are

217 insufficient to induce the structure to have discrete carbonate and bicarbonate units, in lieu of the

218 shared carbonate/bicarbonate character produced by the hydrogen disorder.

219 **High-pressure Raman and infrared spectral results and assignments**

220 Raman spectra of trona have been obtained on both compression and decompression;

221 representative Raman spectra are shown in Figure 7, and the change in frequency for each mode

222 as a function of pressure is plotted in Figure 8, with results tabulated in Table 5. The assignments

223 of the mid- (above ~500 cm^{-1}) and high-frequency Raman and infrared modes of trona have been

224 presented by Bertoluzza et al. (1981) and for the infrared bands by Novak et al. (1963), based on

225 comparisons with $NaHCO_3$-nahcolite, $3NaHCO_3Na_2CO_3$-wegscheiderite, and deuterated samples

226 of these phases and trona (although Novak et al.'s (1963) assignments hinged on the hydrogen

227 being symmetric between carbonate groups, rather than disordered between two sites). The low-

228 frequency Raman vibrations of trona have not previously been assigned. However, based on (1)

229 their minimal shift in frequency with deuteration (Bertoluzza et al. 1981); (2) the ubiquity of

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230   vibrations near 70, 90, 110 and 140 cm^{-1} in the sodium bicarbonate salts (Bertoluzza et al. 1981);

231   and (3) the presence of vibrations near the first three of these frequencies within the well-

232   understood Raman spectrum of NaOH (e.g., Kanesaka et al. 1982), it appears that the assignment

233   of these vibrations to Na-O associated vibrations is robust. Which of these vibrations might be

234   Na-O stretching vibrations or Na-O-Na bending vibrations is less obvious: it is possible, by

235   analogy with NaOH, that the two lowest frequency of these bands are Na-O-Na bending

236   vibrations, with the vibrations between 140 and 180 cm^{-1} being associated with Na-O stretching

237   modes. This interpretation is in general accord with the smaller pressure shifts of the two lowest

238   frequency vibrations: compaction is likely to have less of an effect on interpolyhedral bending

239   vibrations.

240   Infrared spectra between ~550 and 1800 cm^{-1} on compression and decompression are

241   shown in Figure 9a,b, and the hydroxyl stretching vibrations are shown in Figure 10a,b, with

242   mode shifts shown in Figure 11a,b,c. The pressure dependences of the different infrared modes

243   provide insight into their assignments. In particular, the vibrations associated with the carbonate

244   group are readily identified through both their positions and pressure shifts. The infrared in-plane

245   bends (v_4) of the carbonate group at 684 cm^{-1} and 710 cm^{-1} shift smoothly under compression

246   (Figure 12a). The corresponding Raman vibration at 699 cm^{-1} shifts at a rate intermediate

247   between those of the 684 and 710 cm^{-1} infrared bands. The infrared bands modestly increase in

248   their separation with pressure, implying that the distortion of the carbonate group (or of its local

249   environment) may weakly increase with pressure: site group-associated splitting likely produces

250   the separation of the two infrared bands (Greenaway et al. 1986). At ~5.7 GPa, an additional

251   infrared mode for which the pressure shift is compatible with the other in-plane bends becomes

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252   resolvable near 670 cm^{-1}: this band may simply be separating from a highly-absorbing broad

253   feature near 550 cm^{-1}.

254   The IR active mode at 805 cm^{-1} shifts rapidly with increasing pressure and crosses

255   through, but does not appear to resonantly interact with, the carbonate out-of-plane bend (ν_2) at

256   850 cm^{-1} (Figure 11a). The former band has been attributed to an H_2O-associated vibration,

257   based on its non-appearance in deuterated spectra (Novak et al., 1963): the most likely

258   assignment, based on its frequency, is to an H_2O-libration (e.g., Lutz, 1988), and its robust

259   pressure shift is in accord with increasing hydrogen-bonding of the water-molecule under

260   pressure. An alternate possibility, discussed below, is that it could be associated with vibrational

261   transitions associated with the double-well potential of the disordered hydrogen of the hydroxyl

262   unit. The out-of-plane bend at 850 cm^{-1} shifts by -1.0 cm^{-1}/GPa with increasing pressure: this

263   negative shift is in accord with the behavior of this vibration in a wide suite of other carbonates,

264   and is likely generated by increases in cation-oxygen bond strength under pressure (e.g., Kraft et

265   al. 1991; Williams et al. 1992; Gillet et al. 1993; Catalli et al. 2005). The asymmetric stretch (ν_3)

266   of the carbonate unit falls at 1461 cm^{-1}, and evolves a high-frequency shoulder that becomes

267   deconvolvable above ~4 GPa: these bands have almost identical pressure shifts.

268   For the bands between 1550 and 1800 cm^{-1}, our assignments differ from those of Novak

269   et al. (1963) and Bertoluzza et al. (1981). In particular, the band with a zero pressure frequency

270   of 1557 cm^{-1} has a pressure shift that is markedly larger than any other within trona: nearly 12

271   cm^{-1}/GPa. Both the location and pressure shift of this band indicate that it is the first overtone of

272   the vibration at 806 cm^{-1}, shifted to lower frequency by anharmonicity. Furthermore, its behavior

273   strongly suggests that its intensity is enhanced by a resonant interaction with the band at 1749

274   cm^{-1}: at low pressures, its intensity renders it barely resolvable, but it increases in strength as it

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275   approaches the higher frequency peak (Figure 9a). Hence, the symmetry of this overtone is likely

276   the same as that of the band at 1749 cm^{-1}, and the two undergo increased levels of Fermi

277   resonance with one another as pressure is increased. The coupling constant (which is equal to

278   half the closest approach of these bands) of these modes within trona appears to be on the order

279   of 50 cm^{-1}, or a bit over half an order of magnitude larger than previously observed resonant

280   couplings between vibrations in hydrous phases (e.g., Duffy et al. 1995; Knittle et al. 2001). As

281   with prior studies (Novak et al. 1963; Bertoluzza et al. 1981), we do not resolve an unambiguous

282   H-O-H bending vibration in our spectra: given the somewhat broadened (relative to free H_2O) H-

283   O-H angle in trona of 107.4° (Choi and Mighell 1982), such a vibration would be anticipated to

284   occur near 1600 cm^{-1} (e.g., Lutz 1988). Unless the band at 1698 cm^{-1} is the H-O-H stretch, which

285   is unlikely, as this is an anomalously high frequency for such a vibration (particularly given the

286   wide H-O-H angle in this phase: e.g., Lutz 1988), it appears that this vibration is not

287   characterized.

288   The origins of the infrared bands at 1698 and 1749 cm^{-1} are thus problematic: the former

289   band was attributed by Novak et al. (1963) and Bertoluzza et al. (1981) to either a high-lying

290   asymmetric stretch of the carbonate unit, or a water-associated vibration. The latter interpretation

291   is consistent with the shift of these bands on deuteration: the frequency ratio between the

292   hydrogen-bearing vibrations and the deuterium-bearing vibrations is near 1.09 (Novak et al.

293   1963; Bertoluzza et al. 1981). Within crystalline carbonates, it has long been appreciated that

294   overtones and combinations commonly fall in this spectral range as well (Ross and Goldsmith

295   1964): such combinations can be the 2 x ν_2 (e.g., Kraft et al. 1991) or $\nu_1 + \nu_4$ vibrations of the

296   carbonate group (e.g., Catalli et al. 2005), and can often be distinguished by their pressure shifts.

297   However, neither of the bands' pressure shifts appears compatible with an obvious combination

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298   band. The possibility that these bands might be associated with C=O vibrations, which occur in

299   KHCO$_3$ at frequencies as high as 1650 cm^{-1} (e.g., Dopieralski et al. 2010) does not explain their

300   shift on deuteration. With respect to these vibrations, it is worth noting that the disordered

301   hydrogen positions of the hydroxyl unit in trona occupy a symmetric, double-well potential that

302   is almost linearly oriented between the O(2) oxygens within the structure. As noted for trona

303   (among other phases) by Sokolov et al. (1988, 1990), a quantum mechanical analysis of this

304   configuration gives rise to a number of energy levels associated with the protons, and optical

305   transitions between these levels (e.g., Romanowski and Sobczyk 1977). In short, multiple optical

306   transitions can be generated between different proton states, including the ground and excited

307   states. Given the approximate nature of the theory, it is possible that either the 1698 or 1740 cm^{-1}

308   bands could be generated by a transition between either the fundamental and a higher-lying

309   excited state, or between excited states of the proton (which would imply a marked temperature

310   dependence for the absorption). If this were the case, the ground state to first excited state

311   transition in trona would be anticipated to occur at substantially lower frequencies, and could be

312   associated with the 800 cm^{-1} band: this might provide a natural explanation for the strong Fermi

313   resonant coupling constant between the overtone of this transition and the transition between the

314   two excited states. Indeed, Fillaux (1983) proposed that a highly temperature-dependent infrared

315   band near 1870 cm^{-1} in KHCO$_3$ may be associated with transitions between excited states of the

316   hydroxyl stretching vibration within a double minimum potential. An appealing aspect of this

317   explanation is that compaction of the O-O distance generally produces increases in the

318   frequencies of transitions associated with excited states (Romanowski and Sobczyk 1977;

319   Sokolov et al. 1988, 1990), and thus a positive pressure shift of these vibrations would be

320   anticipated, in accord with our observations.

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321   Above 3000 cm^{-1}, we fit three separate peaks to the infrared spectra, with zero pressure

322   frequencies of 3050, 3449 and 3530 cm^{-1}: the locations of the first and third of these are in

323   reasonable agreement with Novak et al. (1963) and Bertoluzza et al. (1981), while the

324   intermediate peak is required to adequately match the shape of the observed hydroxyl stretching

325   envelope. The initial pressure shift of these peaks is generally similar, with each shifting to lower

326   frequencies on compression, implying that hydrogen bonding increases with pressure within

327   trona. The assignment of these peaks to hydroxyl stretching vibrations associated with the water

328   molecule is compatible with the hydrogen bonding lengths of water within trona, based on

329   general correlations between band frequency and O-O separation (e.g., Nakamoto et al. 1955).

330   **High-Pressure Phase Transitions**

331   The low frequency Raman vibrations with ambient pressure frequencies at ~71 and 100

332   cm^{-1} are associated with vibrations of the Na-O polyhedra: they shift non-linearly to higher

333   frequency under compression. At ~7.0 GPa, the lower frequency band splits, and its lower

334   frequency component and the continuation of the 100 cm^{-1} band each abruptly begin to shift to

335   lower frequency. This negative shift persists until ~14.5 GPa (Figure 8a). Other Raman peaks

336   may undergo modest shifts in their pressure-dependence at this pressure (particularly the 139

337   and 155 cm^{-1} bands), but no discontinuities in peak positions are observed. The combination of

338   mode splitting and shifts in pressure-dependences suggests that the phase transition near ~7.0

339   GPa is second order in character and, based on its Raman spectral signature, predominantly

340   involves changes in the geometry of the sodium polyhedra.

341   The infrared spectra are compatible with this interpretation of the ~7.0 GPa transition:

342   specifically, the pressure dependence of the in-plane bending vibration with a zero-pressure

343   frequency of 710 cm^{-1} shifts, and changes in the H$_2$O rotational vibration and its overtone at 805

15

344 and 1557 cm^{-1}, respectively, occur. A shift in sign of the pressure dependence of the O-H

345 stretching vibrations with zero pressure frequencies of 3449 cm^{-1} and 3530 cm^{-1} also occurs at

346 this pressure, indicating that a shift in the hydrogen bonding geometry has occurred associated

347 with this transition. Each of these vibrations involves oxygen anions that form part of the sodium

348 septahedron, and hence this transition is plausibly produced by a shift in the geometry of this

349 sodium polyhedral unit.

350   At ~14.5 GPa, changes in mode frequencies, the appearance of new bands, and

351 disappearance of bands imply that a second phase transition takes place. In particular, a change

352 in the nature of the lowest frequency Raman vibrational modes at ~14.5 GPa suggests that the

353 coordination geometry of the Na-O polyhedra changes significantly (Figure 8a): a new band

354 appears near 85 cm^{-1}, the band with a zero-pressure frequency near 155 cm^{-1} disappears, and the

355 frequency of the mode with a zero pressure frequency near 172 cm^{-1} drops in frequency by ~10

356 cm^{-1}. At higher frequencies, the in-plane bend, the symmetrical stretch, and the asymmetric

357 stretches of the carbonate group each shift discontinuously to lower frequency at this pressure

358 (Figures 8b, 11b), and continue to shift to higher frequency with increases in pressure. The

359 symmetrical stretch peak of the carbonate group becomes asymmetrical at ~11.0 GPa and splits

360 at ~14.5 GPa and remains split up to 25.4 GPa. The pressure dependence of the H_2O vibrational

361 mode at 3049 cm^{-1} changes sign at this transition (and a weak positive discontinuity in mode

362 frequency may be present), and begins to shift positively at pressures greater than 14.5 GPa

363 (Figure 11c). It is near this pressure that a new hydroxyl stretching band appears at ~3580 cm^{-1}:

364 this band ultimately becomes the dominant feature in the hydroxyl region of the spectrum

365 (Figure 10a, 11c). The band with a zero pressure frequency near 1750 cm^{-1} that we have

366 attributed to transitions associated with the O-H$^{...}$O strongly bound hydroxyl unit disappears at

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367   this transition, which may imply that the double-welled potential (and associated H-disorder) is

368   not present within this phase.

369   In terms of its effect on the carbonate group vibrations (a decrease in the frequencies, and

370   hence force constants, of the carbonate group), the manifestations of this higher pressure

371   transition closely resemble those of a transition in $KHCO_3$ that occurs near 2.8 GPa (Kagi et al.

372   2003): a transition associated with tilting of the carbonate units, displacement of molecular layers

373   relative to one another, and an increase in K-coordination from 8- to 10-fold (Allan et al. 2007).

374   Additionally, a splitting of the symmetric stretching vibration of the carbonate group occurs at

375   this transition, indicating that either multiple carbonate group environments may be present in

376   the high-pressure phase, or that the unit cell may be expanded. The weakening of the carbonate

377   bonds may be associated with a displacement in the three-membered sodium polyhedral units

378   (e.g., Figure 2) relative to one another, with accompanying elongation of the C-O bonds within

379   the carbonate units. This transition also appears to be associated with a notable decrease in

380   hydrogen bonding, as manifested by the positive pressure shifts of the hydroxyl stretching bands

381   and the appearance of a new, higher frequency hydroxyl stretching band. This is again

382   compatible with a shift in the neighboring sodium polyhedral units relative to one another. It is

383   also possible that, due to the large number of water molecules present within trona and their

384   closely juxtaposed positions, hydrogen-hydrogen repulsion may become increasingly important

385   within the phase of trona that occurs above 14.5 GPa.

386   This transition is reversible, but with substantial hysteresis: for example, the symmetric

387   stretch of the carbonate group remains split during decompression down to ~2.5 GPa (Figure 8b).

388   Both the carbonate in-plane bend and symmetric stretch return to within a few wavenumbers of

389   their initial peak locations. The low frequency vibrations (Figure 8a) show similar shifts upon

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390   decompression and also return to within a few wavenumbers of their initial peak locations. Thus,

391   the higher pressure transition we observe is, based on the observed hysteresis, likely first-order in

392   character: however, the high-pressure phase cannot be quenched to ambient pressures at 300 K.

393   **Novel Resonance Effects**

394   An interesting feature of the infrared spectrum of trona (Figure 1) is the transmission

395   window that is present at 1050 cm^{-1}. This sharp decrease in absorbance was first noted in trona

396   by Novak et al. (1963), and assigned to a peculiar resonance effect first observed by Evans and

397   Wright (1960) in the infrared spectrum of *m*-toluidine. This effect has been further studied, and

398   quantitatively modeled, by Evans (1960, 1962) and Claydon and Sheppard (1969). Trona may be

399   the single example observed to date of this "Evans window" effect in minerals: in short, a

400   transmission maximum is generated when a broad band overlaps a sharp fundamental band of the

401   same symmetry. A form of Fermi resonance thus occurs, with the intensity of the fundamental

402   band being resonantly redistributed at frequencies surrounding the fundamental, and a

403   transmission window within the broad band being produced at the frequency of the sharp

404   fundamental (Evans and Wright 1960). In the case of trona, the transmission window is the result

405   of the symmetrical carbonate stretch interacting with a broad band at a similar frequency. The

406   nature of the broad band is unclear: it appears that it is a combination band or overtone

407   associated with a hydroxyl or water vibration (presumably a libration or translation), as the

408   transmission maximum disappears within deuterated samples (Novak et al., 1963).

409   We are able to monitor the pressure shift of this transmission window under compression

410   and decompression (Figure 12a,b). The transmission window shifts smoothly with increasing

411   pressure into a diamond absorption region and returns upon decompression (Figure 12a). Its

412   pressure shift is in close accord with the shift of the corresponding Raman (ν_1) symmetric

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413   stretching vibration, confirming the identification of this spectral hole as being associated with

414   this sharp fundamental vibration.

415   **Mode Grüneisen Parameters**

416   Using the pressure derivative of a vibrational frequency ν_i for a mode i, (dν_i/dP), a mode

417   Grüneisen parameter (γ_i) can be calculated using $\gamma_i = K_0/\nu_{0i}$ (dν_i/dP). Here, K_0 is the bulk modulus

418   of trona, which was estimated to be 36 GPa, as calculated from the P- and S- wave velocities in

419   trona-dominated strata and the known density of trona (Ge et al. 2012). This value is of unknown

420   accuracy. However, it lies in the vicinity of that of other water-rich evaporite minerals (for

421   example, the bulk modulus of gypsum is ~45 GPa: Stretton et al. 1997). The ν_{0i} values were

422   determined by infrared and Raman spectroscopy at room temperature and pressure, and the

423   calculated dν_i/dP and γ_i are listed in Table 5. For comparison, the thermodynamic value of the

424   Grüneisen parameter can be determined using our thermal expansion (α), coupled with the bulk

425   modulus of 36 GPa (K_0), the density (ρ), and the heat capacity at 300 K (C_p) from Haynes (2003)

426   using $\gamma_i = \alpha K_0/\rho C_p$. The calculated thermodynamic Grüneisen parameter is 1.06: our overall

427   average mode Grüneisen parameter for the fundamental bands in Table 5 is 0.48. This

428   discrepancy is certainly associated with the oversampling of high-frequency, low-Grüneisen

429   parameter molecular modes in our study, and in particular in our mid-infrared spectral

430   measurements. An averaging of our Raman modes, which sample both low- and high-frequency

431   portions of the trona spectrum, yield an average value of 0.91, which is in substantially closer

432   accord with the thermodynamic value. Unsurprisingly, the dominant contributors to the

433   thermodynamic Grüneisen parameter are low-frequency modes, and particularly modes that are

434   likely to be associated with the Na-O polyhedra.

435   **Implications**

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436   The behavior of trona under extreme conditions is useful for understanding late-stage

437 peralkaline magmatic processes (e.g., Markl and Baumgartner 2002), as well as the behavior of

438 water molecules within a carbonate-dominated framework. Notably, the interactions between

439 water/hydrogen and carbonate units are quite insensitive to pressure: while hydrogen bonding

440 weakly increases with compression in trona (and may decrease across high-pressure polymorphic

441 transitions), the carbonate unit behaves in a similar manner to the carbonate unit in other

442 carbonate minerals under high pressure such as aragonite and dolomite (Kraft et al. 1991; Gillet

443 et al. 1993), siderite and rhodochrosite (Santillan and Williams 2004), and witherite (Lin and Liu

444 1997). Hence, at least within trona, carbonate ions and water molecules behave as largely

445 independent molecular units, with limited interactions, under compression.

446   As an industrial material whose thermal stability is important in its usage as both a

447 sorbent and scrubber of SO_2 (Kong and Wood 2010; Su et al. 2011; Sutcu and Eker 2013) and

448 CO_2 (Ficicilar and Dogu, 2006), the effect of temperature appears to be most notably manifested

449 in the sodium septahedron within the structure. The thermal expansions of two bonds in this

450 polyhedron appear to be anomalous (as is the thermal expansion of the *b*-axis), and this

451 expansion may be a key contributor to the thermal stability limit of trona. In this respect, it is

452 notable that substitution of potassium into trona induces both a change in crystal symmetry and a

453 weak increase in thermal stability from ~330 K (Cho et al. 2008) to 341 K (Adam and Cirpus

454 1996). Hence, enhancing the thermal stability of trona may require substitution into the

455 septahedral site: a site that is not amenable to substitution by heavier elements (Adam and Cirpus

456 1996). Finally, we note that the disordered hydrogen position within trona could be associated

457 with tunneling and quantum correlation effects: these are hinted at by our possible assignment of

458 bands between 1690 and 1750 cm^{-1} to transitions between the ground and excited states of the O-

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459   H···O unit. Such anomalous quantum effects in phases containing protons with multiple sites

460   have been extensively documented within $KHCO_3$ (Fillaux et al. 2006; Fillaux 2007), and the

461   disordered hydrogens associated with the O-H···O units within trona may represent candidates for

462   similar quantum effects.

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473   **References**

474   Adam, A., and Cirpus, V. (1996) Darstellung und Structur der ersten gemischten

475   Alkalimetallhydrogencarbonate $NaA_2[H(CO_3)_2]\cdot 2H_2O$ mit A = K, Rb. *Zeitschrift fur*

476   *Anorganische Allgemeine Chemie, 622*, 2023-2030.

477   Allan, D.R., Marshall, W.G., and Pulham, C.R. (2007) The high-pressure crystal structure of

478   potassium hydrogen carbonate ($KHCO_3$). *American Mineralogist, 92,* 1018-1025.

479   Arakcheeva, A., Bindi, L., Pattison, P., Meisser, N., Chapuis, G., and Pekov, I. (2010) The

480   incommensurately modulated structures of natural natrite at 120 and 293 K from

481   synchrotron X-ray data, *American Mineralogist, 95,* 574-581.

21

482   Bacon, G.E., and Curry, N.A. (1956) A neutron-diffraction study of sodium sesquicarbonate.

483   *Acta Crystallographica, 9,* 82-85.

484   Ballirano, P., and Melis, E. (2009) Thermal behaviour and kinetics of dehydration of gypsum in

485   air from in situ real-time laboratory parallel beam X-ray powder diffraction. *Physics and*

486   *Chemistry of Minerals, 36,* 391-402.

487   Bertoluzza, A., Monti, P., Morelli, M.A., and Battaglia, M.A. (1981) A Raman and infrared

488   spectroscopic study of compounds characterized by strong hydrogen bonds. *Journal of*

489   *Molecular Structure, 73,* 19-29.

490   Brand, H.E.Q., Fortes, A.D., Wood, I.G., Knight, K.S., and Vocadlo, L. (2009) The thermal

491   expansion and crystal structure of mirabilite ($Na_2SO_4 \cdot 10H_2O$) from 4.2 to 300 K as

492   determined by time-of-flight neutron powder diffraction. *Physics and Chemistry of*

493   *Minerals, 36,* 29-46.

494   Brown, C.J., Peiser, H.S., and Turner-Jones, A. (1949) The crystal structure of sodium

495   sequicarbonate. *Acta Crystallographica, 2,* 167-174.

496   Brusentsova, T.N., Peale, R.E., Maukonen, D., Harlow, G.E., Boesenberg, J.S., and Ebel, D.

497   (2010) Far infrared spectroscopy of carbonate minerals. *American Mineralogist, 95,*

498   1515-1522.

499   Candlin, R. (1956) Thermal changes in the structure of sodium sequicarbonate. *Acta*

500   *Crystallographica, 9,* 545-554.

501   Catalli, K., Santillan, J., and Williams, Q. (2005) A high pressure infrared spectroscopic study of

502         $PbCO_3$-cerussite: Constraints on the structure of the post-aragonite phase. *Physics and*

503   *Chemistry of Minerals, 32,* 412-417.

22

504   Catalli, K., and Williams, Q. (2005) A high-pressure phase transition of calcite-III. *American*

505   *Mineralogist*, *90*, 1679-1682.

506   Cho, K.J., Keener, T.C., and Khang, S.-J. (2008) A study on the conversion of trona to sodium

507   bicarbonate, *Powder Technology, 184,* 58-63.

508   Choi C.S., and Mighell A.D., (1982) Neutron diffraction study of sodium sesquicarbonate

509   dihydrate. *Acta Crystallographica, B38,* 2874-2876.

510   Claydon, M.F., and Sheppard, N. (1969) The nature of "A, B, C"-type infrared spectra of

511   strongly hydrogen-bonded systems; pseudo-maxima in vibrational spectra. *Journal of the*

512   *Chemical Society D: Chemical Communications*, 23, 1431-1433.

513   Dolomanov O.V., Bourhis L.J., Gildea R.J., Howard J.A.K., and Puschmann, H. (2009) OLEX2:

514   a complete structure solution, refinement and analysis program.

515   *J. Appl. Cryst. 42,* 339-341.

516   Dopieralski, P.D., Latajka, Z., and Olovsson, I. (2010) Proton-transfer dynamics in the $(HCO_3^-)_2$

517   dimer of $KHCO_3$ from Car-Parrinello and path-integrals molecular dynamics calculations.

518   *Acta Crystallographica, B66,* 222-228.

519   Duffy, T.S., Meade, C., Fei, Y., Mao, H.K., and Hemley, R.J. (1995) High-pressure phase

520   transition in brucite, $Mg(OH)_2$. *American Mineralogist, 80,* 222-230.

521   Ekosse, G.I.E. (2010) X-ray diffraction study of kanwa used as active ingredient in achu soup in

522   Cameroon. *African Journal of Biotechnology*, *9*, 7928-7929.

523   Evans, J.C. (1960) Further studies of unusual effects in the infrared spectra of certain molecules.

524   *Spectrochimica Acta*, *16*, 994-1000.

525   Evans, J.C. (1962) Narrow transmission regions within broad infrared absorption bands in solids.

526   *Spectrochimica Acta*, *19,* 507-512.

23

527   Evans, J.C., and Wright, N. (1960) A peculiar effect in the infrared spectra of certain molecules.

528   *Spectrochimica Acta*, *16*, 352-357.

529   Ficicilar, B., and Dogu, T. (2006) Breakthrough analysis for CO_2 removal by activated

530   hydrotalcite and soda ash. *Catalysis Today, 115,* 274-278.

531   Figg, J., Moore, A.E., and Gutteridge, W.A. (1976) On the occurrence of the mineral trona

532   (Na_2CO_3 $NaHCO_3$ $2H_2O$) in concrete deterioration products. *Cement and Concrete*

533   *Research, 6,* 691-696.

534   Fillaux, F. (1983) Calculations of infrared and Raman band profiles of strong hydrogen bonds.

535   OH stretching bands and proton dynamics in crystalline potassium hydrogen carbonate.

536   *Chemical Physics, 74,* 405-412.

537   Fillaux, F. (2007) Proton transfer in the $KHCO_3$ and benzoic acid crystals: A quantum view.

538   *Journal of Molecular Structure, 844/845,* 308-318.

539   Fillaux, F., Cousson, A., and Gutmann, M.J. (2006) Macroscopic quantum entanglement and

540   'super-rigidity' of protons in the $KHCO_3$ crystal from 30 to 300 K. *Journal of Physics:*

541   *Condensed Matter, 18,* 3229-3249.

542   Ge, M., Wang, H., Schissler, A., and Ramani, R. (2012). Measuring pillar width in trona mines

543   using a body wave based in-seam seismic technique. *International Journal of Rock*

544   *Mechanics and Mining Sciences*, *53*, 10-17.

545   Gillet, P., Biellmann, C., Reynard, B., and McMillan, P. (1993) Raman spectroscopic studies of

546   carbonates: Part 1. High-pressure and high-temperature behavior of calcite, magnesite,

547   dolomite and aragonite. *Physics and Chemistry of Minerals, 20,* 1-18.

24

548   Greenaway, A.M., Dasgupta, T.P., Koshy, K.C., and Sadler G.G. (1986) A correlation between

549   infrared stretching mode absorptions and structural angular distortions for the carbonato

550   ligand in a wide variety of complexes. *Spectrochimica Acta A, 42,* 949-954.

551   Haynes, H.W. (2003) Thermodynamic solution model for trona brines. *AIChE Journal*, *49*, 1883-

552   1894.

553   Kanesaka, I., Tsuchida, M., and Kawai, K. (1982) Vibrational spectra and normal coordinate

554   analysis of NaOX (X = H or D). *Journal of Raman Spectroscopy, 13,* 253-256.

555   Knittle, E., Phillips, W., and Williams, Q. (2001) An infrared and Raman spectroscopic study of

556   gypsum at high pressures. *Physics and Chemistry of Minerals, 28,* 630-640.

557   Kong Y., and Wood M.D. (2010) Dry injection of trona for SO_3 control. *Power, 154,* 114-118.

558   Kraft, S., Knittle, E., and Williams, Q. (1991). Carbonate stability in the Earth's mantle: a

559   vibrational spectroscopic study of aragonite and dolomite at high pressures and

560   temperatures. *Journal of Geophysical Research: Solid Earth*, *96*, 17997-18009.

561   Lennie, A.R., Tang, C.C., and Thompson, A.P. (2004) The structure and thermal expansion

562   behavior of ikaite, $CaCO_3 \cdot 6H_2O$, from T = 114 to T = 293 K. *Mineralogical Magazine,*

563   *68,* 135-146.

564   Lin, C.C., and Liu, L.G. (1997) High-pressure Raman spectroscopic study of post-aragonite

565   phase transition in witherite ($BaCO_3$). *European Journal of Mineralogy*, *9*, 785-792.

566   Liu, X., and Fleet, M.E. (2009) Phase relations of nahcolite and trona at high PT conditions.

567   *Journal of Mineralogical and Petrological Sciences*, *104*, 25-36.

568   Lutz, H.D. (1988) Bonding and structure of water molecules in solid hydrates. Correlation of

569   spectroscopic and structural data. *Structure and Bonding, 69,* 97-125.

25

570   Markgraf, S.A., and Reeder, R.J. (1985) High-temperature structure refinements of calcite and

571   magnesite. *American Mineralogist, 70,* 590-600.

572   Mao, H.K., Xu, J.A., and Bell, P.M. (1986) Calibration of the ruby pressure gauge to 800 kbar

573   under quasi-hydrostatic conditions. *Journal of Geophysical Research, 91,* 4673-4676.

574   Markl, G., and Baumgartner, L. (2002) pH changes in peralkaline late-magmatic fluids.

575   *Contributions to Mineralogy and Petrology*, *144*, 331-346.

576   Nakamoto, K., Margoshes, M., and Rundle, R.E. (1955) Stretching frequencies as a function of

577   distances in hydrogen bonds. *Journal of the American Chemical Society, 77*, 6480-6486.

578   Nielsen, J.M. (1999) East African magadi (trona): Fluoride concentration and mineralogical

579   concentration. *Journal of African Earth Sciences, 29,* 423-428.

580   Novak, A., Saumagne, P., and Bok, L.D.C. (1963) Etude par spectroscopie infrarouge de

581   quelques hydrogenocarbonates alcalins: $NaHCO_3$, $NH_4 HCO_3$, $KHCO_3$, et du

582   sesquicarbonate de sodium $Na_2CO_3^.NaHCO_3^. 2H_2O$. *Journal de Chimie Physique*, *60*,

583   1385-1395.

584   Pertlik, F. (1986) Ein vergleich von ergebnissen routine assiger strukturbestimmungen mittels

585   rontgen- BZW. Neutronen-einkristalldaten am beispiel der trona, $Na_3H[CO_3]_2^.2H_2O$.

586   *Mitteilungen Osterreichischen Mineralogischen Gesellschaft, 131*, 7-14.

587   Robinson, K., Gibbs, G.V., and Ribbe, P.H., (1971) Quadratic elongation: A quantitative

588   measure of distortion in coordination polyhedra. *Science,172*, 567-570.

589   Romanowski, H., and Sobczyk, L. (1977) A stochastic approach to the IR spectra of the OHO

590   symmetrical hydrogen bond. *Chemical Physics, 19,* 361-370.

591   Ross, S.D., and Goldsmith, J. (1964) Factors affecting the infrared spectra of planar anions with

592   D_{3h} symmetry-I. Carbonates of the main group and first row transition elements.

593   *Spectrochimica Acta, 20,* 781-784.

594   Santillan, J., and Williams, Q. (2004) A high-pressure infrared and X-ray study of $FeCO_3$ and

595        $MnCO_3$: comparison with $CaMg (CO_3)_2$-dolomite. *Physics of the Earth and Planetary*

596   *Interiors*, *143*, 291-304.

597   Sheldrick G.M. (2008) A short history of *SHELX*. Acta Cryst. A64, 112-122.

598   Sokolov, N.D., Vener, M.V., and Savel'ev, V.A. (1988) Tentative study of strong hydrogen bond

599   dynamics. Part I. Geometric isotope effects. *Journal of Molecular Structure, 177,* 93-110.

600   Sokolov, N.D., Vener, M.V., and Savel'ev, V.A. (1990) Tentative study of strong hydrogen bond

601   dynamics. Part II. Vibrational frequency considerations. *Journal of Molecular Structure,*

602   *222,* 365-386.

603   Stretton, I.C., Schofield, P.F., Hull, S., and Knight, K.S. (1997) The static compressibility of

604   gypsum. *Geophysical Research Letters, 24,* 1267-1270.

605   Sutcu H., and Eker Y. (2013) The removal of sulfur from Dursunbey and Iskilip lignites in

606   Turkey, using natural trona: 1. The effect of the thermal method. *Energy Sources Part A-*

607   *Recovery Utilization and Environmental Effects,* 35, 83-91.

608   Williams, Q., Collerson, B., and Knittle, E. (1992) Vibrational spectra of magnesite and calcite-

609   III at high-pressures. *American Mineralogist, 77,* 1158-1165.

610   Yoo M., Han S.J., and Wee J.H. (2013) Carbon dioxide capture capacity of sodium hydroxide

611   aqueous solution, *Journal of Environmental Management, 114,* 512-519.

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615   Figure 1. Representative ambient temperature and pressure infrared and Raman spectra of trona.
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617   Figure 2. Crystal structure of trona at 300K looking down the b-axis note: the dynamically
618   disordered H_3 atom is represented with light hatchmarked circles (H-atom positions from Choi
619   and Mighell 1982). Unit cell is outlined in the solid gray line. Image generated using
620   CrystalMaker ® v8.7.6.
621
622   Figure 3. Unit cell volume of trona as a function of temperature.
623
624   Figure 4. Normalized unit-cell parameters as a function of temperature, with lines representing
625   least square fits to our observations. With temperature, the *b*-axis changes by almost a factor of
626   three greater than the *a* and *c* axes.
627
628   Fig 5. Normalized Na-O bond lengths as a function of temperature, with lines representing least
629   square fits to our observations. All Na-O bonds expand with increasing temperature. The long
630   Na_2-O_1 and the short Na_2-O_4 bonds expand substantially more than the any other Na-O bond
631   with temperature.
632
633   Figure 6. Na octahedral and septahedral sites, with changes in Na-O bond angles, and distances
634   between Na_1-Na_1, Na_2-Na_2, O_1-O_1, O_3-O_3, and O_1-O_4 bonds from 100 K to 340 K being labeled.
635   Crystal structure image generated using CrystalMaker ® v8.7.6.
636
637   Figure 7. Representative Raman spectra of trona up to 25.4 GPa (a) fow frequency under
638   compression (b) carbonate v_1 peak under compression (c) low frequency under decompression
639   (d) carbonate v_1 under decompression. Because multiple runs were conducted with trona crystals
640   mounted in different orientations, peak intensities vary between spectra (this is particularly
641   notable in the contrast between the low frequency spectra of samples at 2.0 and 3.9 GPa).
642
643   Figure 8. Peak positions of observed Raman modes in trona as a function of pressure at room
644   temperature, solid circles are compression open circles are decompression. Error bars are smaller
645   than symbols, and vertical dashed lines indicate likely phase transitions. (a) low frequency (b)
646   carbonate asymmetric stretch and I-P bend.
647
648   Figure 9 Representative infrared spectra of trona in the mid-infrared region up to 24.2 GPa (a)
649   under compression (b) under decompression.
650
651   Figure 10 Representative infrared spectra of trona in the hydroxyl stretching region up to 24.2
652   GPa (a) under compression (b) under decompression.
653
654   Figure 11. Peak positions of observed infrared modes in trona as a function of pressure at room
655   temperature. Solid circles are on compression, and open circles are on decompression. Error bars
656   are smaller than the symbols, and vertical dashed lines indicate likely phase transitions. (a)
657   carbonate bending vibrations, H_2O libration, and transmission window; (b) carbonate asymmetric
658   stretches, 1st overtone of 806 cm^{-1}, and a transition or combination band; and (c) O-H stretches of
659   the H_2O molecule.

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661 Figure 12. Infrared spectra of the transmission window shifting as a function of pressure (a)
662 under compression (b) under decompression. Inset in 12b: Schematic diagram of Fermi
663 resonance effect, with the dashed line showing two overlapping modes (one sharp, and one
664 broad) in the absence of a Fermi resonance, and the solid line illustrating the resultant spectrum
665 when Fermi resonance occurs (after Claydon and Sheppard, 1969).
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709   Table 1: Unit cell parameters and experimental details of trona single-crystal refinements.
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T (±2) (K)	100	200	300	320	330	340
Wavelength (Å)	1.54187 (1)	1.54187 (1)	1.54187 (1)	0.61990 (1)	0.61990 (1)	0.61990 (1)
a (Å)	20.366 (3)	20.370 (4)	20.4124 (10)	20.398 (3)	20.402 (4)	20.400 (3)
b (Å)	3.4583 (5)	3.4749 (7)	3.4927 (2)	3.4887 (5)	3.4881 (6)	3.4922 (5)
c (Å)	10.2946 (13)	10.3146 (19)	10.3327 (4)	10.3248 (16)	10.3085 (18)	10.3279 (14)
β (°)	106.483 (9)	106.484 (14)	106.471 (3)	106.545 (8)	106.552 (10)	106.469 (7)
Volume (Å^3)	695.26 (17)	700.1 (2)	706.43 (6)	704.33 (19)	703.20 (2)	705.59 (8)
Z	4	4	4	4	4	4
$N_{reflections}$	624	621	625	1615	1613	1623
N_{unique}	582	560	550	1509	1466	1425
R1 (%)	3.41	4.08	4.26	4.97	4.97	4.18
wR2 (%)	10.65	10.92	11.09	13.88	14.01	13.06
GooF	1.646	1.081	1.112	1.164	1.119	1.167

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713   Table 2: Fractional atomic coordinates as a function of temperature (refined anisotropically).
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Atom	T (K)	x	y	z
Na$_1$	100	0.0000	0.7475 (3)	0.2500
	200	0.0000	0.7466 (3)	0.2500
	300	0.0000	0.7462 (3)	0.2500
	320	0.0000	0.7461 (2)	0.2500
	330	0.0000	0.7460 (2)	0.2500
	340	0.0000	0.7461 (2)	0.2500
Na$_2$	100	0.15092 (4)	0.1598 (2)	0.42574 (7)
	200	0.15081 (5)	0.1620 (3)	0.42569 (9)
	300	0.15064 (5)	0.1641 (3)	0.42549 (8)
	320	0.15053 (3)	0.16492 (17)	0.42604 (6)
	330	0.15050 (4)	0.16531 (19)	0.42606 (6)
	340	0.15053 (3)	0.1657 (16)	0.42604 (6)
C$_1$	100	0.09308 (10)	0.2662 (5)	0.10314 (19)
	200	0.09316 (12)	0.2648 (6)	0.1033 (2)
	300	0.09337 (11)	0.2638 (7)	0.10346 (19)
	320	0.09308 (6)	0.2651 (3)	0.10345 (11)
	330	0.09314 (6)	0.2649 (3)	0.10349 (12)
	340	0.09314 (5)	0.2650 (3)	0.10349 (10)
O$_1$	100	0.15142 (6)	0.4000 (4)	0.10124 (13)
	200	0.15127 (8)	0.4001 (5)	0.10161 (15)
	300	0.15102 (7)	0.3989 (5)	0.10214 (13)
	320	0.15112 (5)	0.3987 (3)	0.10227 (9)
	330	0.15111 (6)	0.3988 (3)	0.10225 (11)
	340	0.15107 (5)	0.3985 (3)	0.10222 (9)
O$_2$	100	0.05416 (7)	0.1293 (4)	0.98697 (13)
	200	0.05436 (6)	0.1299 (5)	0.98764 (15)
	300	0.05424 (8)	0.1300 (5)	0.98804 (13)
	320	0.05441 (5)	0.1298 (3)	0.98799 (9)
	330	0.05457 (5)	0.1300 (3)	0.98818 (10)
	340	0.05448 (5)	0.1303 (3)	0.98812 (9)
O$_3$	100	0.07272 (7)	0.2554 (4)	0.20811 (13)
	200	0.07255 (8)	0.2466 (5)	0.20803 (15)
	300	0.07252 (8)	0.2465 (5)	0.20792 (14)
	320	0.07249 (5)	0.2533 (3)	0.20794 (9)
	330	0.07240 (5)	0.2532 (3)	0.20787 (10)
	340	0.07245 (5)	0.2535 (2)	0.20781 (9)
O$_4$	100	0.21200 (7)	0.6623 (4)	0.35447 (15)
	200	0.21206 (9)	0.6641 (4)	0.35455 (18)

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	300	0.21192 (9)	0.6651 (5)	0.35428 (17)
	320	0.21207 (6)	0.6657 (3)	0.35454 (11)
	330	0.21205 (7)	0.6657 (4)	0.35469 (12)
	340	0.21209 (6)	0.6662 (3)	0.35454 (11)

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717   Table 3: Bond lengths (Å) as a function of temperature and their linear thermal expansion in
718   trona.
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T (±2) (K)	100	200	300	320	330	340	Thermal Expansion
C_1-O_1	1.283 (2)	1.277 (3)	1.228 (3)	1.2760 (13)	1.2756 (15)	1.2747 (13)	-0.0083 (13)
C_1-O_2	1.320 (2)	1.316 (3)	1.321 (3)	1.3152 (14)	1.3127 (16)	1.3151 (13)	-0.0049 (13)
C_1-O_3	1.263 (2)	1.266 (3)	1.268 (2)	1.2649 (13)	1.2640 (14)	1.2651 (12)	0.0021 (12)
Na_1-O_2 x2	2.4139 (13)	2.4244 (16)	2.4327 (14)	2.4297 (10)	2.4265 (11)	2.4327 (10)	0.0188 (18)
Na_1-O_3 x2	2.3750 (15)	2.3813 (18)	2.3893 (18)	2.3869 (11)	2.3862 (12)	2.3857 (10)	0.0107 (18)
Na_1-O_3 x2	2.4134 (15)	2.4162 (18)	2.4255 (18)	2.4232 (10)	2.4225 (12)	2.4237 (10)	0.0103 (18)
Na_2-O_1	2.6479 (15)	2.6640 (18)	2.6786 (19)	2.6769 (12)	2.6754 (14)	2.6801 (12)	0.0322 (19)
Na_2-O_1	2.3588 (15)	2.3665 (18)	2.3738 (17)	2.3697 (11)	2.3661 (13)	2.3689 (11)	0.0101 (18)
Na_2-O_2	2.4453 (15)	2.4518 (18)	2.4609 (17)	2.4546 (11)	2.4551 (13)	2.4553 (11)	0.0101 (17)
Na_2-O_3	2.3744 (15)	2.3773 (18)	2.3829 (16)	2.3787 (12)	2.3769 (13)	2.3828 (11)	0.0232 (16)
Na_2-O_4	2.3596 (14)	2.3689 (19)	2.382 (2)	2.3838 (12)	2.3839 (14)	2.3854 (12)	0.0238 (19)
Na_2-O_4	2.3707 (14)	2.3779 (18)	2.3881 (18)	2.3875 (11)	2.3860 (13)	2.3880 (11)	0.0173 (18)

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724 Table 4: Bond angles of trona as a function of temperature.
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T (±2) (K)	100	200	300	320	330	340
O_1-C_1-O_2	115.95 (16)	116.03 (93)	116.23 (13)	116.17 (10)	116.32 (11)	116.21 (9)
O_1-C_1-O_3	123.63 (17)	123.8 (2)	123.92 (18)	123.66 (11)	123.71 (12)	123.69 (10)
O_2-C_1-O_3	120.42 (17)	120.02 (2)	119.52 (18)	120.16 (10)	119.96 (11)	120.09 (10)
O_2-Na_1-O_2	159.43 (8)	159.64 (9)	159.54 (11)	159.49 (6)	159.48 (7)	159.53 (6)
O_3-Na_1-O_3 x2	179.12 (5)	179.21 (6)	179.18 (7)	179.18 (4)	179.18 (4)	179.14 (4)
O_2-Na_1-O_3 x2	100.48 (5)	100.49 (6)	100.61 (6)	100.60 (3)	100.61 (4)	100.61 (3)
O_2-Na_1-O_3 x2	94.26 (4)	94.15 (5)	94.11 (5)	94.16 (3)	94.17 (4)	94.14 (3)
O_2-Na_1-O_3 x2	79.46 (4)	79.46 (6)	79.34 (6)	79.34 (3)	79.34 (4)	79.34 (3)
O_3-Na_1-O_3 x2	92.47 (5)	92.82 (6)	93.00 (5)	92.98 (3)	93.00 (4)	93.12 (3)
O_3-Na_1-O_3	88.41 (7)	87.97 (8)	87.82 (8)	87.84 (5)	87.83 (6)	87.74 (5)
O_3-Na_1-O_3	86.65 (7)	86.39 (8)	85.74 (6)	86.20 (5)	86.18 (6)	86.02 (5)
O_1-Na_2-O_1	87.18 (5)	87.17 (6)	87.25 (5)	87.24 (4)	87.33 (4)	87.29 (4)
O_1-Na_2-O_2	51.17 (4)	50.73 (5)	50.55 (5)	50.54 (3)	50.53 (4)	50.47 (3)
O_1-Na_2-O_2	83.91 (5)	84.00 (6)	84.10 (6)	84.19 (4)	84.25 (4)	84.28 (4)
O_1-Na_2-O_3	119.33 (6)	119.60 (7)	119.78 (7)	119.96 (4)	119.95 (5)	120.02 (4)
O_1-Na_2-O_3	128.06 (5)	127.81 (6)	127.66 (6)	127.66 (4)	127.57 (4)	127.57 (4)
O_3-Na_2-O_2	85.74 (5)	85.95 (6)	86.04 (6)	86.11 (4)	86.05 (4)	86.09 (4)
O_4-Na_2-O_1	77.16 (5)	76.99 (6)	76.92 (6)	76.87 (4)	76.77 (4)	76.76 (4)
O_4-Na_2-O_1	82.95 (5)	82.92 (6)	83.10 (6)	83.07 (4)	83.03 (4)	83.05 (4)
O_4-Na_2-O_1	145.10 (6)	145.09 (7)	145.17 (7)	145.00 (4)	144.96 (5)	144.98 (4)
O_4-Na_2-O_1	147.85 (6)	147.89 (7)	148.02 (7)	147.85(4)	147.83 (5)	147.86 (4)
O_4-Na_2-O_2	108.49 (5)	108.02 (7)	107.76 (7)	107.74(4)	107.68 (5)	107.57 (4)
O_4-Na_2-O_2	155.58 (6)	155.98 (7)	156.17 (8)	156.41(4)	156.47 (5)	156.51 (5)
O_4-Na_2-O_3	82.90 (5)	82.92 (6)	83.10 (6)	83.19(4)	83.29 (5)	83.25 (4)
O_4-Na_2-O_3	94.53 (5)	94.36 (6)	94.10 (6)	94.07(4)	94.12 (5)	94.06 (4)
O_4-Na_2-O_4	93.96 (5)	94.12 (7)	94.15 (6)	93.97(4)	93.99 (5)	94.04 (4)

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729 Table 5. Raman and infrared modes observed at room temperature and pressure, pressure
730 dependences of peak positions, and calculated mode Grüneisen parameters of trona (some
731 assignments based on Novak et al. (1963), others based on this study).
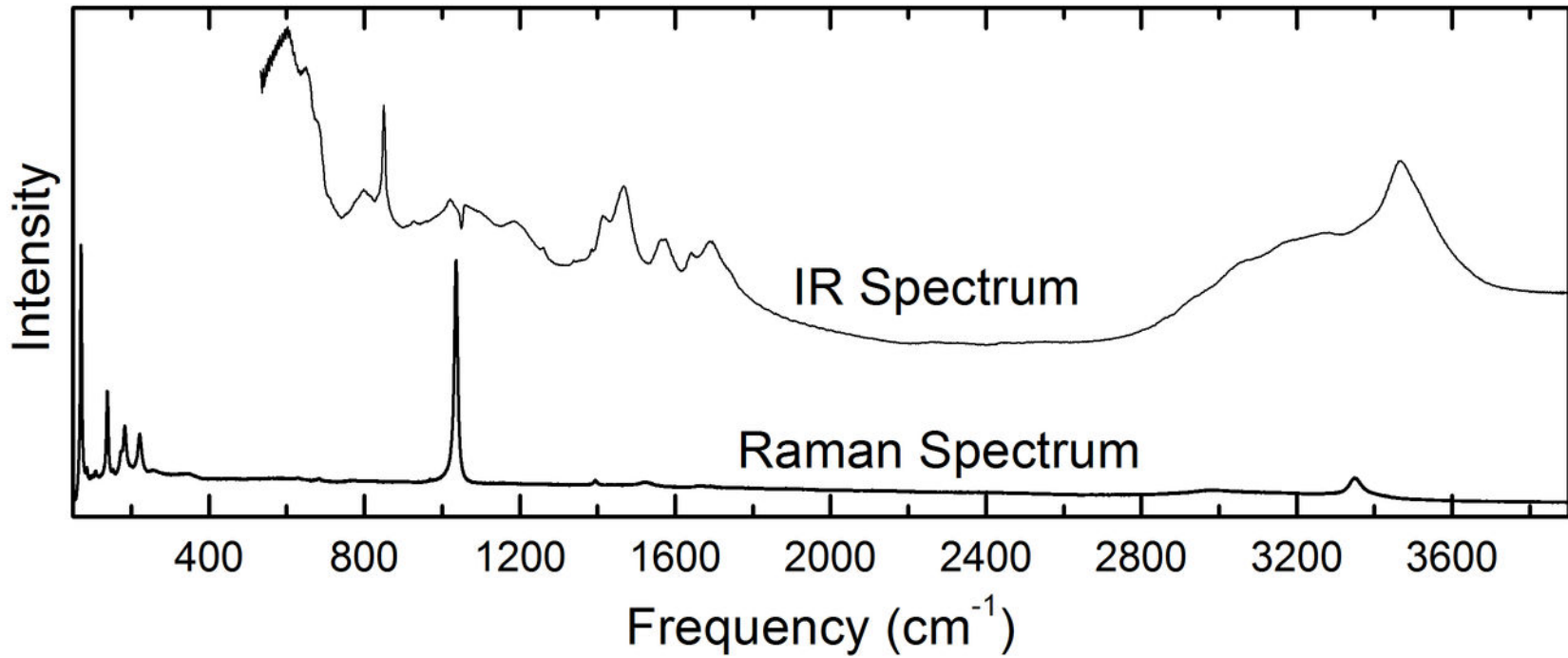732

ν_{0i} (cm^{-1})	Assignment	$(d\nu_{0i}/dP)$ to 7GPa (cm^{-1}/GPa)	γ_i
71	Na-O-Na (R)	1.78 ($\pm$0.24)	0.90
100	Na-O-Na (R)	2.06 ($\pm$0.09)	0.74
108	Na-O (R)	6.03 ($\pm$0.48)	2.01
139	Na-O (R)	4.34 ($\pm$0.31)	1.12
155	Na-O (R)	4.74 ($\pm$0.37)	1.10
172	Na-O (R)	4.69 ($\pm$0.36)	0.98
684	ν_4 (IR)	4.14 ($\pm$0.25)	0.22
699	ν_4 (R)	4.79 ($\pm$0.36)	0.25
710	ν_4 (IR)	5.66 (0.40)	0.29
806	H_2O Lib (IR)	6.21 ($\pm$0.72)	0.28
850	ν_2 (IR)	-1.01 ($\pm$0.10)	-0.04
1051	Transmission Window (IR)	5.89 ($\pm$0.35)	0.20
1060	ν_1 (R)	5.37 ($\pm$0.25)	0.18
1461	ν_3 (IR)	3.80 ($\pm$0.30)	0.09
1557	1st Overtone of 806 (IR)	11.60 ($\pm$1.0)	0.26
1698	O-H··O transition? Combination? (IR)	1.58 ($\pm$0.90)	0.03
1749	O-H··O transition? Combination? (IR)	5.95 ($\pm$0.73)	0.12
3049	H_2O (IR)	-7.98 ($\pm$0.26)	-0.09
3449	H_2O (IR)	-5.46 ($\pm$0.76)	-0.06
3530	H_2O (IR)	-6.10 ($\pm$1.34)	-0.06

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IR Spectrum

Raman Spectrum

Compression

a

25.4 GPa

20.2 GPa

16.4 GPa

14.5 GPa

12.0 GPa

8.8 GPa

5.8 GPa

3.9 GPa

2.0 GPa

0.01 GPa

Intensity

Frequency (cm^{-1})

Compression

b

25.4 GPa

20.2 GPa

16.4 GPa

14.5 GPa

12.0 GPa

8.8 GPa

5.8 GPa

3.9 GPa

2.0 GPa

0.01 GPa

Intensity

Frequency (cm^{-1})

1000 1050 1100 1150 1200

Decompression

21.9 GPa

13.5 GPa

8.1 GPa

2.5 GPa

0.03 GPa

c

Intensity

Frequency (cm^{-1})

100   200   300   700   800

Decompression

d

21.9 GPa

13.5 GPa

8.1 GPa

2.5 GPa

0.03 GPa

Intensity

Frequency (cm^{-1})

Compression

24.2 GPa

17.9 GPa

14.7 GPa

12.5 GPa

10.2 GPa

7.9 GPa

5.7 GPa

4.2 GPa

2.1 GPa

1.3 GPa

0.4 GPa

a

Absorbance

700 800 900 1000   1500 1600 1700 1800

Frequency (cm^{-1})

Decompression

b

20.8 GPa

15.1 GPa

7.8 GPa

1.5 GPa

1.0 GPa

0.3 GPa

Absorbance

Frequency (cm^{-1})

700 800 900 1000   1500 1600 1700 1800

Compression

a

24.2 GPa

17.9 GPa

14.7 GPa

12.5 GPa

10.2 GPa

7.9 GPa

5.7 GPa

4.2 GPa

2.1 GPa

1.3 GPa

0.4 GPa

Decompression

20.8 GPa

15.1 GPa

7.8 GPa

1.5 GPa

1.0 GPa

0.3 GPa

b

Absorbance

Frequency (cm^{-1})

a

Transmission
window

H_2O (Lib)

O-O-P bends (ν_2)

I-P bends (ν_4)

b

Transition or combination?

1st Overtone of 806 cm^{-1}

Asymmetric stretches (ν_3)

C

O-H Stretches
of the H_2O

Compression

a

2.1 GPa

1.3 GPa

0.4 GPa

Absorbance

Frequency (cm^{-1})

1000   1050   1100

Decompression

b

1.5 GPa

1.0 GPa

0.3 GPa

Absorbance

Frequency (cm^{-1})

1000   1050   1100