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Revision 2

Carbonic Acid Monohydrate

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Abstract

In the water-carbon dioxide system, above a pressure of 4.4 GPa, a crystalline phase consisting of an adduct of the two substances can be observed to exist in equilibrium with the aqueous fluid. The phase had been found to be triclinic, and its unit cell parameters determined, but the full crystalline, and even molecular, structure remained undetermined. Here, we report new diamond-anvil cell, x-ray diffraction data of a quality sufficient to allow us to propose a full structure. The crystal exists in the P $\bar{1}$ space group. Unit cell parameters (at 6.5 GPa and 140°C) are a = 5.8508(14) Å, b = 6.557(5) Å, c = 6.9513(6) Å, α = 88.59(2)°, β = 79.597(13)°, and γ = 67.69(4)°. Direct solution for the heavy atoms (carbon and oxygen) revealed CO_3 units, with co-planar, but isolated, O units. Construction of a hydrogen network, in accordance with the requirements of hydrogen bonding and with minimum allowed distances between non-bonded

atoms, indicates that the phase consists of a monohydrate of carbonic acid ($H_2CO_3 \cdot H_2O$) with the carbonic acid molecule in the cis-trans configuration. This is the first experimental determination of the crystalline structure of a H_2CO_3 compound. The structure serves as a guide for ab initio calculations that have until now explored only anhydrous H_2CO_3 solids, while validating calculations that indicated that high pressures should stabilize H_2CO_3 in the solid state. If 4.4 GPa is the lowest pressure at which the phase is thermodynamically stable, this probably precludes its existence in our solar system, although it may exist on larger, volatile-rich exoplanets. If, however, its range of stability extends to lower pressures at lower temperatures (which possibility has not yet been adequately explored) then it might have been be a stable form of CO_2 within the water-rich moons and dwarf planets prior to differentiation, and might still exist on an undifferentiated Callisto.

Keywords: carbonic acid, CO_2, hydrate, high-pressure, single-crystal X-ray diffraction, exoplanets

Introduction

Water and carbon dioxide are ubiquitous compounds in the biological and geological sciences. Their 1:1 adduct, carbonic acid (H_2CO_3), and its two anions, bicarbonate (HCO_3^-) and carbonate (CO_3^{-2}), engage in an important set of reactions governing the solubility of CO_2 and the pH of systems critical to life and planetary processes. However, owing to unfavorable kinetics and equilibrium constants at ambient conditions (Loerting et al. 2000), molecular carbonic acid has

long eluded detailed experimental observation and, as described below, a crystalline structure had not previously been determined. Recently, Wang et al. (2016) claimed to have observed the formation of solid carbonic acid at high pressures, and Abramson et al. (2017) demonstrated that the observed phase can exist in thermodynamic equilibrium with the aqueous fluid for pressures beyond a quadruple point at 4.4 GPa. Preliminary X-ray results indicated that the new phase was triclinic, but their quality did not allow a refinement of the crystal structure. Here, new X-ray diffraction data of the high-pressure phase provide further insight into its structure. Despite remaining uncertainties pertaining to the hydrogen network, the results confirm the presence of H_2CO_3 molecules, and indicate that the crystal consists of a monohydrate of the acid. Our results complete the initial experimental reports describing that phase, validate calculations which indicated that high pressures should stabilize H_2CO_3 in the solid state, and offer a structure for a H_2CO_3 hydrate as a guide to further calculations.

Prior Studies

Over the past three decades, attempts to synthesize H_2CO_3 have led to the development of numerous protocols divided among four main strategies. 1. **The vacuum thermolysis of carbonates** led to the first reported synthesis of H_2CO_3, in the vapor phase; originally using ammonium bicarbonate (Terlouw et al. 1987), the process was more recently accomplished with di-tert-butyl carbonate (Reisenauer et al. 2014). 2. **The irradiation of CO_2 and H_2O ices** produced the first H_2CO_3 solid; the initial experiment involved the proton irradiation of CO_2 + H_2O mixtures (Moore and Khanna 1991), but both UV photolysis (Gerakines et al. 2000; Wu et al. 2003) and electron irradiation of the mixtures (Zheng and Kaiser 2007), as well as the proton

irradiation of pure CO_2 ice (Brucato et al. 1997; Garozzo et al. 2008) have also been successful. 3. **The ionization of CO_2 and H_2O gases** has been used to produce radicals for recombination into H_2CO_3, either directly in the gas phase (Mori et al. 2009, 2011), or in the solid state by deposition of OH radicals onto CO ice (Oba et al. 2010). 4. Finally, **the protonation of carbonates** has been explored to produce H_2CO_3 in various states; short-lived aqueous H_2CO_3 was produced by reacting acids with $NaHCO_3$ (Falcke and Eberle 1990; Lam et al. 2014), Na_2CO_3 (Soli and Byrne 2002), or DCO_3^- (Adamczyk et al. 2009); similarly, solid H_2CO_3 has been synthesized through reactions in aqueous glasses, combining acids with K_2CO_3 or $KHCO_3$ (Hage et al. 1995, 1996; Bernard et al. 2013), or particulate $CaCO_3$ (Bernard et al. 2012); as well, dry vapors of acids reacted with particulate $CaCO_3$ (Al-Hosney and Grassian 2004, 2005; Al-Hosney et al. 2005) have produced adsorbed H_2CO_3.

Following the first synthesis of solid H_2CO_3 (Moore and Khanna 1991), spectral analyses have typically relied upon IR absorption and/or Raman spectroscopies. Direct confirmation of the molecular composition has been confined to the gas phase syntheses, through neutralization-reionization mass spectrometry (Terlouw et al. 1987) and microwave spectroscopy (Mori et al. 2009, 2011); X-ray diffraction patterns were reported for an amorphous solid (Winkel et al. 2007), however attempts to provide diffraction patterns of a crystallized sample were inconclusive (Mitterdorfer et al. 2012; Bernard et al. 2013). These limitations gave room to the belief, for two decades, that two different configurations of H_2CO_3 (then designated as α-H_2CO_3 and β-H_2CO_3) had their own distinct amorphous, crystalline, and vapor phases preserved through sublimation and condensation (Hage et al. 1995, 1996, 1998; Bernard et al. 2011, 2013); not until

2014 was it discovered that only one of these phases (β-H_2CO_3) pertained to H_2CO_3, while the putative α-H_2CO_3 actually consisted of the related monomethyl ester (Reisenauer et al. 2014).

Efforts to predict possible crystalline structure(s) for H_2CO_3 through ab initio calculations have yielded a variety of solutions with differences in energy levels smaller than the uncertainties (Winkel et al. 2007; Reddy et al. 2011). Simulations of the C-H-O system suggest that pressure has a stabilizing effect on H_2CO_3, allowing several of its polymorphs, and a polymerized form, to exist (at 0 K) between ~1 and ~300 GPa (Saleh and Oganov 2016). In contrast to the computational results, experimental studies of the H_2O-CO_2 system under pressure had found only two gas hydrates of CO_2 (Sloan and Koh 2007; Tulk et al. 2014; Amos et al. 2017), both existing only below 1 GPa and decomposing into ices of their component molecules when brought to higher pressures (Hirai et al. 2010; Bollengier et al. 2013; Tulk et al. 2014; Massani et al. 2017). (The cryogenically prepared, amorphous carbonic acid, or its annealed form (Kohl et al. 2009), may be stable at high pressures but, to our knowledge, this possibility has not been tested.)

Recently, a new CO_2-H_2O compound was observed above 2.4 GPa and asserted to be H_2CO_3 based on IR and Raman lines similar to those of the low pressure H_2CO_3 solid (Wang et al. 2016). Following this initial report, we (Abramson et al. 2017) demonstrated that this new phase can exist in equilibrium with an aqueous fluid (starting from a quadruple point with ices H_2O(VII) and CO_2(I), at 4.4 GPa and 165 °C), which allowed the growth of single crystals for purposes of X-ray diffraction. However, non-hydrostatic strains in the crystal degraded the

quality of the data, and only the lattice parameters of the triclinic crystal were determined; its full structure, and chemical composition, remained unknown.

Methodology

A CO_2-H_2O mixture was loaded at the University of Washington into a Merrill-Bassett type diamond-anvil cell (DAC) equipped with a 40 μm thick rhenium gasket. The cell contents were estimated at 30 mol% CO_2 from visual observation of the loaded sample. Pressure was measured to a precision of 0.1 GPa, using the Raman scattering from a chip of cubic boron nitride (cBN) placed inside the sample chamber; excitation was provided by a 20 mW, 488 nm laser source. Temperature was measured to an accuracy of 1 K through use of type K thermocouples. Further details are given in Abramson et al. (2017). Single crystals were grown between pressures of 5 and 6 GPa by slow cooling (2 °C/min) of the H_2O-CO_2 fluid mixture after a few nuclei had been isolated (figure 1); after crystallization, further cooling brought the pressure to 6.5 GPa.

The DAC was brought to the European Synchrotron Radiation Facility in Grenoble, France, for single-crystal X-ray diffraction on beamline ID15b. Prior to data collection, the DAC was placed in an external resistive heating system and brought to 140 ±2 °C to allow partial annealing of residual strains; this produced an appreciable improvement in the sharpness of reflections. Data were acquired using a wavelength of 0.4108 Å and a beam diameter of 10 μm FWHM. The Bragg peaks from one crystal were collected on a MarCCD® flat panel detector (MAR555) using the scan mode from -28° to +28° with an increment of 0.5° and an exposure time of 1 s. The location of the collection spot (indicated in figure 1B) was chosen to provide a maximum

thickness of single crystal, to avoid areas suspected to be subject to a greater non-hydrostatic strain, and to limit shadowing from the gasket.

Data collection was 20.4% complete to 25° in θ. In total, 243 reflections were collected, covering the indices $-6 \leq h \leq 6$, $-3 \leq k \leq 4$, and $-7 \leq l \leq 7$. Of these, 165 reflections were symmetry independent with $R_{int} = 0.0337$. Indexing and unit cell refinement indicated a primitive triclinic lattice. The space group was found to be P $\bar{1}$ (no. 2). The unit cell parameters closely match those previously obtained at the Advanced Light Source in Berkeley (Abramson et al. 2017). Angles ($\alpha = 88.59(2)°$, $\beta = 79.60(1)°$, and $\gamma = 67.69(4)°$) agree within 0.1% while the new cell dimensions ($a = 5.851(1)$ Å, $b = 6.557(5)$ Å, and $c = 6.951(1)$ Å) are 0.5% smaller, possibly due to a slight compression resulting from the elevated temperature of the DAC (pressure was not measured during data collection). The data were integrated and scaled using the CrysAlisPro software (Rigaku Oxford Diffraction, 2015). Empirical absorption corrections were applied using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm (Oxford Diffraction, 2006).

Structure Refinement

A multi-step iterative approach based on plausible constraints was required to provide a full structure for this triclinic crystal. After an initial model was obtained by direct solution, the structure was completed by difference Fourier synthesis with SHELXL (Sheldrick 2015) using scattering factors from Waasmair and Kirfel (1995). All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. The locations of hydrogen atoms were then

155 determined based on the geometry of the carbon-oxygen structures and appropriate hydrogen-
156 bonding behavior. Crystallographic data are provided as supplementary material in a CIF file.
157 The process used to refine the structure is detailed below.
158
159 Initially, the direct solution produced a partial model with two CO_3-resembling electron density
160 maxima per asymmetric unit of the space group. Two isolated oxygen atoms were found in the
161 vicinity of the CO_3 groupings. The CO_3 and O components are co-planar but separated by more
162 than 2 Å, precluding a covalent bond. To refine the CO_3 geometries, their angles and bond
163 lengths were restrained to be as equivalent as possible while adequately fitting the data. In a
164 search for a shorter C-O distance in each grouping (as expected from a double bond), only one
165 out of nine possible permutations of one short and two long bonds per CO_3 gave a satisfying R1,
166 and it was subsequently adopted. Since neither the bond lengths nor the angles were fixed, the
167 existence of one double bond in, and the planarity of, each CO_3 was confirmed.
168
169 The last step in completing the structure consisted of placing hydrogen atoms in geometrically
170 ideal positions. The relative orientations of the CO_3 were examined for possible H-bonds, for
171 which distance and angles matter (figure 2). Starting with the single-bonded oxygens of the CO_3,
172 the closest receptor for the hydrogen of O4 is the double-bonded O3. O3 is also at an appropriate
173 distance to act as a receptor for a hydrogen on O7. The geometries of the water molecules (O7
174 and O8) were then restrained with hydrogens set at 0.8 Å, resulting in a quasi-rigid model
175 allowed to rotate freely. The second hydrogen on O7 was assumed to bond with the closest out-
176 of-plane oxygen acceptor. With O4 and O7 set with H-bonds to O3, the hydrogen on O5 was set

177 towards O8, giving the H_2CO_3 molecule a cis-trans configuration. The hydrogen on O1 aligned
178 appropriately for hydrogen bonding without an added constraint. Once this satisfactory network
179 was complete, a few H···H distances fell in the 2.00-2.07 Å range, slightly below the minimum
180 allowed distance of 2.1 Å, requiring an anti-bumping restraint. All hydrogens (with O-H bonds
181 restrained at 0.8 Å) could finally be assigned an appropriate orientation.
182
183 **Discussion**
184 The limited angular access available in a diamond-anvil cell, the low symmetry of the crystal,
185 and the small scattering cross-section of the hydrogen atoms all contributed to the challenge of
186 determining this structure. However, the direct method unambiguously determined the presence
187 of the CO_3 and O components, yielding the formula with respect to C and O. The distances
188 between neighboring components (CO_3 and O) imply that they are isolated, precluding the
189 presence of more complex C-O-H molecules (notably the orthocarbonic acid H_4CO_4 of
190 equivalent bulk formula (Saleh and Oganov 2016), or dicarbonic acid $H_2C_2O_5$ (Zeller et al. 2005;
191 Zhang et al. 2013)). Since only hydrogen atoms are available to bond with the CO_3, molecular
192 H_2CO_3 is required in the structure. Consequently, the final crystal formula (CH_4O_4), the presence
193 of carbonic acid and its ratio to water, and the co-planar arrangement within the same (110)
194 planes of the oxygen and carbon of the carbonic acid, and oxygen of the water molecules, are
195 definitive conclusions of this work, independent of the subsequent interpretative steps used to
196 refine the hydrogen network. The final structure reached at the end of the last steps is fully
197 compatible with our dataset. As well, the calculated density of 2.194 g/cm^3 exceeds that of

198 H_2O(VII), 1.72 g/cm^3, consistent with the observation that the monohydrate will sink in the same
199 solution in which the latter will float (Abramson et al. 2017).
200
201 In our final structure, the H_2CO_3 and H_2O molecules are organized on parallel, H-bonded sheets
202 in (110) lattice planes (figure 3). Within each sheet, H_2CO_3 molecules form (hydrogen-bonded)
203 chains parallel to the c-axis with water providing in-plane hydrogen bonding between adjacent
204 chains. To our knowledge, ab initio calculations have only investigated pure H_2CO_3 structures so
205 far, limiting the relevance of direct comparisons with the present monohydrate; however, low-
206 pressure structures have indeed been said to favor chain- or sheet-like configurations (with the
207 planes of the individual H_2CO_3 molecules coincident with the crystal planes) (Reddy et al. 2011;
208 Saleh and Oganov 2016), as opposed to 3D networks for higher-pressure, polymerized structures
209 (Saleh and Oganov 2016).
210
211 The main uncertainty in our solution is in the determination of the hydrogen network. The
212 proximity of the H_2CO_3 molecules suggests H bonds exist between them; in turn, the relative
213 orientation of the molecules (i.e. the position of the C=O bonds) suggests that the H_2CO_3 are in a
214 cis-trans configuration (as explained in the Structure Refinement section). Although the cis-cis
215 conformer has been identified as the most stable configuration for the isolated H_2CO_3 molecule,
216 for H-bonded H_2CO_3 molecules, and for H_2CO_3-H_2O complexes (see (Mori et al. 2009) and
217 references therein, and (Bernard et al. 2013)), the cis-trans conformer is considered a close
218 second (in comparison with the clearly less stable trans-trans), as well as a necessary step on the
219 decomposition (formation) pathway to (from) CO_2 + H_2O (Mori et al. 2009).

220

221 **Implications**

222 The present work provides the first characterization of the structure of a crystal containing the
223 H_2CO_3 molecule, which is additionally the only known example of a solid H_2CO_3 compound in
224 conditions of established thermodynamic equilibrium (i.e. a demonstrated, reversible transition).
225 The results validate calculations that indicate that high pressures can stabilize H_2CO_3 in the solid
226 state (Saleh and Oganov, 2016). The confirmation of the existence of a stable H_2CO_3 compound,
227 of its formation in the hydrated state, and of equilibrium with the aqueous fluid, may prove
228 useful both as a guide to future computational searches for stable structures within the H_2O-CO_2
229 system, and in stimulating further experimental exploration of this system.

230

231 In the absence of other H_2O-CO_2 solids reported between 1.0 GPa (the upper limit of the known
232 CO_2 gas hydrates) and 4.4 GPa (the lower end of the proven stability field of the present
233 structure (Abramson et al. 2017)), the H_2CO_3 monohydrate may define the lower pressure
234 boundary of an extended domain of additional H_2O-CO_2 compounds: the present monohydrate
235 was reportedly observed up to 25 GPa (Wang et al. 2016), while simulations suggest a transition
236 around ~300 GPa from various polymorphs and polymers of H_2CO_3 to H_4CO_4 (Saleh and
237 Oganov, 2016). Alternatively, this (or other) carbonic acid hydrate(s) may exist between 1 and
238 4.4 GPa, but at temperatures below the solidus, where sluggish rates of solid-solid transitions
239 would have precluded their observation (note that in common hydrate-forming systems, e.g.,
240 H_2O-$MgSO_4$ (Chou and Seal 2007), lower temperatures favor the formation of higher hydrates).

241

242 Restricting our attention to the present H_2CO_3 monohydrate, if 4.4 GPa is indeed the lower
243 pressure limit of its thermodynamic stability, this would likely preclude its existence in our solar
244 system. Ices within the (now differentiated) water-rich moons and dwarf planets of the outer
245 solar system do not achieve sufficiently high pressures, while in Earth, Neptune and Uranus,
246 temperatures at the requisite pressure are too high. Although radiolysis of mixed H_2O/CO_2 ices,
247 or proton implantation into water ice, is believed to produce H_2CO_3 as a metastable molecule on
248 the surfaces of icy bodies, there has been no evidence that the monohydrate is formed in these
249 processes. If, however, lowering of temperature allows the hydrate to exist stably at lower
250 pressures (and this hasn't yet been explored), then it might have been a stable form of CO_2 within
251 the water-rich moons and dwarf planets prior to differentiation, and might still exist on (a
252 partially differentiated) Callisto. Of course, considering the prevalence of C-H-O fluids in
253 planetary processes, the present H_2CO_3 monohydrate may be supposed to exist in some of the
254 (larger, volatile-rich) exoplanets of current interest.
255

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Figure Captions

Figure 1. (**a**) Photomicrograph of the pressure chamber during growth of euhedral crystals from the fluid phase. (**b**) After cooling to room temperature. The small, dark cross-hairs indicate the approximate location of X-ray impingement during data collection.

Figure 2. ORTEP of the structure with thermal ellipsoids at the 50% probability level.

Figure 3. (**a**) Illustration of the layered structure of the crystal with the (110) sheets. The box of solid, black lines represents the unit cell dimensions. (**b**) View perpendicular to a (110) sheet, showing the cis-trans configuration of the carbonic acid molecules and hydrogen-bonded chains of H_2CO_3 along the c-axis. C, O and H atoms are depicted as black, red and pink spheres, respectively.

Figure 1

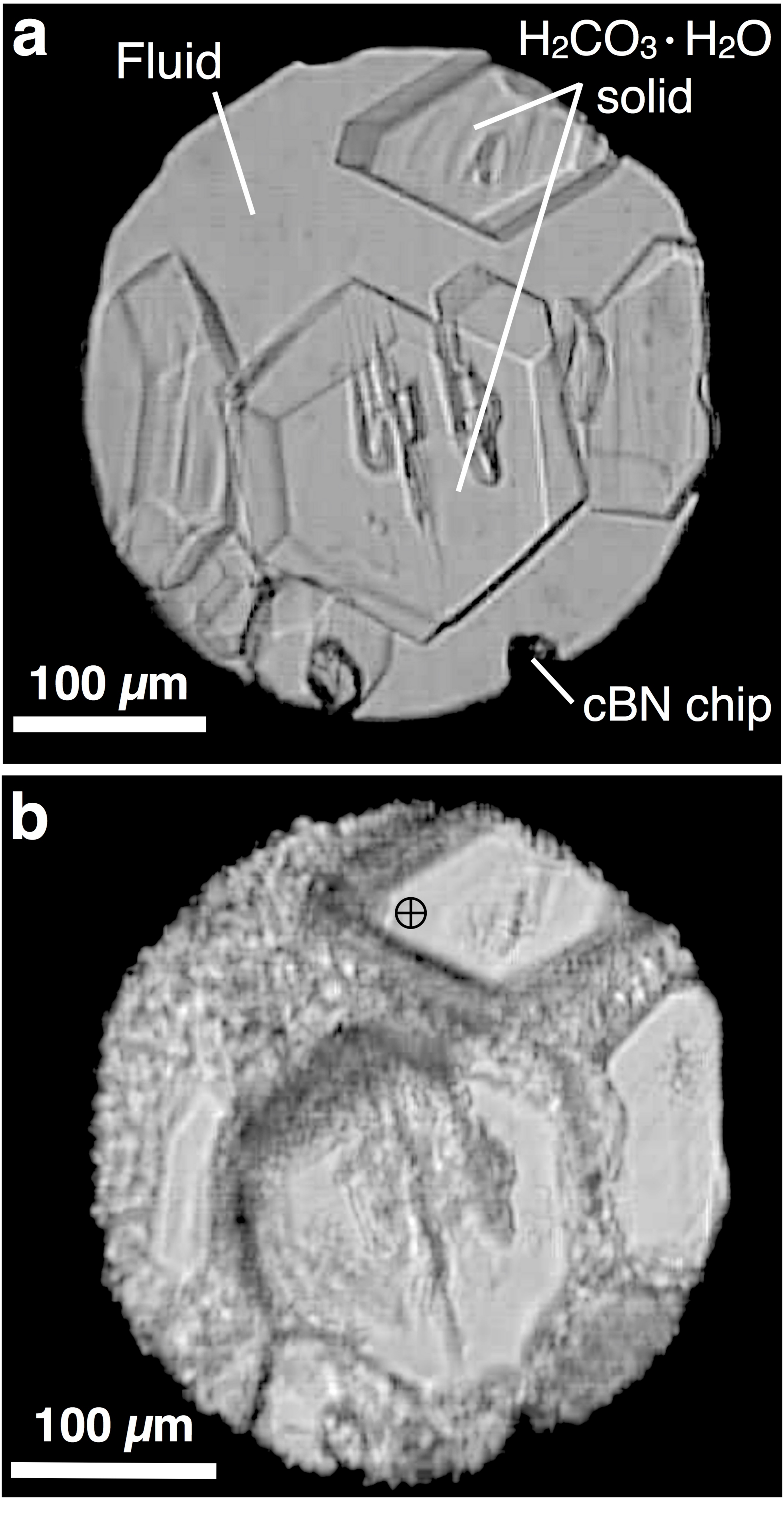

Figure 2

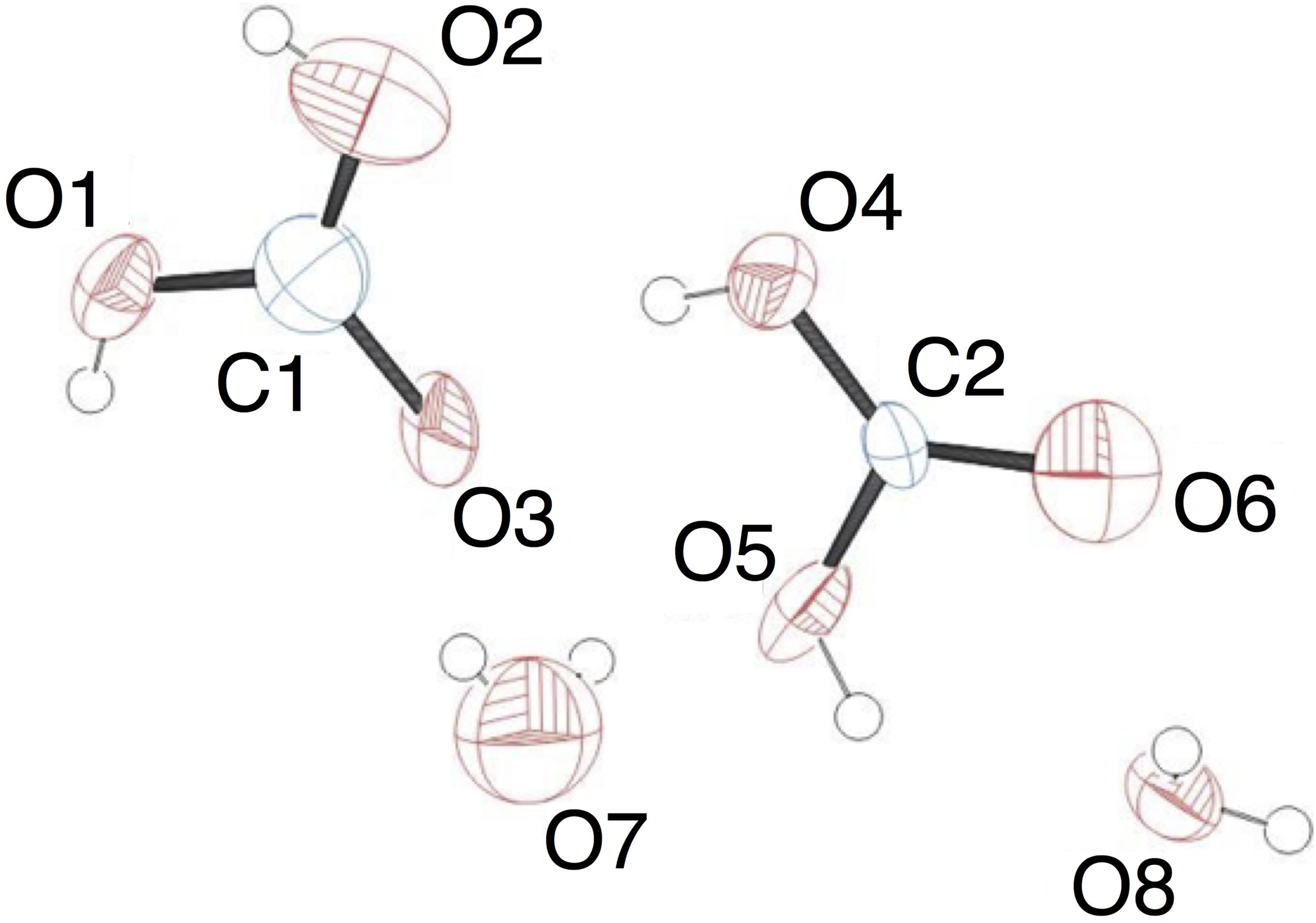

Figure 3