

Thermodynamics of the C-O-H System at High Pressures. E. H. Abramson¹, O. Bollengier¹, and J. M. Brown¹,
¹Department of Earth and Space Sciences, University of Washington, Seattle (WA), United States (corresponding author: obollengier@gmail.com)

Introduction: An understanding of C-O-H fluids at high pressure in deep oceans and in deeper rock layers is prerequisite in efforts to understand the availability of carbon in habitable environments. How carbon is transported and sequestered (and in which phases) depends on fluid speciation and details of phase equilibria. Our investigations of the water-carbon dioxide system at high pressure are highlighting problems inherent in current geochemical models.

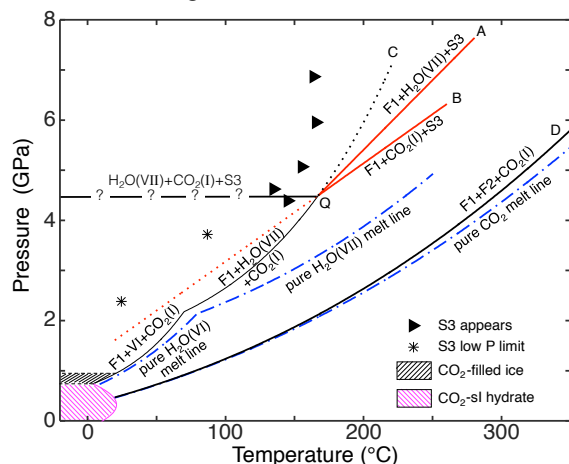


Figure 1 : Phase boundaries of the low-temperature water-carbon dioxide binary [1].

Approach: Below 1 GPa, two CO₂ hydrates (a sI clathrate and a filled ice) have been reported (Fig.1). Filled triangles demark where the new phase (S3) has been observed to nucleate upon heating. Asterisks indicate pressures below which S3 was seen to decompose. The black dotted line indicates the metastable extension of the CO₂-saturated H₂O(VII) solidus to higher temperatures in the absence of S3, and the red dotted line the metastable extension of the solidus of S3 to lower temperatures. Curves labeled "A" through "D" correspond to an eutectic, a peritectic, another eutectic, and a melting point, respectively. F1 is an aqueous solution, while melting of CO₂ produces a fluid, F2, dominated by that compound. The invariant quadruple point, "Q" (H₂O(VII) + CO₂(I) + S3 + F1), lies at 4.4 GPa and 165°C.

Figure 2 presents the Raman spectra of a 26 mole% solution of carbon dioxide in water contain a line due to dissolved, aqueous CO₂ at ~1390 cm⁻¹ (right inset); pressure is raised, this line is seen to disappear [2]. At the same time, another line (left inset) appears at ~1040 cm⁻¹. Clearly, the already dissolved, CO₂(aq) is reacting to form a new species. This shift in speciation

occurs in conjunction with a rapid dissolution of the majority CO₂ fluid into the aqueous phase, and can be assumed to explain the greatly enhanced solubility.

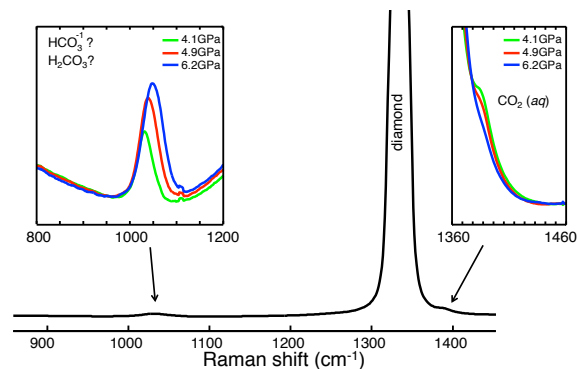


Figure 2

We find that a solid phase containing H₂O and CO₂ (possibly carbonic acid, H₂CO₃) forms in equilibrium with the fluid phase beyond a quadruple point at 4.4 GPa and 165°C [3]. Single-crystal X-ray diffraction revealed a triclinic crystal with unit cell parameters (at 6.5 GPa) of $a = 5.88 \text{ \AA}$, $b = 6.59 \text{ \AA}$, $c = 6.99 \text{ \AA}$, $\alpha = 88.7^\circ$, $\beta = 79.7^\circ$, and $\gamma = 67.7^\circ$.

The two-fluid phase immiscibility surface extends to 7 GPa and 450 °C [3]. A key finding is that commonly used equations of state for water and carbon dioxide are unable to correctly describe the experimentally determined fluid-fluid phase relationships. The primary cause of this discrepancy is that at higher pressures, in contrast to the assumption commonly made in computer calculations or when parametrizing equations of state, dissolved carbon dioxide no longer exists as the aqueous molecule.

References: [1] Abramson, E. H. (2017a). accepted for publication in *J. Phys.: Conf. Ser. Joint 25th AIRAPT International* [2] Abramson, E.H., et al. (2017b). Submitted to *Scientific Reports*. [3] Abramson, E.H., et al. (2017c). In prep. for *Geochemica et Cosmochimica Acta*.