SUPPORTING INFORMATION: Carbon Dioxide, Bicarbonate and Carbonate lons in Aqueous Solutions at Deep Earth Conditions

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Determination of the acidic/basic character of the solution

Due to a strong dependence on pressure and temperature of the self-ionization constant of water $K_w^{1,2}$, the relation between the concentration of hydroxide ions and the concentration of hydronium ions

$$[H_3O^+][OH^-] = K_w$$
(1)

implies that the neutralility conditions of $[H_3O^+] = [OH^-]$ is no longer pH = 7, but varies according to thermodynamic conditions of the solution. For this reason, to properly determine the acidity/basicity of the solution we considered directly the ratio $[H_3O^+]/[OH^-]$, specifically the quantity

$$f = pH - pOH = -\log_{10} \frac{[H_3O^+]}{[OH^-]}$$
(2)

Regardless on temperature and pressure conditions, the neutrality is identified by f = pH - pOH = 0. However, to calculate such quantity, we considered experimental K_w values² corresponding to the thermodynamic contitions of our simulations

Table S1 Autoionization constant of water at different thermodynamic contitions, obtained by Holzapfel².

P [GPa]	log ₁₀ K _w				
	1000 K	1600 K			
2	-5.488	_			
3	-4.626	-4.718			
4	-4.035	-4.085			
5	_	-3.653			
6	_	-3.221			
7	-2.839	_			
8	-2.436	_			
9	_	-1.953			
10	_	-1.636			
11	-1.398	-			

We ran simulation containing three different solvated carbon species: CO_2 , HCO_3^- , or CO_3^{2-} . The proton-exchange reaction determine whether the solution becomes acidic or basic.

\mathbf{CO}_2

When the solvated species is CO_2 , it can react into HCO_3^- or CO_3^{2-} . In both cases the solution can only become acidic because the reaction

$$CO_2 + 2H_2O \Longrightarrow HCO_3^- + H_3O^+$$

produces one hydronium ion $\mathrm{H}_3\mathrm{O}^+$ and the reaction

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$$

produces a further hydronium ion.

In this case, the equilibrium relation is $[H_3O^+]_{eq}[OH^-]_{eq} = ([H_3O^+]^* + x)x = K_w$ where the subscript 'eq' identifies the overall concentration at the equilibrium and the quantity $[H_3O^+]^*$ is the concentration of hydronium ion produced from the proton-exchange reaction. Solving for the x, which stands for the concentration of hydronium/hydroxide ions at the investigated thermodynamic conditions relative to the considered K_w, we obtain that

$$[H_{3}O^{+}]_{eq} = \frac{[H_{3}O^{+}]^{*}}{2} + \frac{\sqrt{[H_{3}O^{+}]^{*2} + 4K_{w}}}{2}$$

$$[OH^{-}]_{eq} = \frac{-[H_{3}O^{+}]^{*}}{2} + \frac{\sqrt{[H_{3}O^{+}]^{*2} + 4K_{w}}}{2}$$
(3)

which contain only known quantities and can be used to calculate the quantity reported in Eq. 2.

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 CO_{3}^{2-}

When the solvated species is CO_3^{2-} , it can react into HCO_3^- or CO_2 and this case is very similar to the previous one with the only difference that the solution can only become basic. In fact the reaction

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^{-} + OH^{-}$$

produces one hydroxide ion OH^- and the reaction

$$HCO_3^- + H_2O \rightleftharpoons CO_2 + OH^-$$

produces a further hydroxide ion. Following the above procedure, it is found that $[H_3O^+]_{eq}[OH^-]_{eq} = x(x+[OH^-]^*) = K_w$ where $[OH^-]^*$ is the concentration of hydroxide ion produced from the aforementioned reactions. Now the two ion concentrations read as

$$[H_{3}O^{+}]_{eq} = \frac{-[OH^{-}]^{*}}{2} + \frac{\sqrt{[OH^{-}]^{*2} + 4K_{w}}}{2}$$

$$[OH^{-}]_{eq} = \frac{[OH^{-}]^{*}}{2} + \frac{\sqrt{[OH^{-}]^{*2} + 4K_{w}}}{2}$$
(4)

HCO₃

Finally, when the solvated species is HCO_3^- the results of the proton-exchange reaction can either turn the solution more acidic or more basic. In fact, when it becomes CO_2

$$HCO_3^- + H_2O \Longrightarrow CO_2 + OH^-$$

a hydroxide ion is produced, while when it becomes CO_3^{2-}

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$$

a hydronium ion is produced. Hence, Eq. 1 now becomes $([H_3O^+]^* + x)(OH^-]^* + x) = K_w$ because at the equilibrium both the concentration have changed. The solution of the equation produces the two equilibrium concentrations

$$[H_{3}O^{+}]_{eq} = \frac{[H_{3}O^{+}]^{*} - [OH^{-}]^{*}}{2} + \frac{\sqrt{([H_{3}O^{+}]^{*} + [OH^{-}]^{*})^{2} + 4(K_{w} - [H_{3}O^{+}]^{*}[OH^{-}]^{*})}}{2}$$

$$OH^{-}]_{eq} = \frac{-[H_{3}O^{+}]^{*} + [OH^{-}]^{*}}{2} + \frac{\sqrt{([H_{3}O^{+}]^{*} + [OH^{-}]^{*})^{2} + 4(K_{w} - [H_{3}O^{+}]^{*}[OH^{-}]^{*})}}{2}$$
(5)

The calculated value for the quantity in Eq. 2 are reported together with molecular fractions in the following Section.

Molecular composition of carbon in aqueous solution as a function of temperature, pressure and pH

Table S2 Fraction of carbon species in aqueous solution at T = 1000K. In the first column is reported the starting molecule in solution.

CO_{3}^{2-}
0.0
0.0
22.2
16.2
20.5
24.7
18.7
25.0
35.3
-

Table S3 Fraction of carbon species in aqueous solution at T = 1600K. In the first column is reported the starting molecule in solution.

	P [GPa]	рН-рОН	CO_2/H_2CO_3	HCO_3^-	CO_{3}^{2-}
CO ₂	3.3 ± 0.9	-3.19	80.5	19.5	0.0
	5.3 ± 1.0	-2.38	77.5	22.5	0.0
	8.9 ± 1.1	-2.26	1.7	77.0	20.3
HCO ₃ ⁻	3.8 ± 0.9	1.84	13.0	82.6	4.5
	5.6 ± 1.0	-1.89	3.5	78.4	17.1
	10.2 ± 1.2	-0.66	3.1	72.6	24.3
CO ₃ ^{2–}	4.0 ± 0.9	3.98	12.5	69.2	18.3
	5.6 ± 1.0	3.08	9.5	64.4	26.1
	10.4 ± 1.2	0.75	5.4	14.9	89.7

Solvation shell of solvated carbon species at T = 500 K



Fig. S1 Atomistic representation of the solvation shell at T = 500K. (a) CO₂, (b) HCO₃⁻, (c) CO₃²⁻. Blue sphere represents the carbon atom, red spheres represent oxygen atoms and white spheres represent hydrogen atoms. CO₂does not form any hydrogen bond.

Solvation shell of solvated carbon species as a function of pressure and temperature



Fig. S2 Radial distribution functions between carbon atom and the water oxygens at different thermodynamic contitions. Top panels: g(r) for carbon dioxide as initial species in solution (not enough data at T = 1000K, T = 1600K and high pressure). Middle panels: g(r) for bicarbonate ion as initial species in solutions. Bottom panels: g(r) for carbonate ion as initial species in solutions.

Diffusion as a function of pressure and temperature



Fig. S3 Mean square displacement of water molecules calculated for both oxygen and hydrogen atoms for different pressures and different temperature. At lower temperature and high pressure, or high temperature and low pressure, the two species diffuse with the same velocity, while at high temperature and pressure the two MSD starts two diverge from the first picoseconds. This suggests the onset of a transition from the molecular to the ionic phase, as the water autoionization constant at these conditions is estimated to approach $K_w \sim 1.^2$. The calculated diffusion coefficients are: $D_H = 11.29$ Å/ps² and $D_O = 11.28$ Å/ps² for panel a, $D_H = 27.1$ Å/ps² and $D_O = 26.5$ Å/ps² for panel b, and $D_H = 18.28$ Å/ps² and $D_O = 16.72$ Å/ps² for panel c. The difference is, respectively, < 0.1%, 2.2%, and 9.3%.

Notes and references

[1] S. D. Hamann and M. Linton, Transactions of the Faraday Society, 1969, 65, 2186–2196.

[2] W. B. Holzapfel, The Journal of Chemical Physics, 1969, 50, 4424-4428.