OCEANS ON MARS: WHITHER CARBONATE? John Longhi and Taro Takahashi, Lamont-Doherty Earth Observatory, Palisades, NY 10964 (longhi@ldeo.columbia.edu)

Calculations of carbonate stability in bodies of standing water under martian surface conditions are the basis for positing carbonate deposits as major CO$_2$-reservoirs in climate history models (e.g.,1). To date, extensive deposits of carbonate have not been reported, whereas extensive deposits of Ca-sulfate have been detected (2). The failure to observe extensive carbonate deposits on Mars either from orbit or by rover has cast some doubt on the one-time existence of a thick (P $\geq$ 1 bar) CO$_2$ atmosphere that might have warmed the surface enough to stabilize an extensive water ocean (3). Widely referenced sets of carbonate stability calculations (4,5) did not include the effects of sulfate ions on carbonate stability. Here we present here some simple calculations that map out part of the range of carbonate and sulfate stability in a martian ocean.

Carbonate stability is typically calculated in aqueous environments by first considering the set of equilibria that define the dissolution of CO$_2$ gas into water, followed by reaction of CO$_2$ with water to form HCO$_3^-$ and CO$_3^{2-}$ ions, and ultimately combination of Ca$^{2+}$ and carbonate species to form crystalline carbonate. Apparent dissociation constants (K) for these equilibria are then cast in terms of concentrations “(xy)” of the various species and the various equations are solved simultaneously to obtain approximate concentrations for the parameters of interest in units of moles/kg. The values of the K-terms depend on the salinity of the aqueous solution and for want of better constraints and to make our calculations as consistent with previous calculations as possible, we employ values derived for terrestrial seawater at 5°C (6). Thus:

$$\text{(0) } \text{CO}_2 \text{ atm} = \text{CO}_2 \text{ aqu } \Rightarrow \text{(CO}_2\text{)} \text{ aqu} = K_0 \text{pCO}_2 \text{ atm} \text{ where } K_0 = 5.2 \times 10^{-2}$$

$$\text{(1) } (\text{CO}_2\text{)} \text{ aqu} + (\text{H}_2\text{O}) = (\text{HCO}_3\text{)} \text{ aqu} + (\text{H}^+) \text{ aqu } \Rightarrow K_1 = (\text{HCO}_3\text{)} \text{ aqu} (\text{H}^+) \text{ aqu}/(\text{CO}_2\text{)} \text{ aqu} = 9.1 \times 10^{-7}$$

$$\text{(2) } (\text{HCO}_3\text{)} \text{ aqu} = (\text{CO}_3^{2-}) \text{ aqu} + (\text{H}^+) \text{ aqu } \Rightarrow K_2 = (\text{CO}_3^{2-}) \text{ aqu} (\text{H}^+) \text{ aqu}/(\text{HCO}_3\text{)} \text{ aqu} = 5.1 \times 10^{-10}$$

$$\text{(3) } K_1 K_2 = (\text{CO}_3^{2-}) \text{ aqu}(\text{H}^+) \text{ aqu}/(\text{CO}_2\text{)} \text{ aqu}$$

$$\text{(4) } (\text{H}_2\text{O}) = (\text{H}^+) \text{ aqu} + (\text{OH}^-) \text{ aqu } \Rightarrow K_w = (\text{H}^+)(\text{OH}^-) = 1.0 \times 10^{-14}$$

$$\text{(5) } (\text{CaCO}_3 \text{)} \text{ xtl} = (\text{Ca}^{2+}) \text{ aqu} + (\text{CO}_3^{2-}) \text{ aqu } \Rightarrow K_{\text{calcite}} = (\text{Ca}^{2+})(\text{CO}_3^{2-}) = 4.3 \times 10^{-7}$$

Charge balance requires:

$$\text{(6) } 2(\text{Ca}^{2+}) \text{ aqu} + (\text{H}^+) \text{ aqu} = (\text{HCO}_3^-) \text{ aqu} + 2(\text{CO}_3^{2-}) \text{ aqu} + (\text{OH}^-) \text{ aqu}$$

With appropriate substitutions, we obtain an expression with (H$^+$) and pCO$_2$ as variables.

$$\text{(7) } (2K_{\text{calcite}}/(K_0 K_1 K_2 p\text{CO}_2))(\text{H}^+) + (\text{H}^+)^3 - (K_0 K_1 p\text{CO}_2 + K_w) (\text{H}^+) = 2K_0 K_1 K_2 p\text{CO}_2$$

which can be solved for (H$^+$), (Ca$^{2+}$), (CO$_3^{2-}$), and total CO$_2$. By adding a solubility equation for gypsum, $K_{\text{gyp}} = (\text{Ca}^{2+})(\text{SO}_4^{2-}) = 1.0 \times 10^{-4}$, to the set of equations, we can derive 2 more sets of simultaneous solutions: one for a “calcite + gypsum” ocean and the other for a gypsum–saturated ocean without carbonate.

Results of the calculations for a calcite-saturated ocean, given in Table 1, show that the ocean is weakly acidic under greenhouse conditions and that at calcite saturation Ca$^{2+}$ and CO$_3^{2-}$ will vary considerably with pCO$_2$. Specifically, increasing the atmospheric pCO$_2$ at calcite saturation will not only increase (H$^+$) and total dissolved CO$_2$, but will also cause Ca$^{2+}$ to
increase by dissolving carbonate. Because Pollack et al (4) fixed Ca$^{2+}$ at terrestrial levels, they limited the applicability of their calculations to a restricted set of conditions. Not only does water chemistry change in response to CO$_2$ partial pressure, but it may also change considerably at constant pCO$_2$ if the saturation conditions change. What could cause the saturation conditions to change? Because sulfate is a strong electrolyte, its activity (concentration) remains constant at constant at a given temperature. Therefore, addition of sulfur to the system by volcanism, once the ocean is saturated gypsum, will cause precipitation of gypsum in order to maintain constant sulfate activity. Precipitation of gypsum also causes the ocean to become more acidic and to decrease Ca$^{2+}$ and CO$_3^{2-}$, thereby destabilizing carbonate.

Thus volcanism on Mars may have promoted sulfate precipitation while limiting carbonate. In view of the observation of sulfates on the scale of at least hundreds of square kilometers in the northern lowlands by the OMEGA/MEX imaging spectrometer (2) combined with the apparent absence of large-scale carbonate deposits on Mars (3), an implication of these calculations is that the weathering processes that released Ca$^{2+}$ into the oceans, may not have been sufficiently robust on a large scale to supply the Ca necessary to maintain calcite saturation. Alternatively, carbonates may have precipitated during episodes of evaporation or of loss of atmosphere to space, only to be succeeded and covered by Ca-sulfate, as is the case in terrestrial evaporite sequences.

CO$_2$-pressure might also play an important role in limiting carbonate deposition. CO$_2$ solubility in water increases and carbonate stability decreases with pressure under nearly isothermal conditions (7). The upper levels of the terrestrial oceans are supersaturated with carbonate, mainly due to biological activity (8), but at depth (∼3 km), however, the oceans become undersaturated due to the pressure effect. Absent a strong biological carbonate production, any carbonate that did form near the surface might be limited to the upper layers until the final evaporation of the ocean.


<table>
<thead>
<tr>
<th>Table 1 Chemical Variation in a Martian Ocean</th>
<th>pCO$_2$ (atm)</th>
<th>(H$^+$) (mol/kg)</th>
<th>pH</th>
<th>Ca$^{2+}$ (mol/kg)</th>
<th>(CO$_3^{2-}$) (mol/kg)</th>
<th>(SO$_4^{2-}$) (mol/kg)</th>
<th>Tot CO$_2$ (mol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>calcite only</td>
<td>1x10$^{-4}$</td>
<td>2.4x10$^{-9}$</td>
<td>8.6</td>
<td>1.0x10$^{-3}$</td>
<td>4.2x10$^{-4}$</td>
<td>--------</td>
<td>1.8x10$^{-3}$</td>
</tr>
<tr>
<td>calcite only</td>
<td>1</td>
<td>1.1x10$^{-6}$</td>
<td>6.0</td>
<td>2.1x10$^{-2}$</td>
<td>2.0x10$^{-5}$</td>
<td>--------</td>
<td>6.2 x10$^{-2}$</td>
</tr>
<tr>
<td>calcite + gypsum</td>
<td>1</td>
<td>7.3x10$^{-7}$</td>
<td>6.1</td>
<td>9.6x10$^{-3}$</td>
<td>4.5x10$^{-5}$</td>
<td>1.0x10$^{-2}$</td>
<td>1.2 x10$^{-1}$</td>
</tr>
<tr>
<td>gypsum only</td>
<td>1</td>
<td>2.2x10$^{-4}$</td>
<td>3.7</td>
<td>1.0x10$^{-2}$</td>
<td>5.1x10$^{-10}$</td>
<td>1.0x10$^{-2}$</td>
<td>5.2 x10$^{-2}$</td>
</tr>
</tbody>
</table>