

## Experimental Inhibition of Carbonate Precipitation by Sulfite Minerals

Itay Halevy<sup>1</sup> and Daniel P. Schrag<sup>1</sup>, <sup>1</sup>Earth and Planetary Sciences, Harvard University, Cambridge, MA, USA (ihalevy@fas.harvard.edu)

**Introduction:** Volcanic and hydrothermal supply of reducing gases to the early atmosphere of Mars likely surpassed the slow supply of oxidizing power from hydrogen escape to space, resulting in a neutral or mildly reducing atmosphere and in geochemical cycles that operated very differently than they do on the modern Earth. We have recently suggested that one such difference between the modern and ancient geochemical cycle of sulfur is the possible existence of a SO<sub>2</sub> climate feedback on early Mars [1], analogous to the negative climate feedback between atmospheric CO<sub>2</sub> concentrations and the rate of silicate weathering on the modern Earth [2].

Being both a more effective greenhouse gas (when added to a CO<sub>2</sub>-rich atmosphere) and a stronger acid than CO<sub>2</sub>, small atmospheric concentrations of SO<sub>2</sub> suffice for it to become the dominant control on climate, on the pH of surface waters and through these on the rate of silicate weathering and supply of alkalinity to surface water bodies. Precipitation of hannebachite (CaSO<sub>3</sub>·1/2H<sub>2</sub>O) is an alkalinity, and therefore climate-dependent mineral sink for SO<sub>2</sub>, which completes the requirements for operation of a negative climate feedback. A prediction from the aqueous chemistry of SO<sub>2</sub> is that under these conditions sulfite minerals should precipitate at the expense of carbonates [1]. In a series of mineral precipitation experiments we show that this is indeed the case and that oxidation of the precipitates gives rise to mineral assemblages similar to those detected on the surface of Mars.

**Aqueous Chemistry of SO<sub>2</sub>:** SO<sub>2</sub> is a weak diprotic acid that speciates in solution in an analogous way to dissolved CO<sub>2</sub> (Fig. 1, table 1). Because SO<sub>2</sub> is a stronger acid than CO<sub>2</sub>, most of the S<sup>4+</sup> at a pH between 2 and 6 is present in solution as the bisulfite ion (HSO<sub>3</sub><sup>-</sup>), while most of the carbon is as aqueous CO<sub>2</sub> (Fig. 1). Even small amounts of SO<sub>2</sub>, relative to CO<sub>2</sub>, are enough for it to control the pH of an aqueous solution (Fig. 2), and to depress the concentration of the carbonate ion (CO<sub>3</sub><sup>2-</sup>). Consequently, despite being about a hundred times more soluble than calcite (table 1), for a ratio of the partial pressure of SO<sub>2</sub> to that of CO<sub>2</sub> (*p*SO<sub>2</sub>:*p*CO<sub>2</sub>) equal to or exceeding ~5 × 10<sup>-8</sup> hannebachite reaches saturation at a lower calcium concentration than does calcite (Fig. 3). Hannebachite precipitation then limits the Ca<sup>2+</sup> concentration and prevents the precipitation of calcite.

These predictions, made on the basis of aqueous solubility calculations, do not account for kinetic factors, which affect the precipitated mineral assemblage. It is known from calcite precipitation experiments, for example, that nucleation occurs at several times supersaturation, may require an incubation period of minutes to days and is inhibited by both organic and inorganic compounds in solution. The kinetics of sulfite mineral precipi-

Table 1: Equilibrium constants of relevant reactions. K<sub>H</sub> is Henry's law constant, K<sub>a1</sub> and K<sub>a2</sub> are the first and second acid dissociation constants and K<sub>sp</sub>s are solubility constants.

Reaction		K <sub>eq</sub>
SO <sub>2</sub> (g)	⇌ SO <sub>2</sub> (aq)	K <sub>H</sub> = 10 <sup>+0.09</sup>
SO <sub>2</sub> (aq)	⇌ HSO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	K <sub>a1</sub> = 10 <sup>-1.86</sup>
HSO <sub>3</sub> <sup>-</sup>	⇌ SO <sub>3</sub> <sup>2-</sup> + H <sup>+</sup>	K <sub>a2</sub> = 10 <sup>-7.21</sup>
CaSO <sub>3</sub> ·1/2H <sub>2</sub> O	⇌ Ca <sup>2+</sup> + SO <sub>3</sub> <sup>2-</sup>	K <sub>sp</sub> = 10 <sup>-6.51</sup>
CaCO <sub>3</sub>	⇌ Ca <sup>2+</sup> + CO <sub>3</sub> <sup>2-</sup>	K <sub>sp</sub> = 10 <sup>-8.48</sup>

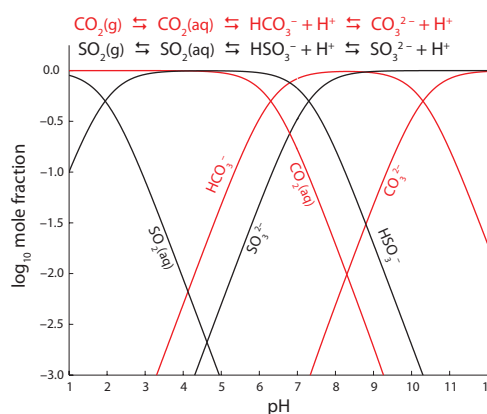


Figure 1: The pH-dependent speciation of carbon (red) and tetravalent sulfur (black).

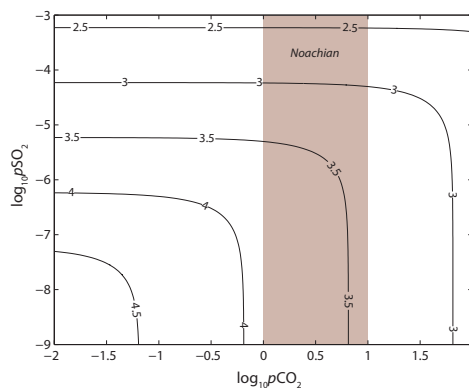


Figure 2: pH contours of an aqueous solution in equilibrium with CO<sub>2</sub> and SO<sub>2</sub>. Where the contours are horizontal the pH is controlled by SO<sub>2</sub>. In the range of *p*CO<sub>2</sub> relevant to warming Mars during the Noachian, shown by the shaded region, *p*SO<sub>2</sub> greater than 10<sup>-5</sup> bar is enough for it to dominate the pH of surface waters.

at the conditions relevant to the early history of Mars have not been studied, nor have the competitive kinetics of a mixed carbonate-sulfite system.

**Methods:** We conducted mineral precipitation experiments under a range of *p*SO<sub>2</sub>:*p*CO<sub>2</sub>, ionic strength and

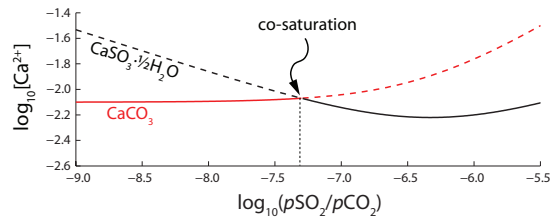


Figure 3: The calcium concentration at calcite ( $\text{CaCO}_3$ , red) and hannebachite ( $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ , black) saturation. The phase represented by the line limits the  $\text{Ca}^{2+}$  wherever the line is solid.

Fe:Mg:Ca. Desired concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  were attained by dissolving  $\text{CaCl}_2$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  in de-oxygenated, de-ionized water, held in a glove tent with positive  $\text{N}_2$  pressure. We added  $\text{NaHCO}_3$  and  $\text{NaHSO}_3$  in the proportions required to reach the desired  $p\text{SO}_2:p\text{CO}_2$  in the headspace and then sealed the reaction bottles. The value of  $p\text{SO}_2:p\text{CO}_2$  in the headspace, the pH of the sealed solutions and the initial degree of supersaturation of  $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$  and  $\text{CaCO}_3$  were calculated from thermodynamic equilibrium and assuming slow kinetics of  $\text{SO}_2$ -species oxidation and disproportionation. We verified these calculations by comparing the calculated pH against measurements in a series of test bottles and found that the calculated pH was within 0.1 pH units of the measurements.

The solutions were left to stand until precipitates formed or long enough to ascertain that none will (up to two weeks). The precipitates were identified by X-ray diffraction and imaged with a scanning electron microscope (Fig. 4). To examine how exposure to oxic conditions alters the mineral assemblage, we left moist and submerged aliquots of precipitates from a few experiments exposed to air and periodically measured the pH and reanalyzed the mineral assemblage.

**Results:** In experiments containing  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$  and either  $\text{CO}_2$  or  $\text{SO}_2$ , we found that hannebachite precipitated at a lower degree of supersaturation than calcite, suggesting less severe kinetic inhibition to nucleation of the former. When both  $\text{CO}_2$  and  $\text{SO}_2$  were included,  $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$  precipitated at the expense of  $\text{CaCO}_3$  for values of  $p\text{SO}_2:p\text{CO}_2$  as low as  $\sim 5 \times 10^{-8}$ , as predicted by the solubility calculations. This occurred in solutions of both low and high ionic strength ( $\sim 0.05$  and  $\sim 0.57$ , respectively) and despite the fact that  $\text{CaCO}_3$  was supersaturated in all of the experiments (up to 10 times supersaturation). The presence of  $\text{Mg}^{2+}$  did not significantly change the value of  $p\text{SO}_2:p\text{CO}_2$  above which sulfite precipitation inhibits carbonate precipitation. In addition, no correlation was observed between Mg:Ca in the solution (in the range 0–20) and the amount of  $\text{Mg}^{2+}$  incorporated into the hannebachite crystal structure. In experiments that contained  $\text{Fe}^{2+}$ , green rust ( $\text{Fe}_6(\text{OH})_{12}\text{CO}_3$ ) precipitated together with hannebachite.

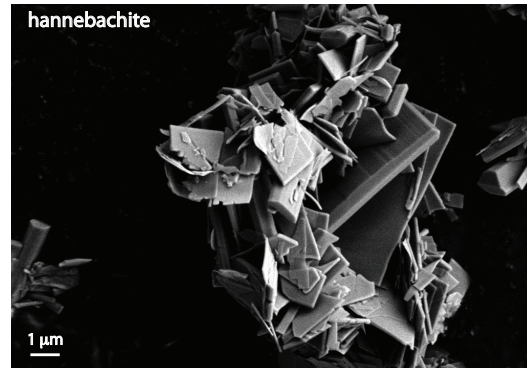
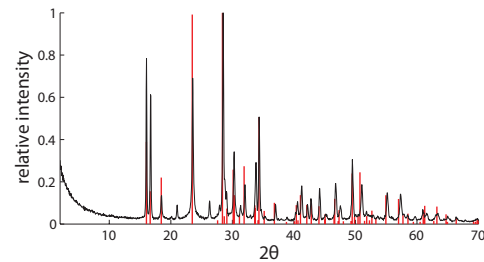


Figure 4: Upper panel: an example of a hannebachite X-ray diffraction pattern. The red lines are from the International Center for Diffraction Data. Lower panel: an SEM image of precipitated hannebachite.

When exposed to air, the pH of the precipitates dropped as the sulfurous acid (aqueous  $\text{SO}_2$ ) was replaced by sulfuric acid ( $\text{H}_2\text{SO}_4$ ). Hannebachite was replaced by gypsum and green rust by iron oxides.

**Discussion** Our results show that even a miniscule amount of  $\text{SO}_2$  (i.e.  $\sim 100$  ppb), in equilibrium with a surface water reservoir, would have been enough to inhibit carbonate mineral precipitation in favor of sulfites. Even if  $\text{SO}_2$  did not reach radiatively important atmospheric concentrations, during periods of volcanic activity its abundance was almost certainly high enough to dominate the aqueous chemistry on the surface of Mars, potentially explaining the scarcity of carbonates [3]. Inhibition by sulfite precipitation, unlike other explanations proposed [4, 5], occurs at  $\sim$ neutral pH and may also explain how clays were able to form early in Martian history [6] unaccompanied by carbonate minerals. Finally, exposure of the sulfites to oxidizing solutions is shown to *i*) release acidity, consistent with evidence for acidic conditions during subsequent periods of Martian history [7], and *ii*) result in mineral assemblages similar to those observed on the surface of Mars [6, 7].

- [1] Halevy I. et al. (2007), *Science*, 318, 1903. [2] Walker J. C. G. et al. (1981), *JGR*, 86, 9776. [3] Christensen P. R. et al. (2001), *JGR*, 106, 23823. [4] Banin A. et al. (1997), *JGR*, 102, 13341. [5] Fairen A. G. et al. (2004), *Nature*, 431, 423. [6] Bibring J. P. et al. (2006), *Science*, 312, 400. [7] Squyres S. W. and Knoll A. H. (2005), *EPSL*, 240, 1.