

Siderite Dissolution Kinetics in Mars-Analog Brines. M. D. Cullen¹, C. M. Phillips-Lander¹, and M.E. Elwood Madden¹ ¹ School of Geology and Geophysics, University of Oklahoma, Norman OK, USA, melwood@ou.edu

Introduction: Current evidence for salty liquid water on Mars, and the processes that accompany it, can be inferred by the widespread presence of salt deposits that likely formed from evaporating or freezing brines [1, 2]. This is crucial to understanding and interpreting mineral assemblages in SNC meteorites and outcrops on Mars because it implies that geochemical processes such as mineral alteration and dissolution in brines likely occurred at the surface.

Data obtained by CRISM indicate, among other phases, the presence of modern magnesium chlorate/perchlorate salts [3], as well as widespread sulfate assemblages in older rocks [4]. Minerals observed on the surface include various phosphate, sulfate, and carbonate species [5, 6, 7]. This includes jarosite and alunite, which both indicate acidic aqueous conditions [8, 9]. This implies that rocks at the surface of Mars were likely in contact with acidic brines at some point in Mars history.

Siderite (an Fe²⁺ carbonate) has been observed both on the surface of Mars [10] and in SNC meteorites [11]. While carbonates have been identified in a few large scale outcrops on Mars and are commonly observed as a minor phase in Mars dust deposits, they are generally less prevalent than expected, given the relatively high CO₂ concentration in the atmosphere [10]. Previous modeling studies have suggested that acidic fluids may have dissolved many of the carbonate deposits [12], leading to the sparse carbonate outcrops observed on modern Mars. To test this hypothesis, this study investigates the kinetics of siderite dissolution in acidic magnesium-based brines with varying composition and concentration to determine how both anion chemistry and concentration affect siderite dissolution rates and preservation.

Methods: Anoxic magnesium chloride (MgCl₂) and magnesium sulfate (MgSO₄) brines were prepared at three different concentrations: 0.01 M, 1 M, and 3 M. First, HCl and H₂SO₄ (for MgCl₂ and MgSO₄ brines, respectively) were used to reduce the pH of UPW to 2. Dissolved O₂ was then boiled out and solutions cooled under flowing N₂. These solutions were then transferred to an anaerobic chamber where 250mL of each of the six brines were prepared.

The siderite was micronized and BET analysis was used to measure the surface area (0.601 m²/g). Each experiment used 0.075 ± 0.005 g siderite. 75mL of each brine was put in brown glass serum vials to minimize photolytic reactions which may affect dissolved Fe. The vials were capped and sealed from ambient air before being placed on an orbital shaker for about sev-

en weeks. Experiments were run in duplicate, resulting in 12 reactors. Sampling took place each week using needled syringes to maintain anoxic conditions within the reactor and filtered using 0.2 micron acetate syringe filters. A portion of each sample was refrigerated for elemental aqueous analysis at the end of the experiments, and the remainder was used to measure pH.

Dissolved Fe concentrations in each sample were analyzed using matrix-matched flame Atomic Absorption Spectroscopy. Fe concentrations were plotted as a function of time. The first 4 sample points were fitted with a 2nd order polynomial, and differentiated to determine the initial dissolution rate.

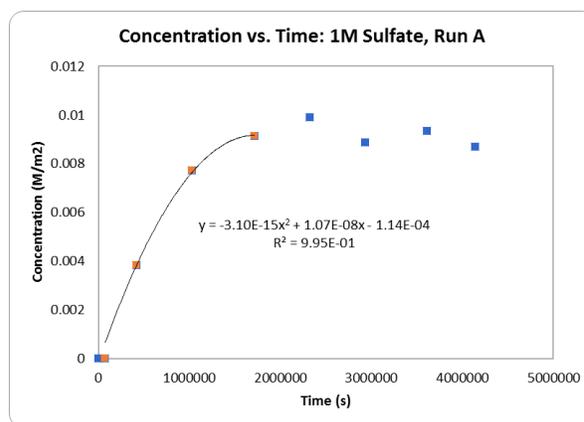


Figure 1. Sample graph of results showing the concentration of aqueous iron over time. Concentration has been normalized to the surface area of the original sample.

Results and Discussion: In both MgCl₂ and MgSO₄ brine, the initial dissolution rate changed with increasing brine concentration, however in different ways.

Siderite dissolution rates in magnesium sulfate decrease slightly as concentration increases between 0.01 M and 1 M, and decrease significantly between 1 M and 3 M (see Table 1), likely due to the decrease in the activity coefficient of water from 1 to 0.91 as the concentration increases to 3 M [13]. However, as brine concentration increases, the total iron released to solution after 7 weeks increases. Higher Fe concentrations in the high salinity brines are likely due to Fe complexes which form with sulfate ions. Because iron forms these complexes as it is dissolved, the activity of free aqueous Fe is lower than in the more dilute brines, al-

lowing more iron to enter the solution as Fe^{2+} and resulting in a greater total siderite solubility.

Batch	Brine	Brine Molarity (M)	Rate (mol/s/m ²)	Final Fe Concentration (M/m ²)
A	MgCl ₂	0.01	7.93E-09	5.38E-03
B	MgCl ₂	0.01	8.86E-09	5.36E-03
A	MgCl ₂	1.0	N/A	7.09E-03
B	MgCl ₂	1.0	N/A	8.00E-03
A	MgCl ₂	3.0	N/A	7.46E-03
B	MgCl ₂	3.0	N/A	7.77E-03
A	MgSO ₄	0.01	9.98E-09	8.74E-03
B	MgSO ₄	0.01	1.15E-08	8.43E-03
A	MgSO ₄	1.0	1.07E-08	8.69E-03
B	MgSO ₄	1.0	9.54E-09	9.15E-03
A	MgSO ₄	3.0	2.88E-09	1.98E-02
B	MgSO ₄	3.0	5.03E-09	1.73E-02

Table 1. Initial dissolution rates in pH 2 MgCl₂ and MgSO₄ brines. 1 M and 3 M MgCl₂ rates could not be determined since most of the sample dissolved before the first sampling point.

Dissolution rates were only determined for the 0.01 M MgCl₂ brine experiments because the siderite in the higher concentration brines was almost totally dissolved before the first sample was taken (1 week), preventing a rate from being accurately quantified. However, this demonstrates that magnesium chloride behaves differently than magnesium sulfate as salt concentration increases. Since the siderite completely dissolved prior to the first sampling point in the 1 M and 3 M MgCl₂ brines, the dissolution rate must have been significantly slower in the 0.01 M MgCl₂ brine since complete dissolution took 4-5 weeks to occur. Therefore, increasing MgCl₂ concentration results in increased dissolution rates, even though the activity of water in the high concentration MgCl₂ brines is significantly less than the activity of water in the sulfate brines containing the same mole fraction of salt [14].

Thus, Cl⁻ ions may accelerate siderite dissolution by forming complexes with iron in the MgCl₂ experiments, resulting in faster dissolution rates as Cl⁻ concentration increases, while decreased activity of water appears have greater effects than Fe-sulfate complex formation in the MgSO₄ experiments. However, siderite dissolution rates in the dilute MgCl₂ experiments were slightly slower than those observed in similar salinity MgSO₄ brines, suggesting that Fe release is accelerated only when Cl⁻ is present in high concentrations. MgCl₂ brines see the largest increase in total Fe released between 0.01 M and 1 M with no significant change between 1 M and 3 M (see Table 1), whereas MgSO₄ brines see the largest increase in solubility between 1 M and 3 M concentrations.

Chloride complexation with Fe was also proposed by Pritchett et al. (2012) to explain increases in jarosite dissolution rates at high CaCl₂ brine concentration [9].

However, in jarosite experiments, this mechanism was dependent on a charge imbalance caused by gypsum precipitation. If this same mechanism occurs in the MgCl₂-siderite, then Mg²⁺ activity must decrease in the solution, either through precipitation or formation of Mg-CO₃ complexes to produce a similar charge imbalance.

Implications for Mars: Using the rates established in this study, we can constrain the duration of brine alteration processes in samples/outcrops that contain both siderite and evaporite phases. We have shown that in the presence of both MgCl₂ and MgSO₄ acidic brines, wholesale dissolution of micron-sized siderite grains occurs on a scale of 4-5 weeks in dilute brines, and in some cases over a period of a few days in the case of more concentrated MgCl₂ brines. Therefore, any outcrop or meteorite that contains siderite and salts, along with jarosite or other minerals indicative of acidic conditions likely experienced only a short period of aqueous alteration. These experiments provide data for interpreting post-Noachian alteration processes, when acidic aqueous conditions appear to dominate. Future experiments investigating siderite dissolution in brines at higher pH will provide further data for constraining aqueous alteration assemblages formed under more alkaline conditions in the Noachian [12].

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