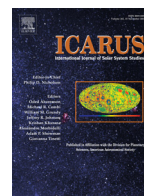




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# Carbonate dissolution rates in high salinity brines: Implications for post-Noachian chemical weathering on Mars

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## ABSTRACT

A diverse suite of carbonate minerals including calcite ( $\text{CaCO}_3$ ) and magnesite ( $\text{MgCO}_3$ ) have been observed on the martian surface and in meteorites. Terrestrial carbonates usually form via aqueous processes and often record information about the environment in which they formed, including chemical and textural biosignatures. In addition, terrestrial carbonates are often found in association with evaporite deposits on Earth. Similar high salinity environments and processes were likely active on Mars and some areas may contain active high salinity brines today. In this study, we directly compare calcite and magnesite dissolution in ultrapure water, dilute sulfate and chloride solutions, as well as near-saturated sulfate and chloride brines with known activity of water ( $a_{\text{H}_2\text{O}}$ ) to determine how dissolution rates vary with mineralogy and  $a_{\text{H}_2\text{O}}$ , as well as aqueous cation and anion chemistry to better understand how high salinity fluids may have altered carbonate deposits on Mars. We measured both calcite and magnesite initial dissolution rates at 298 K and near neutral pH (6–8) in unbuffered solutions containing ultrapure water ( $18 \text{ M}\Omega \text{ cm}^{-1}$  UPW;  $a_{\text{H}_2\text{O}} = 1$ ), dilute ( $0.1 \text{ mol kg}^{-1}$ ;  $a_{\text{H}_2\text{O}} = 1$ ) and near-saturated  $\text{Na}_2\text{SO}_4$  ( $2.5 \text{ mol kg}^{-1}$ ,  $a_{\text{H}_2\text{O}} = 0.92$ ), dilute ( $0.1 \text{ mol kg}^{-1}$ ,  $a_{\text{H}_2\text{O}} = 1$ ) and near-saturated NaCl ( $5.7 \text{ mol kg}^{-1}$ ,  $a_{\text{H}_2\text{O}} = 0.75$ ). Calcite dissolution rates were also measured in dilute and near-saturated  $\text{MgSO}_4$  ( $0.1 \text{ mol kg}^{-1}$ ,  $a_{\text{H}_2\text{O}} = 1$  and  $2.7 \text{ mol kg}^{-1}$ ,  $a_{\text{H}_2\text{O}} = 0.92$ , respectively) and  $\text{MgCl}_2$  ( $0.1 \text{ mol kg}^{-1}$ ,  $a_{\text{H}_2\text{O}} = 1$  and  $3 \text{ mol kg}^{-1}$ ,  $a_{\text{H}_2\text{O}} = 0.73$ , respectively), while magnesite dissolution rates were measured in dilute and near-saturated  $\text{CaCl}_2$  ( $0.1 \text{ mol kg}^{-1}$ ,  $a_{\text{H}_2\text{O}} = 1$  and  $9 \text{ mol kg}^{-1}$ ,  $a_{\text{H}_2\text{O}} = 0.35$ ).

Initial calcite dissolution rates were fastest in near-saturated  $\text{MgCl}_2$  brine, while magnesite dissolution rates were fastest in dilute ( $0.1 \text{ mol kg}^{-1}$ ) NaCl and  $\text{CaCl}_2$  solutions. Calcite dissolution rates in near-saturated  $\text{Na}_2\text{SO}_4$  were similar to those observed in the dilute solutions ( $-8.00 \pm 0.12 \text{ log mol m}^{-2} \text{ s}^{-1}$ ), while dissolution slowed in both NaCl solutions ( $0.1 \text{ mol kg}^{-1}$ ;  $-8.23 \pm 0.10 \text{ log mol m}^{-2} \text{ s}^{-1}$  and  $5.7 \text{ mol kg}^{-1}$ ;  $-8.44 \pm 0.11 \text{ log mol m}^{-2} \text{ s}^{-1}$ ), as well as near-saturated  $\text{MgSO}_4$  brine ( $2.7 \text{ mol kg}^{-1}$ ;  $-8.35 \pm 0.05 \text{ log mol m}^{-2} \text{ s}^{-1}$ ). The slowest calcite dissolution rates observed in the near-saturated NaCl brine. Magnesite dissolution rates were ~5 times faster in the dilute salt solutions relative to UPW, but similar to UPW ( $-8.47 \pm 0.06 \text{ log mol m}^{-2} \text{ s}^{-1}$ ) in near-saturated  $\text{Na}_2\text{SO}_4$  brines ( $-8.41 \pm 0.18 \text{ log mol m}^{-2} \text{ s}^{-1}$ ). Magnesite dissolution slowed significantly in near-saturated  $\text{CaCl}_2$  brine ( $-9.78 \pm 0.10 \text{ log mol m}^{-2} \text{ s}^{-1}$ ), likely due to the significantly lower water activity in these experiments. Overall, magnesite dissolution rates are slower than calcite dissolution rates and follow the trend: All dilute salt solutions  $> 2.5 \text{ mol kg}^{-1} \text{ Na}_2\text{SO}_4 \approx \text{UPW} > 5.7 \text{ mol kg}^{-1} \text{ NaCl} \gg 9 \text{ mol kg}^{-1} \text{ CaCl}_2$ . Calcite rates follow the trend  $3 \text{ mol kg}^{-1} \text{ MgCl}_2 > 2.5 \text{ mol kg}^{-1} \text{ Na}_2\text{SO}_4 \approx \text{UPW} \approx$  all dilute salt solutions  $> 2.7 \text{ mol kg}^{-1} \text{ MgSO}_4 \approx 5.7 \text{ mol kg}^{-1} \text{ NaCl}$ . Magnesite dissolution rates in salt solutions generally decrease with decreasing  $a_{\text{H}_2\text{O}}$  in both chloride and sulfate brines, which indicates water molecules act as ligands and participate in the rate-limiting magnesite dissolution step. However, there is no general trend associated with water activity observed in the calcite dissolution rates. Calcite dissolution accelerates in near-saturated  $\text{MgCl}_2$ , but slows in near-saturated NaCl brine despite both brines having similar water activities ( $a_{\text{H}_2\text{O}} = 0.73$  and  $0.75$ , respectively). High Mg calcite was observed as a reaction product in the near-saturated  $\text{MgCl}_2$ , indicating  $\text{Mg}^{2+}$  from solution likely substituted for  $\text{Ca}^{2+}$  in the initial calcite, releasing additional  $\text{Ca}^{2+}$  into solution and increasing the observed calcite dissolution rate. Calcite dissolution rates also increase slightly as  $\text{Na}_2\text{SO}_4$  concentration increases, while calcite dissolution rates slow slightly with

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increasing concentration of  $\text{MgSO}_4$  and  $\text{NaCl}$ . However, all of the carbonate rates vary by less than 0.5 log units and are within or near the standard deviation observed for each set of replicate experiments.

Carbonate mineral lifetimes in high salinity brines indicate magnesite may be preferentially preserved compared to calcite on Mars. Therefore, Mg-carbonates that have experienced post-depositional aqueous alteration are more likely to preserve paleoenvironmental indicators and potential biosignatures. Rapid weathering of carbonates in circum-neutral pH sulfate brines may provide a potential source of cations for abundant sulfate minerals observed on Mars, Ceres, and other planetary bodies.

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## 1. Introduction

Carbonate minerals, including calcite, magnesite, and siderite have been detected on Mars using both orbital and rover instrument data (Wray et al., 2016; Niles et al., 2013; Sutter et al., 2012; Boynton et al., 2009; Palomba et al., 2009; Ehlmann et al., 2008; Kounaves et al., 2010a, b; Christensen et al., 2004; Bandfield et al., 2003; Carrozzo et al., 2017; Michalski et al., 2017) and in martian meteorites (Gooding and Wentworth, 1991; Mittlefehldt, 1994; Bridges and Grady, 2000; Bridges et al., 2001). Globally, martian dust consists of ~2–5% carbonate based on global Thermal Emission Spectrometer data from the Mars Global Surveyor (Bandfield et al., 2003), significantly less than predicted based on the  $\text{CO}_2$ -rich atmosphere (Ehlmann et al., 2014). Multiple hypotheses exist to explain the paucity of carbonate minerals on Mars's surface, including isochemical alteration in the subsurface isolated from the  $\text{CO}_2$ -rich atmosphere (Ehlmann et al., 2011; Niles et al., 2013), chemical weathering in acidic environments inhibiting the formation of carbonates (Bullock and Moore, 2007; Fairen et al., 2004), and/or carbonate formation and subsequent alteration under acid-sulfate conditions (Bibring et al., 2006). While Ehlmann et al. (2009) suggest carbonates may have formed from the interaction of subsurface rocks with groundwater flux, other studies have postulated low levels of atmospheric  $\text{CO}_2$  during the Noachian may have inhibited carbonate formation (Chevrier et al., 2007; Bristow et al., 2017). The abundance of Fe/Mg smectites relative to carbonates during basalt alteration at pH ~ 4 has been used as evidence to suggest acid pH may have dominated Mars' aqueous alteration history, resulting in the smectite rich, carbonate poor mineralogy observed in Noachian terrains (Peretyazhko et al., 2016; Dehouck et al., 2016). However, Wray et al. (2016) demonstrated there may be other potential carbonate deposits that have not been previously identified based on their spectral features; for example they contain some, but not all, the carbonate spectral features required for confirmation. If these deposits are found via other methods to contain carbonates, these locations would significantly expand regional carbonate detections on Mars. Therefore, previous carbonate detections may underestimate the total abundance of carbonate deposits in Mars' geologic record and carbonate deposits may be more widespread than previously assumed (Wray et al., 2016).

Indeed, orbital data indicates martian dust globally consists of 2–5 wt.% carbonates, which are dominated by Mg-carbonates (Bandfield et al., 2003). This observation is supported by the detection of 3–5 wt.% Ca-carbonate identified in the martian soil using TEGA at the Phoenix landing site (Boynton et al., 2009). Siderite or siderite + magnesite was also detected in low abundance (<1 wt.%) in the Rocknest sediments analyzed by EGA aboard MSL (Leshin et al., 2013) and Spirit detected <5 wt.% carbonates in Gusev Crater soils using mini-TES (Christensen et al., 2004).

Mg-rich carbonates have been observed in outcrops on Mars including 16–34% carbonate in the Comanche Outcrop within Gusev Crater using Mossbauer and mini-TES (Morris et al., 2010; Carter and Poulet, 2012) and in McLaughlin Crater (Michalski et al., 2013).

Carbonates are also observed in what has been interpreted as a high-temperature alteration assemblage observed in Coprates Chasma (Viviano-Beck et al., 2017). Recent CRISM data analysis by Wray et al. (2016) indicates the presence of Mg-carbonates in Huygens basin, including Lucaya Crater, and a crater in Hesperia Planum's floor and central peak. Fe/Mg-rich carbonates (up to 20 wt.%) have also been observed in Nili Fossae region (Edwards et al., 2015; Bishop et al., 2013; Brown et al., 2010; Ehlmann et al., 2008) and Ca/Mg-rich carbonates have been detected in nearby NE Syrtis (at ~10 wt.%; Palomba et al., 2009). Fe/Ca-carbonates are observed in Leighton crater (Michalski and Niles, 2010) and central crater uplifts within Terra Tyrrhena (Ehlmann et al., 2008; Carrozzo et al., 2017), crater walls in Eridania basin (Korn and Gilmore, 2015), as well as various locations across Valles Marineris (Jain and Chauhan, 2015), and "western Noachis Terra" (Wray et al., 2016; these deposits were previously interpreted as phyllosilicates by Buczkowski et al., 2010, 2013; Le Deit et al., 2012). In many cases these carbonates are observed mixed with hydrated phases (Wray et al., 2016; Bishop et al., 2013; Bultel et al., 2015; Ehlmann et al., 2008). Outcrops of Mg–Ca–Fe carbonates associated with saponite, serpentine, and sulfides have been recently interpreted as hydrothermal deposits which may be associated with crustal spreading in Eridania Basin (Michalski et al., 2017).

Carbonates have also been observed in SNC (Shergotty–Nakhla–Chassigny) meteorites, however the total volumetric carbonate abundance in these meteorites ranges from ~1–2% (Bridges et al., 2001). Carbonates (<100  $\mu\text{m}$ ) present in SNC meteorites occur primarily within cracks and crushed zones in primary minerals and likely formed during hydrothermal alteration (Hicks et al., 2014; Niles et al., 2013; Changela and Bridges, 2010; Lee et al., 2015). Cross-cutting relationships, including impact-related features overprinting alteration textures and minerals and weathering features predating the fusion crust, as well as non-terrestrial isotopic compositions indicate the carbonate-bearing alteration assemblages observed in SNC meteorites are of pre-terrestrial origin (Niles et al., 2013; Gooding et al., 1988). The oldest carbonates (~3.9 Ga) in SNC meteorites were detected in ALH84001 (Lapen et al., 2010; Borg et al., 1999). Magnesite and siderite are the dominant carbonate phases in ALH84001, however calcite is also present (McSween and Harvey, 1998; Harvey and McSween, 1996). Carbonates in ALH84001 and nakhlite meteorites may have formed at low temperatures in the shallow subsurface based on isotopic (Halevy et al., 2011) and microscopic investigations (Changela and Bridges, 2010; McSween and Harvey, 1998; Treiman, 1995). However, carbon (Golden et al., 2001; Niles et al., 2005), hydrogen (Leshin et al., 1996) and oxygen (Leshin et al., 1998) isotopic studies as well as the amount of calcium substitution (Harvey and McSween, 1996) indicate these carbonates formed under hydrothermal conditions (>150 °C).

In many other instances, carbonates in SNC meteorites are observed in close association with salts, implying carbonate-brine interactions. For example, sulfate salts and Ca, Mg-carbonates (Gooding and Wentworth, 1991; Gooding et al., 1988), including individual crystals of calcite and magnesite (Wentworth and Gooding, 1994), as well as high magnesium calcite, are intermixed in

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