

CARBONATE PRECIPITATION KINETICS IN ANOXIC WATER-ROCK SYSTEMS: IMPLICATIONS FOR THE MARTIAN “MISSING CARBONATES”. L. E. Kissick^{1*} and N. J. Tosca¹, ¹Department of Earth Sciences, University of Oxford, Oxford, UK, *lucy.kissick@earth.ox.ac.uk*.

Introduction: Reconciling climate models with geological and geochemical evidence for liquid water on early Mars remains a key challenge in planetary research. Carbon dioxide is traditionally considered the main Noachian atmospheric constituent, yet carbonate-bearing bedrock exposures (namely the iron (II) carbonate siderite; FeCO_3) remain surprisingly uncommon at the martian surface [1, 2]. Nevertheless, carbonates have long been recognised within Martian meteorites, often associated with minerals that require at least neutral pH to form [e.g., 3]. In addition, re-analyses of Martian orbital data have shown that carbonate-rich rocks, though rare, are becoming increasingly recognised in ancient Noachian terrains, especially where subsurface lithologies are exposed [2]. Together, this suggests that some environments produced carbonates on Mars, while others did not. What factors may have controlled this distribution?

At least two possibilities may account for the relative paucity and stratigraphic distribution of carbonate minerals on Mars: either 1) the partial pressure of Noachian CO_2 was significantly lower than the ~1 bar required to stabilise liquid water [4], raising to question what alternative atmosphere supported the early Martian surface; or 2) carbonate formation on early Mars was strongly controlled by kinetic factors that may have restricted deposition to only the most favourable aqueous environments.

In this study, we experimentally investigate anoxic water-rock interactions between acidified fluids and ferromagnesian minerals to more closely examine the processes that control the precipitation of Fe(II)-carbonate minerals. Kinetic data for Fe(II)-carbonate precipitation are generally lacking, yet they are expected to comprise the majority of carbonate alteration products on early Mars. This tests the rigidity of a purely thermodynamic approach to constraining early atmospheric CO_2 .

Materials and methods: Water-rock experiments were conducted in closed vessels at varying water-rock ratios (W/R), initial pH, and dissolved CO_2 content. Water-rock ratio was varied to represent open system aqueous environments at the early martian surface in contact with the atmosphere on the one hand (high W/R), and rock dominated sub-surface systems (low W/R) on the other. Experiments were conducted with synthetic pure fayalite (Fe_2SiO_4), pure natural forsterite (Mg_2SiO_4 ; $\text{Fo}_{>90}$) or mixtures of the two. Strictly anoxic conditions were maintained dur-

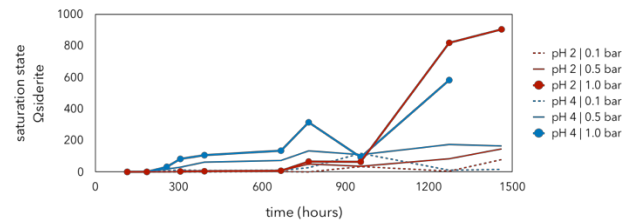


Figure 1. ICP-OES plot of siderite saturation state through time (60 days, ~1450 hours) with starting substrates of fayalite and forsterite.

ing experimentation: all experiments were conducted within a Coy polymer anoxic glovebox under a mix of 4% H_2 /96% N_2 gas. pH and oxidation-reduction potential were monitored over a period of up to 60 days, and 10 samples (10% of total solution) extracted. Upon each experiments' termination, solution samples were analysed via inductively coupled plasma optical emission spectrometry (ICP-OES) and solids via powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS).

Results – Siderite inhibition: Solution samples analysed via ICP-OES reveal that, in almost all cases where initial dissolved CO_2 was equivalent to >0.5 bar, siderite was continuously super-saturated. This is defined by any Ω_{siderite} (equal to IAP/K_{sp} , where $\text{IAP} = a_{\text{Fe}^{2+}} \cdot a_{\text{CO}_3^{2-}}$ and K_{sp} is the solubility product of siderite) over the value of 1, where, thermodynamically, a precipitate is expected to form (Fig. 1). Some experiments reached saturation levels equivalent to Ω_{siderite} of almost 1000 in the case of pH 2 at 1.0 bar of CO_2 (Fig. 1). This particular experiment ran for 60 days using fayalite and forsterite as starting substrates.

Despite significant supersaturation, in all experiments no trace of siderite or related iron carbonate minerals (such as chukanovite, metastable with relation to siderite, or amorphous iron carbonate) were found. XRD diffraction patterns revealed only pure fayalite/forsterite (Fig. 2), and iron carbonate [5] was not identified in any samples via SEM or EDS.

These results were obtained in every set of CO_2 -containing experiments at low and high W/R where starting pH was 4 and CO_2 levels were 0.5 bars or over.

Discussion: Many attempts to explain the relative absence of carbonates across Mars have been made.

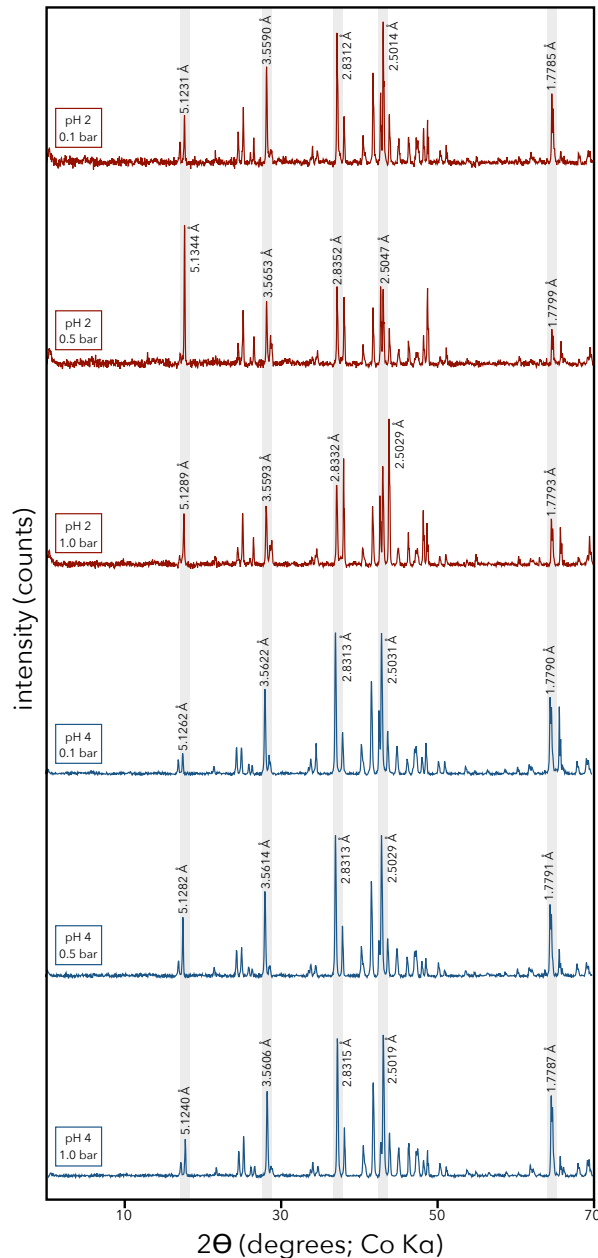


Figure 2: X-Ray diffraction spectra of solids (fayalite and forsterite) after 60 days of experimentation under varying pH and dissolved CO₂.

These include formation deep below the surface [6], formation and subsequent burial [2, 7], preclusion from formation by acidic waters [8], or a lack of significant atmospheric CO₂ [4]. Our data suggest that Fe(II)-carbonate precipitation in anoxic water-rock systems on early Mars was very likely controlled by kinetic factors. These factors, in total, increase the supersaturation threshold for nucleation of new Fe(II)-carbonate material and may have led to low rates of

crystal growth of previously precipitated material. It follows, then, that a lack of siderite cannot by itself be taken as evidence of low atmospheric CO₂, even in systems characterised by anoxia and relatively neutral to weakly basic pH (i.e., Gale Crater diagenetic pore waters [9]).

However, siderite has been identified as a pre-terrestrial alteration product from several martian meteorites [3, 10], and Fe-carbonate appears abundant in at least some sub-surface lithologies exposed by impact craters as identified by orbital spectroscopy [11]. A reasonable inference, based on our data, is that high water-rock ratio aqueous environments, especially those residing at the early martian surface and buffered by high $p\text{CO}_2$, may have been less likely to cross requisite nucleation thresholds for Fe(II)-carbonate. On the other hand, sub-surface environments where alkalinity produced from wall-rock alteration may overwhelm acidity contributed by a high $p\text{CO}_2$ atmosphere, may have been more likely to overcome kinetic barriers and generate new carbonate material (i.e., as observed in meteorites and from orbital data). Together, our results provide geochemical context to the “carbonate problem”. They represent a first step in reconciling climate models predicting relatively high $p\text{CO}_2$ in the early Martian atmosphere with orbital and *in situ* data.

Conclusions: Our experiments demonstrate that the iron carbonate precipitation is subject to strong kinetic control under simulated Noachian Mars-like conditions, even where over 0.5 bars of CO₂ are present. These kinetic factors explain, at least in part, why carbonate minerals formed via low temperature water-rock interaction may be rare at the martian surface but more abundant with depth. This hypothesis can be tested by continued kinetic studies under Mars-relevant conditions, and by new *in-situ* observations made by current and future Mars exploration missions.

References: [1] Leshin L. A. et al. (2013) *Science*, 341, 1238937. [2] Wray J. J. et al. (2016) *JGR: Planets*, 121, 652-677. [3] McSween H. Y. and Harvey R. P. (1998) *Int. Geol. Rev.*, 40, 774-783. [4] Bristow T. F. et al. (2017) *PNAS*, 114, 2166-2170. [5] Jimenez-Lopez C. and Romanek C. S. (2004) *GCA*, 68, 557-571. [6] Ehlmann B. L. et al. (2008) *Science*, 322, 1828-1832. [7] Niles P. B. and Michalski J. R. (2009), *Nat. Geosci.*, 2, 215. [8] Fairén A. G. et al. (2004) *Nature*, 431, 423. [9] Tosca N. J. et al. (2018) *Nat. Geosci.*, 11, 635. [10] Bridges J. C. et al. (2001) *Space Science Rev.*, 96, 365-392. [11] Michalski J. R. and Niles P. B. (2010) *Nat. Geosci.*, 3, 751.