

THE SEDIMENTARY ARCHIVE OF ATMOSPHERIC CO₂ ON MARS. L. E. Kissick¹, N. J. Tosca¹, and T. A. Mather¹, ¹Department of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN, UK (*lucy.kissick@earth.ox.ac.uk*).

Introduction: Mars' "missing" carbonates

Carbon dioxide was likely the main constituent of Mars' Noachian atmosphere given expected outgassing behaviour during crustal formation, yet carbonate-bearing bedrock exposures (namely the Fe(II)-carbonate siderite; FeCO₃) remain surprisingly rare at the 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]. Carbonate-rich rocks have also been recognised from orbit in Noachian terrains, especially where subsurface lithologies are exposed [e.g., 2]. This suggests that some environments on the early martian surface produced carbonates while others did not.

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 CO₂ 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 specific environments.

In this study we experimentally investigate the latter, and reproduce in the laboratory anoxic water-rock interactions between acidified fluids and ferromagnesian minerals to more closely examine the processes that control the precipitation of Fe(II)-carbonates.

Methods: Experimental geochemistry

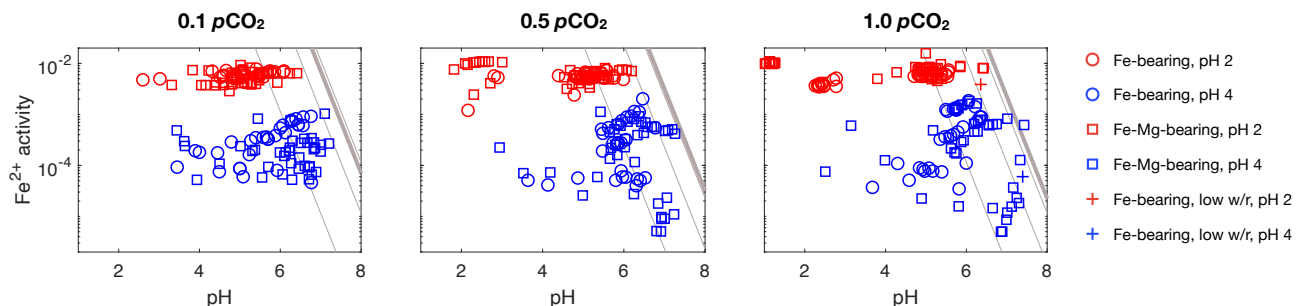
We conducted water-rock interaction experiments within closed vessels at varying water-rock ratios (W/R; at 1:1 or 1:500), initial pH (2 or 4), and dissolved CO₂ content (0.1, 0.5, and 1.0 bars equivalent atmospheric CO₂). As a planet in atmospheric decline from ~3.7-3.0 Ga, Mars is expected to have grown drier and more acidic through time; our variety of parameters reflect both Mars' earlier, more clement conditions, as well as its transition to the present day's aridity. These solutions were added to either pure synthetic fayalite (Fa: Fe₂SiO₄), or a mixture of both fayal-

ite and natural forsterite (Fo: Mg₂SiO₄; Fo_{>90}). Fe²⁺ and Mg²⁺ are two common cations derived from Mars' mafic crust and so are readily available to react with both ground- and surface waters. Strictly anoxic conditions were maintained to simulate Mars' lack of O₂ by conducting all experiments and analytical preparation techniques within N₂/H₂ glove-boxes maintained at 0 ppm O₂. Experiments ran over intervals of 12 hours to 85 days, were each sampled regularly at 10 intervals, and the solutions filtered for later analysis. Upon each experiment's termination, solids were filtered.

Results: Conditions for carbonate precipitation

Solution samples were analysed via both Inductively Coupled Plasma Optical Emission Spectrometry and Inductively Coupled Plasma Mass Spectrometry. In all experiments, under the equivalent of 0.1 to 1.0 bar of atmospheric CO₂, multiple solution samples exceeded the saturation point of siderite. Thermodynamically, this predicts the formation of a precipitate. This is graphically represented in *Figure 1*, where the Fe²⁺ activity of all solution samples ($a_{\text{Fe}^{2+}} = c_{\text{Fe}^{2+}} \times \gamma_{\text{Fe}^{2+}}$, where a is activity, c is Fe²⁺ molar concentration, and γ is the activity coefficient of Fe²⁺) is displayed against the corresponding solution pH in separate graphs for dissolved CO₂ levels. From left to right in each graph, the grey lines represent saturation states (or Ω , where $\Omega = [a_{\text{Fe}^{2+}}][a_{\text{CO}_3^{2-}}]/K_{\text{sp}}$, and K_{sp} is the solubility product of siderite) of 1 (beyond which a precipitate is thermodynamically predicted), 100, and 5000, the latter two being highly super-saturated. The heavier grey line is the limit beyond which Fe(II)-carbonate spontaneously nucleates from solution as amorphous Fe(II)-carbonate (AFC) [8], which is a metastable precursor to siderite.

Figure 1: Fe²⁺ activity and pH of all solution samples for anoxic water-rock interaction experiments conducted under 0.1-1.0 bar CO₂. Grey lines represent siderite saturation states of 1, 100, and 5000 (left-right); heavy grey line is the AFC line [8]. Initial pH of experiments are red (pH 2) or blue (pH 4).



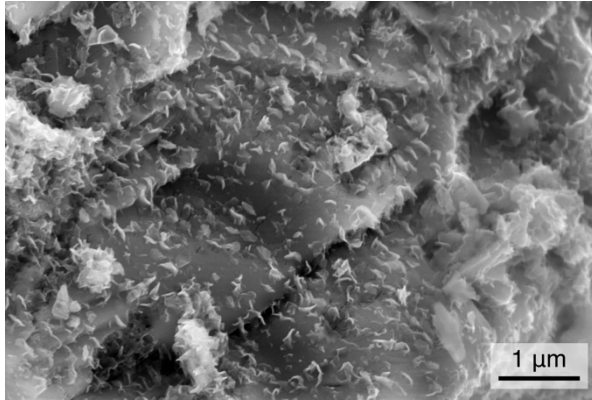


Figure 2: Aligned nanometre-scaled precipitates upon a fayalite grain. EDS shows elevated carbon levels for this sample than unreacted or other reacted solids.

While many solution samples display siderite saturation states that exceed 1, only experiments bearing both fayalite and forsterite (denoted by squares) exceed supersaturation levels of 100, and most of these are experiments begun at pH 4 (blue, 11 out of 14) and more commonly where CO₂ levels are highest (9 samples for 1.0 compared to 1 for 0.1). This suggests under a wide range of conditions, siderite saturation state failed to reach the point of spontaneous nucleation. Only one datapoint exceeds the AFC line: one bearing Fa/Fo, begun at pH 4, and under 1.0 bar CO₂.

The corresponding experiment for this datapoint reached the highest pH recorded (8.2). It was the only experiment of 162 to yield a possible precipitate: nanometre-scale plates were observed via Scanning Electron Microscopy (SEM; see *Figure 2*). Energy Dispersive X-Ray Spectrometry (EDS) determined elevated levels of carbon present in the phase; due to their size, the specific phase could not be determined with the analytical techniques employed thus far.

Discussion: CO₂ in the Martian rock record

What are the prerequisites for carbonate formation? Set in a kinetic framework, our experimental data indicate that anoxic water-rock systems on Mars evolve along a chemical pathway that only surpasses the threshold for spontaneous Fe(II)-carbonate nucleation under the combined conditions of: high Fe²⁺ activity; high alkalinity; and high dissolved CO₂, whereby pH and Fe²⁺ activity must reach higher levels in a 0.1 bar scenario than a 1.0 bar. We can best explain Fe(II)-carbonate distribution on Mars by asking, where would these criteria best combine, and accordingly, where is siderite saturation likely to be the highest?

Where should carbonates form? The main carbonate-forming environments on Mars include within brines [e.g., 6], hydrothermal fluids [e.g., 9], and by in-situ carbonation [e.g., 10]. These are all commonly connected by occurring within the subsurface, where deep, alkaline crustal fluids may migrate to the surface

after sufficient residence time within a mafic substrate. Under such an environment, migrating fluids become buffered to highly alkaline pH from mafic wall-rock alteration, which may overwhelm the acidity contributed by a high pCO₂ atmosphere. Oxygen species are also lost, and Fe remains in the reduced state. Fe²⁺ in solution then precipitates in the presence of high alkalinity and CO₂, which may migrate into the system from the atmosphere, to produce Fe(II)-carbonate. This is in contrast to surface waters, which, in equilibrium with a CO₂-rich atmosphere, will be buffered to mild acidity and be less likely to cross requisite nucleation thresholds for Fe(II)-carbonate.

The above scenarios require liquid water, reducing conditions, and a source of CO₂, which are all met in the Noachian era of anticipated higher temperatures and a substantial CO₂ atmosphere. This is consistent with Fe(II)-carbonate identification in some of the oldest terrains on Mars exposed via impact [e.g., 2, 7, 9]. These exposures are windows into an ancient, aqueous, Fe²⁺-rich, neutral-to-alkaline environment once in contact with CO₂-bearing fluids, which agrees with the criteria for Fe(II)-carbonate formation observed in our experimental research. Attributing a lack of Fe(II)-carbonates on Mars to a lack of atmospheric CO₂ is therefore unreasonable considering strict parameters of pH and a Fe²⁺ must also be met for their precipitation.

Conclusions:

Our experiments demonstrate that Fe(II)-carbonate precipitation is subject to strong kinetic control under chemical conditions relevant to the early Martian surface. This can explain why carbonate minerals are rare at the surface but more abundant with depth, and is consistent with the current inventory of Fe(II)-carbonates. This research also suggests the rarity of carbon stored in the Martian sedimentary record can be attributed not to low atmospheric CO₂ but to a rarity of both deep carbonate exposures and the combined factors that enable their precipitation.

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