CARBONATE IN OLIVINE-RICH UNIT(S) ON MARS MAY HAVE FORMED AT LOW P(H₂O).

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Summary: We offer a new hypothesis for formation of carbonate, with little or no serpentine, in the olivine carbonate unit(s) observed on Mars, particularly in the Nili Fossae region. Whereas several papers invoke water-rock reaction as an origin for the carbonate in these units, a key observation is the paucity of brucite, serpentine and/or talc in orbital spectroscopy over most of the unit. We propose that the carbonate formed via weathering in the presence of an atmosphere with low P(H₂O). Our simple, end-member thermodynamic calculations indicate that at current conditions, with average P(CO₂) ~ 0.006 bars and P(H₂O) ~ 2 x 10⁻⁶ bars [1], Mg-rich olivine is stable above ~ 0°C with respect to serpentine + brucite, but unstable with respect to Mg-carbonate + quartz. Conversely, in the presence of liquid H₂O, serpentine + brucite would be likely to form, together with Mg-carbonate.

Introduction: Olivine-rich units are common on Mars, as documented by orbital and surface observations [reviews in 2-4]. They are particularly abundant in the circum-Isidis Planitia region, including the Nili Fossae region and the Jezero Crater area, the landing site for the Mars 2020 Rover, where they may be olivine-rich pyroclastic rocks and their eroded, reworked equivalents [4-6] or post-Isidis lavas [3,7,8]. Within this region many of these olivine-rich units also contain ~ 20% Mg-rich carbonate minerals [9-12], which have been interpreted as alteration products of olivine (± other silicates). However, brucite, serpentine and talc – hydrous Mg-rich minerals that can be detected from orbital data – are rare in these rocks [13-15]. This information on mineral parageneses poses a challenge in quantifying the conditions of carbonate alteration.

Figure 1: Phase diagram calculated using computational methods provided by ENKI, a software framework for thermodynamic modeling of natural materials. The Python interface to ENKI provides access to thermodynamic properties of phases, from which the affinity of reaction can be constructed. For each reaction, affinity is minimized over a range of temperatures using standard root-finding routines. Thermodynamic properties of minerals from the Berman database, H₂O from a combination of reference state models (Standard Water Interpolative Model, SWIM), and CO₂ from the Duan & Zhang equation of state [16]. Stability fields for H₂O vapor, ice and liquid are shown as light, medium and dark grey fields, respectively. Crosses at 0°C illustrate current, Martian average P(CO₂) in red and P(H₂O) in blue. The 2nd blue cross, at 45°C and P(H₂O) ~ 10⁻⁴ bars, is discussed in the text.
Previous work: Ehmann et al. [9] proposed multiple mechanisms for formation of carbonate in olivine-rich unit(s) in the Nili Fossae region including carbonate formation under cold, dry conditions resembling weathering of olivine-rich meteorites in Antarctica [17]. Alternatively, they and later workers [e.g., 11] invoked low-temperature, in situ carbonation similar to processes in the Samail ophiolite in Oman [e.g., 18]. However, such processes form abundant brucite, serpentine and/or talc, as well as Mg-carbonates.

Thermodynamic studies [19-21] modeled carbonate formation via alteration in aqueous fluids with dissolved CO₂. While 100% consumption of olivine in such processes can produce abundant carbonate + quartz and/or amorphous silica (SiO₂(a)), as in Oman and elsewhere [e.g., 22], such processes also form zones rich in brucite, serpentine and/or talc at lower water/rock ratios. Thus, explicitly or implicitly, such modeling predicts the abundant brucite, serpentine and/or talc, as well as Mg-carbonates, and these predictions may be inconsistent with observations.

Olivine + gas reactions at low P(H₂O): Here we present simple, end-member thermodynamic calculations for equilibria involving Mg-olivine (Forsterite, Mg₂SiO₄) and an atmosphere with low P(H₂O) (Figure 1). For Mg-endmembers, current average Martian conditions (P(CO₂) ~ 0.006 bars, P(H₂O) ~ 2 x 10⁻⁶ bars lie close to equilibrium values for olivine + H₂O = serpentine (chrysotile, Mg₃Si₂O₇(OH)₄) and brucite (Mg(OH)₂) at temperatures above about 0°C. However, olivine is unstable with respect to magnetite (MgCO₃) + quartz (SiO₂) at temperatures below about 100°C. Thus, reaction of olivine with the current Martian atmosphere at temperatures above 0°C favors formation of magnetite but not serpentine + brucite. (Mg-talc, Mg₃Si₂O₇(OH)₄), is not stable with respect to serpentine + brucite in olivine-rich compositions with molar Mg/Si > 1.5 [23], and with respect to serpentine (chrysotile) + quartz below about 15°C [24]).

At 0°C and higher P(H₂O), or current P(H₂O) and lower T, serpentine + brucite could form via weathering of olivine. However, close to equilibrium the affinity driving this reaction is small, much less than for olivine carbonation, as seen in the large difference between equilibrium and observed P(CO₂) (Fig. 1).

At higher temperature and pressure, the relative stability of olivine with respect to serpentine + brucite would have been similar if P(H₂O) remained low. Thus at ~ 45°C, olivine is stable with respect to serpentine + brucite at < 10⁴ bars P(H₂O). If the CO₂/H₂O ratio at these conditions remained ~ 3000, and the Martian atmosphere still contained nearly 100% CO₂, this corresponds to atmospheric pressure of 0.3 bars.

Even at lower T and/or higher P(H₂O), a low affinity for olivine hydration may lead to low rates, compared to the large affinity and faster rates for carbonation (e.g., Kelemen & Matter 2008, Figure 5 [18]). Thus, weathering of olivine-bearing meteorites in Antarctica may not have produced brucite, serpentine or talc in 10⁴ to 10⁵ years [17]. However, given evidence for ongoing serpentinization at Earth surface conditions [18,24-27], it seems unlikely that terrestrial weathering could produce carbonate without hydrous minerals over longer times, especially at > 20°C.

Carbonate formation in olivine-rich Martian units may have occurred before emplacement of the overlying, carbonate-poor, mafic cap rocks in the Nili Fossae region, prior to fluvial erosion, and thus at high P(H₂O). However we wonder if this is correct. Instead, the relative abundance of carbonate in the olivine-rich and overlying lava units could stem from bulk composition, rather than timing, as in Oman where peridottes are extensively carbonated, while gabbros are not.

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