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THE NAKHLITE METEORITES PROVIDE EVIDENCE FOR MINERALIZATION OF MARTIAN CO$_2$ BY CARBONATION OF SILICATES. T. Tomkinson[1], M. R. Lee[2], D. F. Mark[1], F. M. Stuart[1]. [1]Scottish Universities Environmental Research Centre, East Kilbride E75 0QF, U.K. E-mail: tim.tomkinson@glasgow.ac.uk., [2]School of Geographical and Earth Sciences, University of Glasgow, Glasgow G12 8QQ U.K.

Introduction: Climate models suggest that the Noachian atmosphere of Mars could have been CO$_2$-rich and much thicker than at the present-day [1, 2]. These predictions can be tested by attempting to locate the 'missing' CO$_2$. Numerous mechanisms for the loss of CO$_2$ from the planet's early atmosphere have been proposed, including escape to space, trapping as ice and clathrates, and storage in carbonate deposits [3-6]. The latter scenario is supported by the detection of carbonates within Martian dust, bedrock outcrops and meteorites [6-11]. However, the volumes so far located are insufficient to account for all the CO$_2$ that is predicted to have been once present within the atmosphere.
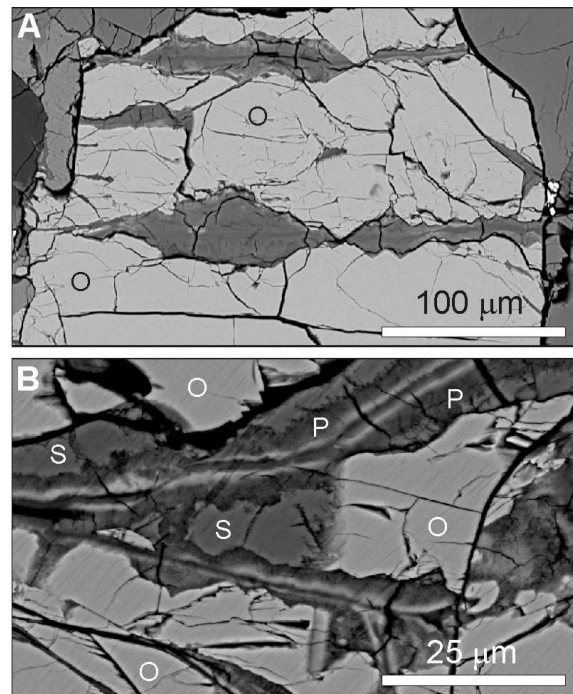
Here we propose that large quantities of CO$_2$ were removed from the Noachian atmosphere and stored in the crust by 'carbonation'. This is a water-mediated reaction whereby silicate minerals that are rich in divalent cations (e.g. olivine) are replaced by carbonates; on Earth carbonation of ultrabasic and basic rocks is an efficient way to irreversibly sequester CO$_2$. For example, the carbonation of terrestrial basalt consumes ~1.8×10^8 tons CO$_2$ yr^{-1} globally [12], and if all of the peridotite in the Samail ophiolite of Oman was converted to carbonate it would consume 77 trillion tons of CO$_2$ [13].

Our study has used the nakhlite meteorite Lafayette as an analogue for the Noachian crust. Lafayette is an Amazonian olivine-bearing clinopyroxenite that contains a suite of secondary minerals, principally carbonates and hydrous silicates, that crystallized from liquid water [14].

Methods: A carbon coated thin section of Lafayette was studied using a FEI Quanta field-emission SEM equipped with an EDAX Genesis energy-dispersive X-ray spectrometer (EDX) and TSL electron backscatter diffraction (EBSD) system. Backscattered electron (BSE) images were obtained at 20 kV and under high vacuum. The crystallographic orientation of the olivine grains was determined by EBSD mapping at low vacuum (~50-70 Pa), 20 kV, and with a relatively high beam current. Kikuchi patterns were acquired at a rate of ~20 patterns/sec. and at a step size of ~0.3 µm. The patterns were indexed using the structure file for olivine in the TSL database.

Results: The Lafayette carbonates occur within serrated veins that cross-cut olivine grains (Fig. 1A), and are also present within the mesostasis. The axes of most of the olivine-hosted veins are oriented parallel to (001)$_{olivine}$. The veins contain Ca-siderite (Ca$_{0.31}$Mn$_{0.24}$Fe$_{0.45}$CO$_3$), several generations of phyllosilicates that can be distinguished from each other in BSE images by contrasts in their crystal size, and Fe-oxides (Fig. 2). The siderite is always in contact with olivine, and occurs either between closely-spaced veins (Fig. 1B) or it fills coarse serrations on vein walls (Fig. 2). The geometry of the siderite-olivine interface is controlled by the olivine crystal structure and is typically parallel to {111}.
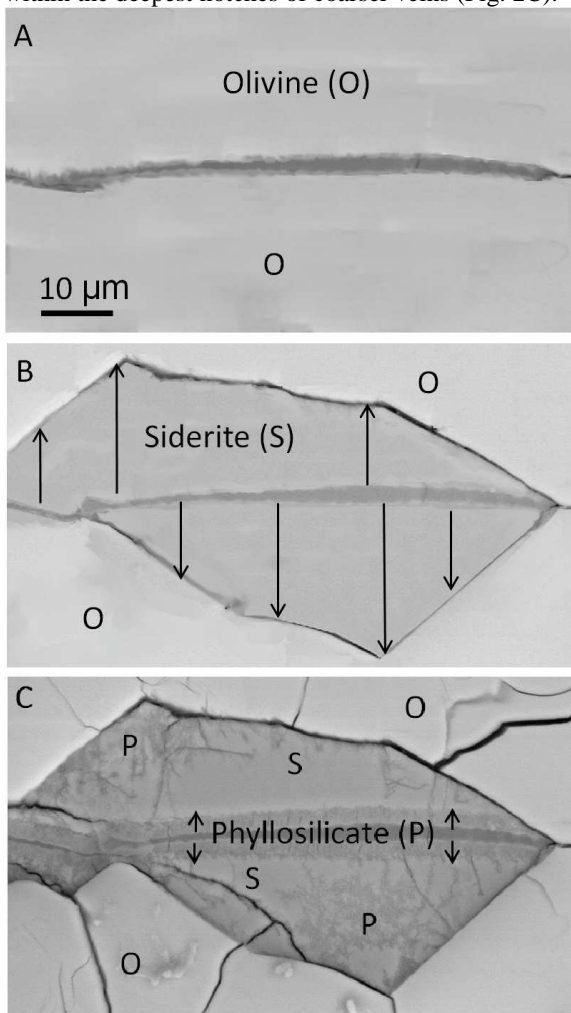

Figure 1: BSE images of olivine-hosted secondary mineral veins. [A] Part of an olivine grain (O) surrounded by augite (medium grey). The olivine is cross-cut by veins with coarsely serrated walls whose axes lie parallel to olivine (001). [B] An 'island' of olivine (O) between two veins that has been partially replaced by siderite (S). Among the constituents of the veins is phyllosilicate (P) and films of Fe-oxide (white).

Siderite is always intergrown with a coarsely crystalline phyllosilicate, and the petrographic relationships between the two minerals show that the phyllosilicate has replaced the carbonate [14, 15]. The axes of the veins are occupied by films of Fe-oxide (Fig. 1B) and nanocrystalline smectite.

Discussion: The petrographic relationships between Ca-siderite and olivine indicate that the carbonate has replaced the silicate, and the sequence of

events is shows schematically in Figure 2. The siderite is inferred to have replaced the walls of an intracrystalline sheet pore (Fig. 2A), and the trajectory of the reaction interface was controlled by the olivine crystal structure (Fig. 2B). A very similar sawtooth interface between terrestrial olivine and replacive Ca-Mg carbonates has been previously observed [16]. The limited degree of replacement of olivine suggests that siderite crystallized for only a brief period of time. Following exhaustion of carbonate anions, the carbonate was partially or completely replaced by phyllosilicates, again working inwards from the vein axis (Fig. 2C). In narrow veins all of the siderite has been replaced by phyllosilicate so that it survives only within the deepest notches of coarser veins (Fig. 2C).

Figure 2: Edited backscatter electron (BSE) images of a secondary mineral vein within olivine (O) showing its sequence of formation. [A] Generation of (001)-parallel sheet pores by dissolution/fracturing. [B] Formation of siderite by crystallographically controlled replacement of olivine. [C] Replacement of siderite by phyllosilicate (P), working inwards from the vein axis.

Implications: Lafayette provides direct evidence for carbonation of the Martian crust. On Earth this reaction can be initiated by the exposure of soluble silicate minerals such as olivine to carbonic acid-rich solutions. Dissolution of olivine supersaturates solutions at the reaction interface with respect to the carbonate by simultaneously increasing their pH value and liberating divalent cations [17]. Given the composition of Lafayette olivine ($\sim Fa_{67}$), it may be expected that the replacive carbonates would have been Fe- and Mg-rich, yet the siderite contains Ca and Mn, and is almost devoid of Mg. Therefore the solutions that mediated replacement must have imported carbonate anions, Ca and Mn to the reaction interface, and exported Mg. However, enrichment in Ca and depletion of Mg is commonplace in the carbonation of terrestrial olivine-rocks, and is due to kinetic inhibition of magnesite crystallization owing to hydration of Mg ions [17].

Large volumes of carbonate did not form in the nakhlite parent rock owing to the paucity of water and carbonate anions. However, we predict that carbonation would have been far more efficient and widespread in the Noachian crust if the atmosphere had been warmer, wetter and richer in CO_2. Crucially however Lafayette shows that the carbonates selectively replace olivine over other silicates owing to its much higher solubility. Therefore, the Noachian carbonates may be finely disseminated throughout the Martian crust and so difficult to detect by orbiters and rovers.

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