ANCIENT MARTIAN FLOODS IN A PLAUSIBLE VARIABLE CLIMATIC ENVIRONMENT AS REVEALED FROM THE SEQUENTIAL GROWTH OF ALLAN HILLS 84001 CARBONATE GLOBULES.

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Introduction: Until samples are returned from Mars, the achondrite meteorites are the only Martian rocks available for study in our laboratories. They provide valuable information about current and ancient environmental conditions on Mars because they have different crystallization ages and relevant information about their formation regions on the red planet [1]. Here we focus in the Allan Hills 84001 meteorite (hereafter ALH 84001) that can be used for constraining conditions on early Mars because it formed more than 4 Gyr ago. Due to its age and long exposure to the Martian environment, ALH 84001 has unique features capable of recording early processes: a highly fractured texture, gases trapped during the ejection event or during formation of the rock, and the presence of spherical Fe-Mg-Ca carbonates. Here we describe the importance of carbonates within the ALH 84001,82 thin section (Fig. 1) [2].

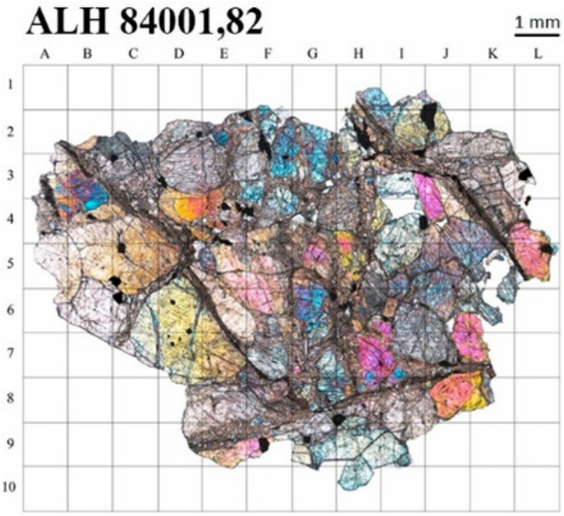

Figure 1. High-resolution mosaic of the ALH 84011,82 section in transmitted light and crossed nichols. A grid to identify the regions of interest (ROIs) is superimposed.

Instrumental procedure: As the focus of this study is the carbonates in the thin section (Fig. 2), we have used several SEM and microprobe techniques to determine the chemical composition of the carbonate globules. In particular, quantitative chemical analyses and BSE images of the carbonate globule walls were obtained using a JEOL JXA-8900 electron microprobe equipped with five wavelength-dispersive spectrometers at the UCM.

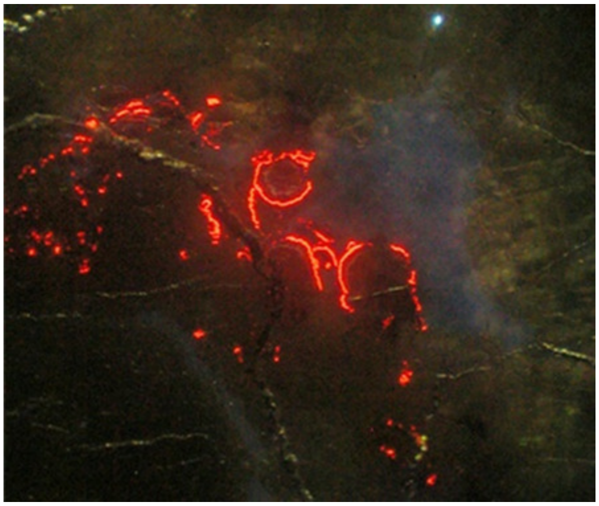

Figure 2. Cathodoluminescence image obtained of the D5 ROI in Fig. 1 (note the curved crack for further identification) using an accelerating voltage of 20-24 keV. As Fe is a typical quencher, the right red areas correspond to Fe-poor and Mn-rich carbonate layers that nicely delineate the carbonate globule walls.

Results: The carbonate globule chemical data, previously presented in [2], are clear evidence for a sequential growth of the carbonate. Such progressive growth could be explained by the precipitation of the ALH 84001 carbonates after (or during) at least two/three different events while the rock was forming part of the ancient Mars' crust about 4 Gyr ago. Indeed, the two main fracture systems of the analysed thin section and the presence of fracturing and corrosion predating precipitation of some layers [2] point towards two or even three different formation episodes with clearly distinct bulk chemistry. For the sake of brevity, such overall results could be exemplified in one of the studied carbonate globules (see Fig. 3).

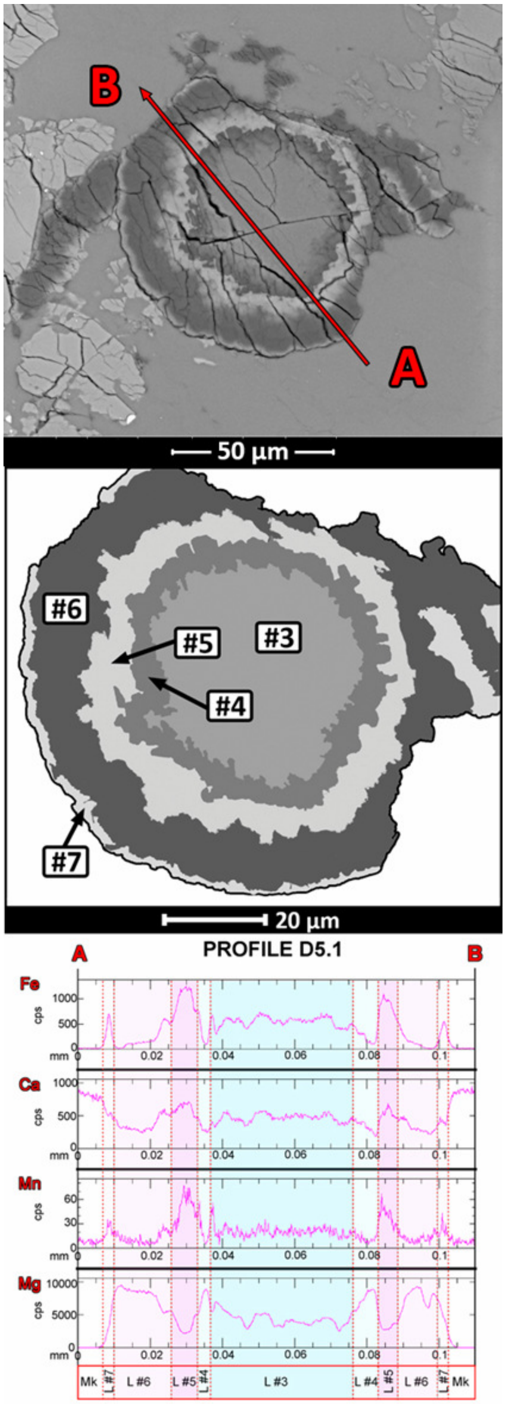

Figure 3. BSE and schematic images showing layers #3 to #7 in one carbonate globule in D5, plus the Fe, Ca, Mn, and Mg microprobe line profiles from one side to the other.

Discussion: We notice a sharp change in composition that suggests a change in solution chemistry and saturation state (e.g., the concentration in CO_2 or pH) between formation of the inner (#1 to #4) and outer (#5 to #7) layers. The microprobe data thus reveal two trends that are consistent with the idea of at least two episodes of precipitation to form the carbonate globules. The distribution coefficients for Fe and Mn into carbonates are higher than 1, meaning that any Fe^{2+} or Mn^{2+} in the fluid will preferentially partition into the carbonate [3]. Assuming that the system was closed so that there was no continuous influx of fluid, Fe and Mn would be depleted relative to Mg, and this process may be responsible for creating the geochemical patterns observed in the layers. The studied carbonates display two compositional patterns (at layers #1 to #4 and again at #5 to #7), which implies that a second carbonate formed as an overgrowth on the first generation. Indeed, the contrasting trends imply that the fluids responsible for carbonate precipitation differed in composition, possibly pointing to distinct aqueous alteration events, which could be related with the already mentioned necessity of at least two episodes of fracturing. Our previous globule growth interpretation is also in accordance with experimental data [4].

Conclusions: The petrographic features and compositional properties of these carbonates indicate that a Mg- and Fe-rich solution saturated the rock, leading to their precipitation in at least two different episodes. This is supported by the presence of distinct chemical trends indicating that these carbonates grew in two or more stages. In conclusion, 1) we have found clear evidence of carbonate globule formation when a fluid soaked the host rock of this meteorite, with chemical variations probably associated with atmospheric changes and volcanic outgassing. 2) The presence of these carbonates suggests that secondary minerals produced by aqueous alteration should be more common in the oldest Martian terrains, as suggested by recent remote-sensing studies and their study can provide valuable clues on the long-standing action of water on the Martian environment.

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References: [1] Moyano-Cambero C.E. et al. (2013), In *The Early Evolution of the Atmospheres of Terrestrial Planets*, J.M. Trigo-Rodríguez, F. Raulin, C. Muller and C. Nixon (eds.), Springer, New York, 165–172, 2013. [2] Moyano-Cambero C.E. et al., (2017) *MAPS* 52, 1030-1047. [3] Rimstidt J. D., et al. (1998) *GCA* 62:1851-1863. [4] Golden D. C., et al. (2001) American Mineralogist 86:370-375.