

Chemical Composition of Carbonate Globules from the Martian Meteorite ALH84001: A Test of Thermal Metamorphism Origin

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Introduction

The carbonate globules found in the Martian meteorite ALH84001 have been the subject of intense study and considerable controversy since McKay et al. [1] suggested they contained possible evidence of ancient microbial life on Mars. Thomas-Keprta et al. [2] have shown that a significant fraction of the magnetite grains extracted from the ALH84001 carbonate globules are quite similar in size, shape, and composition to the magnetite grains produced by terrestrial magnetotactic bacteria, and they claim that the properties of the terrestrial biogenic magnetite are sufficiently distinct to distinguish these magnetite grains from those produced by natural geological activity. However, Golden et al. [3, 4] have performed thermal decomposition experiments on carbonate that has a chemical composition similar to that of the most abundant carbonate in the ALH84001 carbonate globules. Golden et al. [3, 4] report that they can produce all of the features detected in the ALH84001 carbonate globules, including magnetite of the correct size and shape, by this simple thermal decomposition. If, as suggested by Golden et al. [3, 4], all the features in the ALH84001 carbonate globules can be produced by a single, nonbiogenic process, this would significantly undermine the suggestion by McKay et al. [1] that the carbonate globules and the associated magnetite in the ALH84001 meteorite provide evidence for ancient life on Mars.

The ALH84001 carbonate globules consist of four regions: (1) a core of Fe-rich carbonate, (2) a thin inner magnetite band, (3) a band of Mg-rich carbonate (usually called "rim carbonate"), and (4) a thin outer magnetite band. We previously performed bulk chemical analyses, by x-ray fluorescence (XRF), of isolated chips of core and rim carbonate from the ALH84001 carbonate globules by using the x-ray microprobe (XRM) at beamline X-26A at the National Synchrotron Light Source at Brookhaven National Laboratory [5], and we mapped the trace element distribution in a section of an ALH84001 carbonate globule that was $\sim 4 \mu\text{m}$ thick by using the GSECARS XRM at sector 13 at the APS [6, 7]. The section we analyzed on the GSECARS XRM measured about $40 \times 40 \mu\text{m}$ in size and included material from all

four distinct regions. The results from the mapping suggested that the Cr concentration in the inner magnetite band was too high to be explained by simple thermal decomposition of the core carbonate [7]. If so, this would indicate that Golden et al.'s [3, 4] claim that all the features of the ALH84001 carbonate globules can be produced by a simple thermal decomposition of the Fe-rich core carbonate is not correct, and a second process would be required to incorporate Cr into the inner magnetite band. However, we were concerned that the GSECARS XRM analysis of the inner magnetite band, which is variable in width from ~ 1 to $\sim 4 \mu\text{m}$, might have been compromised by including material from the carbonate bands as well, since the analysis beam spot was $\sim 3 \mu\text{m}$ in size. We have now employed the XRM at beamline station 2-ID-D at the APS to characterize an ALH84001 carbonate globule at a spatial scale significantly smaller than the width of the magnetite bands in order to remove any uncertainty in the prior analyses.

Methods and Materials

We extracted a carbonate globule from a freshly broken surface of a chip from the ALH84001 meteorite provided to us by the Astromaterials Curatorial Facility at the NASA Johnson Space Center in Houston, TX. A chip from this carbonate globule was embedded in epoxy, and an ultramicrotome section was cut and deposited on a transmission electron microscope (TEM) grid.

We mapped the spatial distribution of most of the elements from Mg to Zn, with $<200\text{-nm}$ spatial resolution, in a section of this ALH84001 carbonate globule containing all four distinct regions. We used the XRM at beamline station 2-ID-D at the APS. We obtained element maps by plotting the signal intensity at each pixel for each element region-of-interest in the XRF spectrum. We obtained a bulk chemical analysis of each of the four regions in the globule by integrating the single-pixel XRF spectra over all the pixels corresponding to each of the four distinct regions. The resulting integrated spectra are shown in Fig. 1.

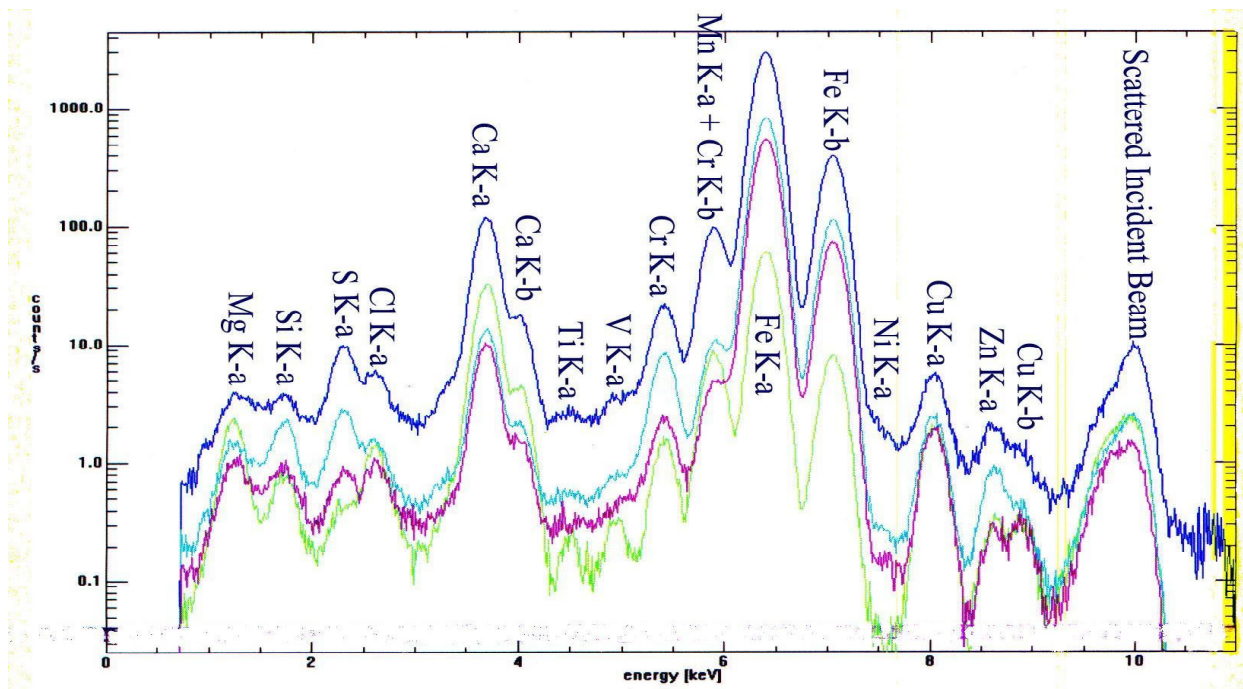


FIG. 1. XRF spectra integrated over the four distinct regions of an ultramicrotome section of an ALH84001 carbonate globule: the Fe-rich core carbonate (purple), the inner magnetite band (light blue), the Mg-rich rim carbonate (green), and the outer magnetite band (blue).

Results

The core carbonate (purple spectrum in Fig. 1) is Fe-rich and contains easily detectable amounts of the elements Mg, Si, S, Cl, Ca, Cr, Mn, Fe, and Ni. The Cu peak seen is the XRF spectrum dominated by fluorescence from the Cu TEM grid. Further analysis is required to determine how much of the Zn is also from the TEM grid. This Fe-carbonate is the presumed starting material for the thermal decomposition proposed by Golden et al. [3, 4], and in the simple model that they propose, this core carbonate should be the source of the trace elements that are found in the rim material (both magnetite bands and the rim carbonate). For closed-system thermal decomposition, the required mass balance is that the rim carbonate and the two magnetite bands sum to the core carbonate composition.

The rim carbonate (green spectrum in Fig. 1) is enriched in Mg and depleted in Fe relative to the core, as expected from the reports of other investigators. This Mg enrichment is not large enough to exclude the Fe-carbonate as its source, since the magnetite bands have lower Mg than does the core carbonate and thus the required mass balance may be achieved. The spectrum in Fig. 1 shows that this rim carbonate is also enriched in Mn, Ti, and V when compared with the core carbonate. The core carbonate does not appear to contain sufficient

Mn, Ti, or V to supply these elements to the rim in the simple, closed-system, thermal decomposition model.

The inner magnetite band (light blue spectrum in Fig. 1) is enriched in Cr relative to the core carbonate. The individual element maps show that the Cr in the inner magnetite band is concentrated in a few submicron hot spots, consistent with the presence of several discrete chromite grains in this band. The inner magnetite band contains a significant amount of Si, presumably in the clay that has been reported on by other investigators. The Fe-concentration of the inner magnetite band is significantly lower than that of the outer magnetite band, indicating that the inner magnetite band is not pure magnetite, again consistent with a substantial concentration of clay.

The outer magnetite band (dark blue spectrum in Fig. 1) has a higher Fe content than does the inner magnetite band, indicating that there is less dilution of the magnetite by other materials (such as clay) in the outer magnetite band. The Cr is lower in the outer magnetite band than in the inner magnetite band. However, there is significant Mn in the outer magnetite band.

Discussion

The presence of substantial Si and Cr in the inner magnetite band but not in the outer magnetite band suggests that the two bands of magnetite formed at

different times and under different conditions. The high Cr content of the inner magnetite band is inconsistent with the closed-system thermal decomposition of the low-Cr, Fe-rich core carbonate, which does not contain enough Cr to provide this amount of Cr through thermal decomposition. The high Mn, Ti, and V in the rim carbonate may also be inconsistent with the thermal decomposition of the Fe-rich core carbonate that provides these elements, but we have not yet performed a detailed mass balance. The high Mn in the outer magnetite band is inconsistent with the thermal decomposition of the low-Mn, Fe-rich core carbonate that provides this amount of Mn through thermal decomposition.

The detection of V in the rim carbonate may be particularly significant, since the oxidization state of V is particularly sensitive to redox conditions. Thus, it may be possible to constrain the formation conditions of the rim carbonate by performing micro-x-ray absorption near-edge structure (micro-XANES) spectroscopy on the V in the rim carbonate.

We cannot determine if the Mg-rich rim carbonate and the magnetite in ALH84001 were produced by thermal decomposition of the core (Fe-rich) carbonate, but the fact that trace elements were found in the rim carbonate and the magnetite bands is inconsistent with their having been formed by a single, closed-system thermal decomposition process, as proposed by Golden et al. [3, 4]. Providing the minor elements that we detected in the two magnetite bands and in the rim carbonate would require other processes that would need to occur simultaneously with or after the thermal decomposition event; this substantially complicates the simple, single-step thermal decomposition mechanism that Golden et al. [3, 4] have invoked. Rather, these measurements of the minor elements in the magnetite bands and the rim carbonate of the ALH84001 carbonate globules support the idea that these materials originated by several stages of modification and element addition. Evidence for multiple episodes of aqueous alteration in ALH84001 and other meteorites from Mars is discussed in a review by Bridges et al. [8].

Acknowledgments

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