

# X-ray Microprobe Analysis of the ALH84001 Mars Meteorite: Implications for the Chronology and Formation of the Carbonate

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## Introduction

McKay et al. suggested that carbonate globules in the ALH84001 meteorite from Mars contained evidence consistent with the development of bacterial life early in the history of Mars [1]. This result provoked an extensive study of the ALH84001 meteorite. More recently, Thomas-Keprta et al. [2] published a study showing that the magnetites associated with carbonate rims are of the size and shape produced by terrestrial bacteria. That paper has revived interest in ALH84001.

The typical ALH84001 carbonate globule consists of four regions (shown in Fig. 1): a core of Fe-rich carbonate, a thin magnetite-rich band, a rim of Mn-rich carbonate, and another thin magnetite-rich band. Trace element analysis of each of these phases may allow us to address three important issues regarding these carbonates. First is the origin of the magnetite-rich bands in the ALH84001 carbonate globules. If the magnetites are derived from the underlying core carbonate through thermal decomposition (as proposed by Golden et al. [3]), then we expect to see “inherited” trace elements in these magnetite bands. Second is the origin of the rim carbonate. This may be constrained by determining if the core carbonate has the same trace elements as the rim carbonates. Third is the age of the rim carbonate. Borg et al. [4] dated the formation age of the carbonate by using a Rb/Sr chronometer. They performed their measurements on progressive leachates of a carbonate-rich separate that had a wide range of Rb/Sr ratios.

We had previously measured the trace element contents of chips from core and rim carbonates from an ALH84001 carbonate globule by using an x-ray microprobe on beamline X26A at the National Synchrotron Light Source (NSLS) [5]. These measurements showed the rim carbonate had a very low Rb content, with  $Sr \gg Rb$ , inconsistent with the ~5 parts per million (ppm) Rb and the approximately equal Rb and Sr contents reported by Borg et al. [4]. The large (~15  $\mu\text{m}$ ) analysis spot of the NSLS x-ray microprobe precluded analysis of the magnetite bands.

We have revisited this question by using the GeoSoilEnviro Consortium for Advanced Radiation

Sources (GSECARS) x-ray microprobe at the APS. The GSECARS microprobe has superior element detection limits and a smaller analysis beam spot than the NSLS instrument, allowing significant improvement over our earlier measurements.

## Methods and Materials

Two carbonate globules were removed from ALH84001 and embedded in epoxy, and ~4- $\mu\text{m}$ -thick slices were prepared by ultramicrotomy. The samples, which showed the same four zones as those in Fig. 1, measure about  $40 \times 40 \mu\text{m}$ . They were placed on ~8- $\mu\text{m}$ -thick Kapton® films for analysis.

The GSECARS x-ray microprobe uses an undulator x-ray source, a silicon (111) cryogenic monochromator, Kirkpatrick-Baez microfocusing mirrors, and a germanium solid-state fluorescence detector (as described

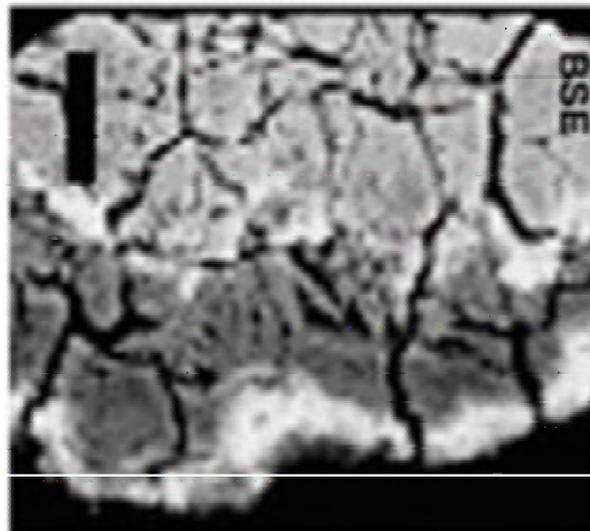


FIG. 1. SEM backscattered electron image of a polished section of a carbonate from ALH84001 showing the four distinct zones: the Fe-rich core carbonate (dark, top), a thin magnetite band (bright), the rim carbonate (dark), and another magnetite band (bright, bottom).

by Sutton et al. [6]). X-ray spectra were collected with 15-min dwell times, in 1- $\mu\text{m}$  steps (by using an  $\sim 3\text{-}\mu\text{m}$  analysis beam spot along a line traversing the entire sample from the core carbonate to the outer magnetite-rich band).

## Results

Element abundances for Ca, Ti, V, Cr, Mn, Fe and Sr were measured. Tungsten contamination from the needle used to mount the sample precluded measurement of the elements from Zn through Br because W L-lines made significant contributions in this energy range.

The highest Cr concentration was observed in the inner magnetite band (see Fig. 2). The two inner magnetite band analysis spots that have minimal carbonate contamination have a Cr concentration of  $\sim 0.14\%$ , while the underlying core carbonate has a mean Cr concentration of  $\sim 0.03\%$ . More striking is the Cr/Fe ratio, which is  $\sim 0.014$  in the inner magnetite band but almost an order of magnitude lower,  $\sim 0.003$ , in the high-Fe core carbonate. This indicates that the magnetite band cannot be derived by a simple thermal decomposition of the core carbonate, which would preserve the Cr/Fe ratio in the magnetite band. The Sr/Ca ratio is relatively constant over the core carbonate and the inner magnetite band (see Fig. 3), with a Sr/Ca ratio of  $\sim 20 \times 10^{-4}$ .

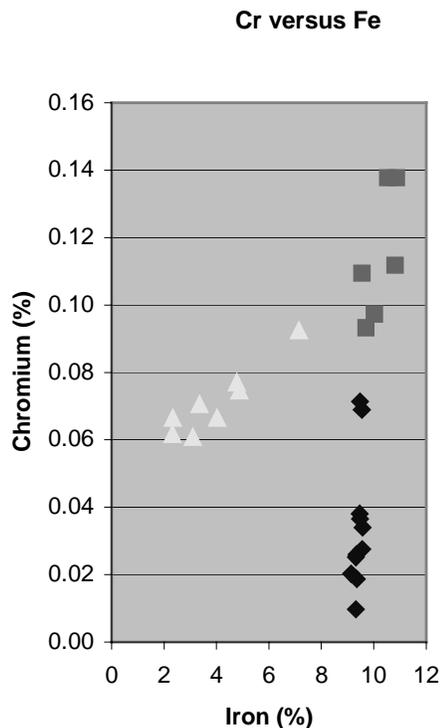
Since Ca and Sr generally have rather similar geochemical behavior, the relatively constant Sr/Ca is

expected. But in the rim carbonate, Sr/Ca shows a negative correlation, with a mean Sr/Ca of  $\sim 9 \times 10^{-4}$ , about one-half the ratio in the core carbonate. This result suggests the rim carbonate did not form as a reaction product of the core carbonate or from a fluid with the same Sr/Ca as the core carbonate.

Rb was measured at a concentration of 0.4 to  $0.5 \pm 0.2$  ppm in rim carbonate in the first sample [7], and Rb was below the detection limit of  $\sim 0.6$  ppm in all spots on the carbonate in the second sample. This is much lower than the Rb concentration of 1.3 to 6.4 ppm in the carbonate-rich leachates reported by Borg et al. [4] but consistent with the much lower Rb concentrations reported by ion microprobe measurements on ALH84001 carbonate [8]. Our result suggests that the Rb measured by Borg et al [4] may not be hosted in rim carbonate but may be in some minor, unidentified, Rb-rich phase.

## Discussion

X-ray microprobe analysis of carbonate globules from the ALH84001 meteorite provides chemical evidence that (1) the magnetite bands did not form from a simple thermal decomposition of the underlying Fe-rich core carbonate, (2) the rim carbonate did not form from the core carbonate or from a fluid with the same Ca/Sr as the core carbonate, and (3) the carbonate contains much less Rb than the carbonate-rich leachates of Borg et al. [4], suggesting that the carbonate formation age estimates by these authors may be erroneous.



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