

# Stable Isotope Evidence for Low Temperature Carbonate Concretions in the Martian Meteorite ALH84001.

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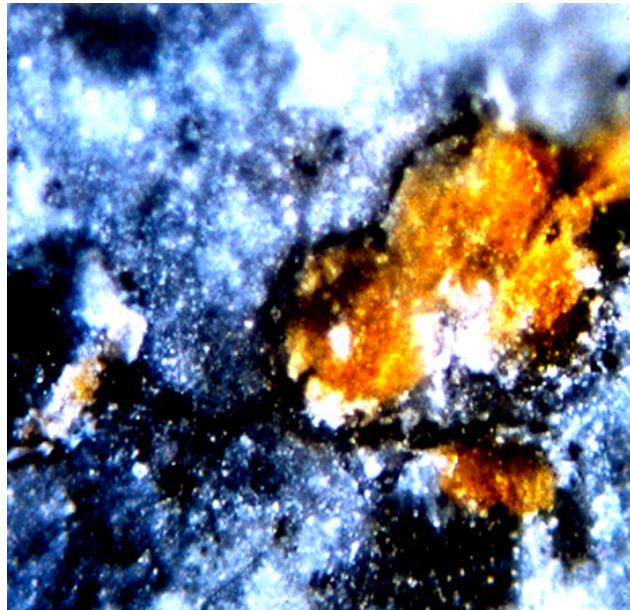
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## Introduction

The recent discovery of possible relic nanobacteria in a Martian meteorite represents the first potential demonstration of life elsewhere than on Earth. Debate has centred on the interpretation of these possible biogenic structures and on the temperature of formation of their host carbonate concretions

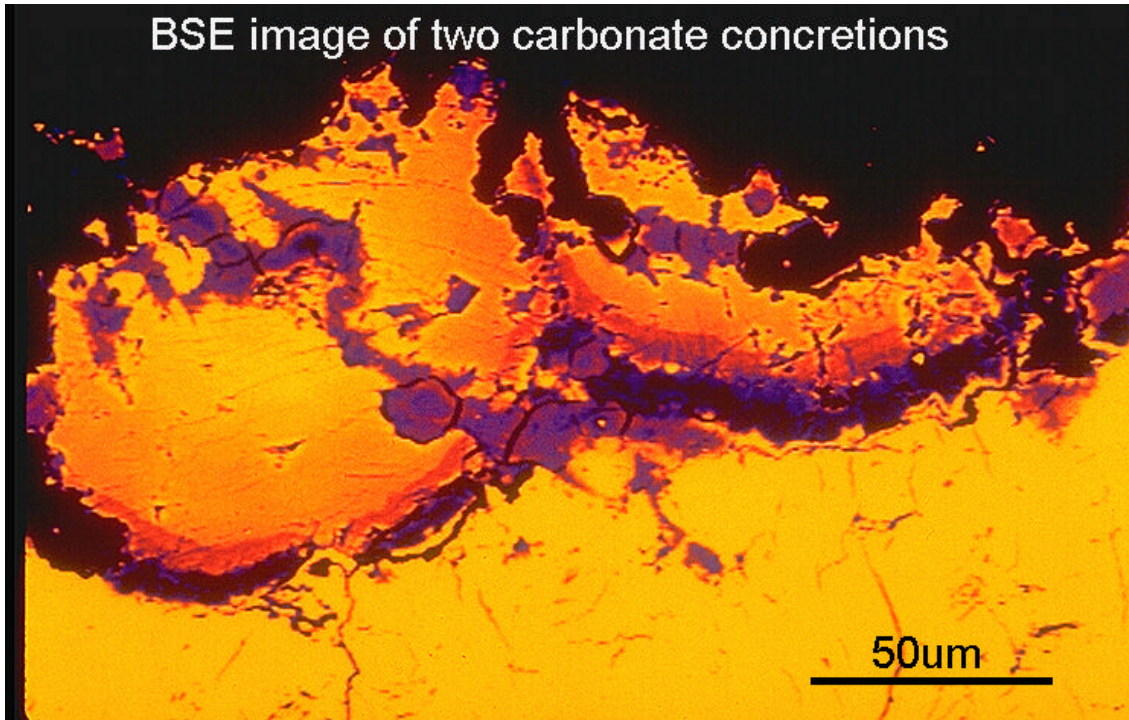
Temperatures of carbonate formation are controversial; the unusual chemistry of the carbonates suggest temperatures in excess of 650°C (Harvey and McSween 1996), while stable isotopic analyses of the carbonates were interpreted to indicate temperatures around 100°C (Romanek et al. 1994).

Temperatures in excess of 100-150°C are not favourable for the establishment of carbon-based life as we know it. Previous conventional analyses of the carbonates have varied from -9 to 26 ‰SMOW in  $\delta^{18}\text{O}$  and -21 to 53 ‰PDB in  $\delta^{13}\text{C}$  may represent mixtures of heterogeneous material.

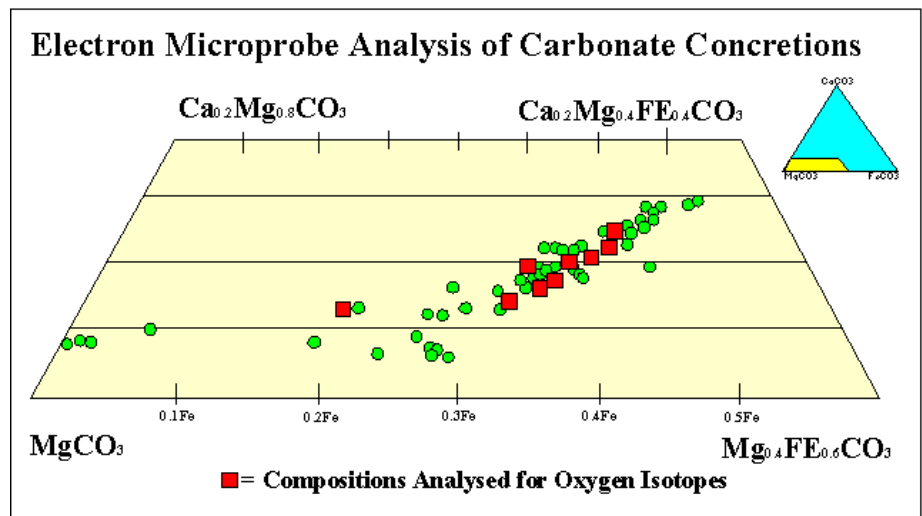


In order to provide more accurate estimates of the temperatures of carbonate formation, and to constrain scales of isotopic and chemical equilibrium, carbonate and silicate minerals in a small piece of ALH84001 have been analysed in situ for  $^{18}\text{O}/^{16}\text{O}$  and  $^{13}\text{C}/^{12}\text{C}$  by ion microprobe, supported by detailed electron microprobe analyses.

## Mineralogy



The ALH84001 meteorite is composed dominantly of orthopyroxene with minor clinopyroxene, olivine, chromite, pyrite, apatite, shocked feldspathic glass and  $\text{SiO}_2$ . The sample is highly fractured, probably by impact events, and secondary carbonates occur in some fractures as disk-shaped concretions typically hundreds of microns in diameter.



Concretions show concentric core to rim chemical zonation from  $\text{Ca}_{0.15}\text{Mg}_{0.45}\text{Fe}_{0.40}\text{CO}_3$  to nearly pure  $\text{MgCO}_3$ ; a compositional break is observed between orange Fe-rich cores and thin ( $\sim 10\mu\text{m}$ ) white mantles of nearly pure magnesite

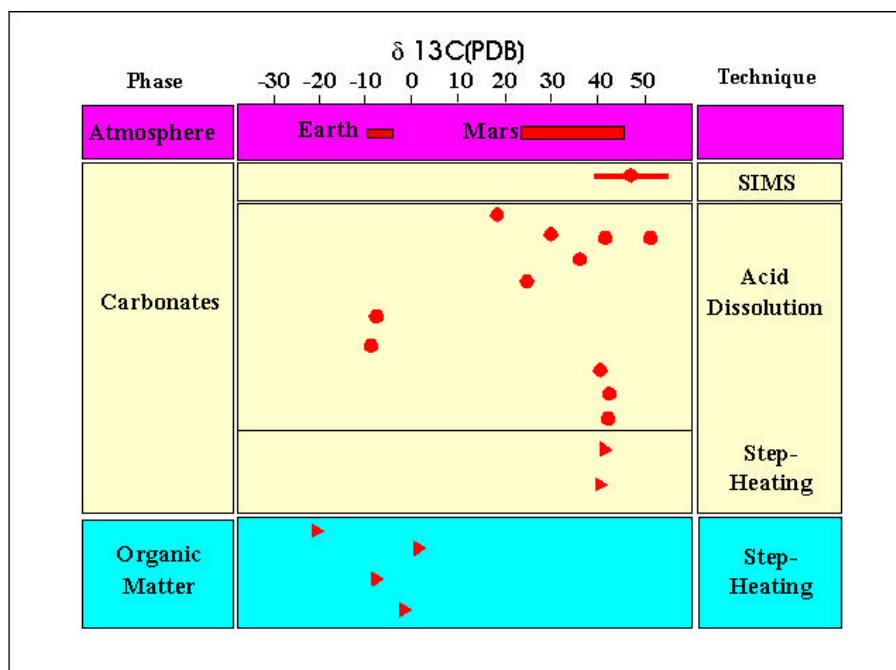
## Methodology

Stable isotope analyses were made using the high energy offset technique described by Valley et al. 1997a. The spot size was about 20 $\mu$ m for oxygen and 30-40 $\mu$ m for carbon. Analyses of ALH84001 were preceded by - and interspersed with - over 500 analyses of 12 homogeneous carbonate standards, nine of which were Ca-Mg-Fe carbonates, in order to derive matrix corrections (Eiler et al. 1998).

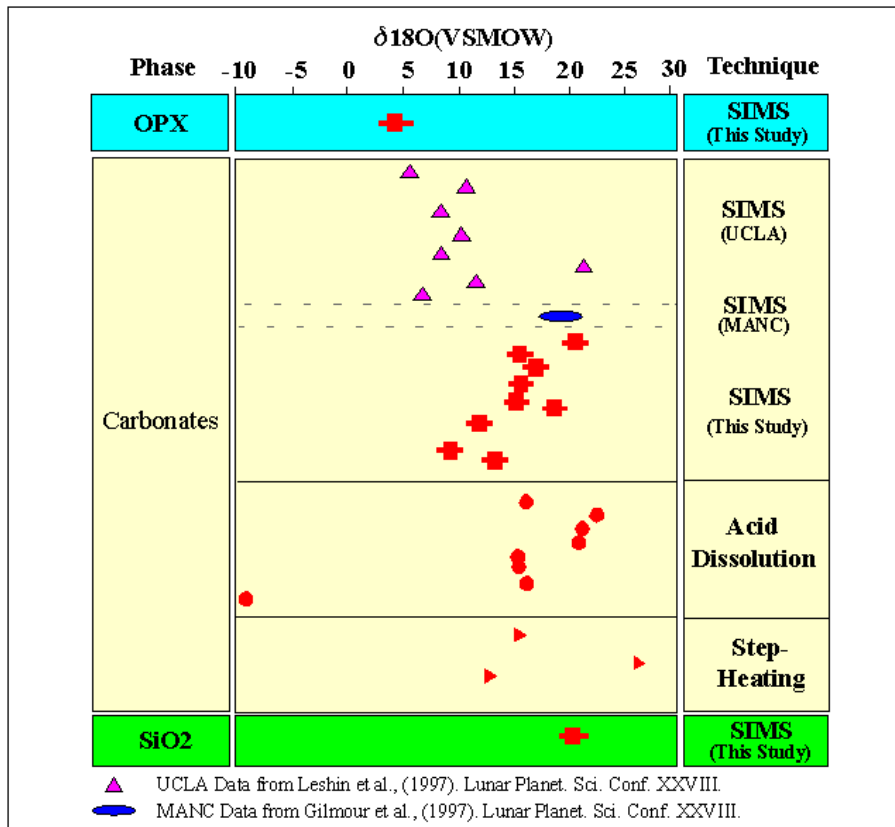
Within the limited compositional range of the orange carbonate concretions, differences in chemistry correspond to calibration differences of 1‰. Analytical precision on standards was about  $\pm 1$  ‰ for  $^{18}\text{O}/^{16}\text{O}$  and  $\pm 1.5$  ‰ for  $^{13}\text{C}/^{12}\text{C}$ . In the meteorite the precision was comparable for  $^{18}\text{O}/^{16}\text{O}$ , but  $^{13}\text{C}/^{12}\text{C}$  analyses were truncated because of heterogeneities encountered at depths of  $\sim 1$ -4 $\mu$ m. At the beginning of each analysis, the  $^{13}\text{C}/^{12}\text{C}$  ratio and the count rates were steady, but at depths of  $\sim 1$ -4 $\mu$ m the count rates increased, then decreased, and the measured isotope ratios fell by  $\sim 48$ ‰. Since these analyses are bracketed by reliable analyses of carbonate standards, these changes must result from real changes in the sample; possibly contamination by epoxy or by the presence of another carbon rich phase in the meteorite.

## Results

Nine analyses of  $^{18}\text{O}$  and 4 analyses of  $\delta^{13}\text{C}$  were made in two carbonate concretions. 10 analyses were made of host orthopyroxene and one of a crosscutting vein of  $\text{SiO}_2$



Values of  $\delta^{13}\text{C}$  measured in the Martian meteorite ALH84001 by SIMS and compared with powders analysed by acid dissolution or step-heating. Samples are either carbonates or suspected organic matter. The  $\delta^{13}\text{C}$  of  $46 \pm 8$ ‰ for the core of one concretion is 40-50‰ higher than typical terrestrial values and consistent with equilibration with a reservoir of similar  $\delta^{13}\text{C}$  to the Mars atmosphere



Values of  $\delta^{18}\text{O}$  measured in the Martian meteorite ALH84001 by SIMS and compared with powders analysed by acid dissolution or fluorination. Samples are carbonates (Mg-rich and Fe-rich), orthopyroxene (OPX) and quartz ( $\text{SiO}_2$ ). Oxygen isotope compositions of carbonate concretions range from +9.5 to +20.5‰. Most of the core of one concretion is homogeneous (16.7‰), and over 5‰ higher than  $^{18}\text{O}$  in the second concretion. Orthopyroxene is homogeneous ( $\delta^{18}\text{O}=4.6\pm 1.2\text{‰}$ ). Secondary  $\text{SiO}_2$  has  $\delta^{18}\text{O}=20.4\text{‰}$ .

## Discussion

The  $^{18}\text{O}$  of the orthopyroxene is homogeneous and comparable to terrestrial mantle values. On Earth  $^{18}\text{O}$  values as high (>16‰) as those measured in ALH84001 carbonates are restricted to rocks which have interacted with isotope reservoirs formed at low temperatures (<100°C). However, the  $\delta^{18}\text{O}$  of the ancient Martian atmosphere or hydrosphere is not known. The  $^{18}\text{O}$  of  $\text{SiO}_2$  in the pyroxene is comparably  $\delta^{18}\text{O}$  enriched to the most  $\delta^{18}\text{O}$  rich carbonate. Equilibration temperatures calculated from  $\delta^{18}\text{O}$  of coexisting carbonates and silicates are in the range <100 to ~300°C; however there is no textural evidence to support equilibration of carbonate and silicate phases.

All chemical and isotopic evidence from this and other studies of ALH84001 indicate disequilibrium isotopic and chemical gradients over distances of <10µm, which together with phase equilibrium constraints (Valley et al. 1997) provide strong evidence against the high temperature hypothesis. Low temperature carbonate minerals (e.g. aragonite and high-Mg calcite) commonly form by kinetic processes of biogenic or abiogenic origin. Although results strongly support the low temperature genesis of the carbonate concretions, the precise temperatures of carbonate precipitation in relation to plausible temperatures favourable for the establishment of carbon-based life as we know it on Earth (<100-150°C) remain to be established.

## References

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