CHEMICAL AND MORPHOLOGICAL CHARACTERIZATION OF SIDERITE FORMED BY IRON-REDUCING BACTERIA.

C. Zhang[1], H. Vali[2], C. S. Romanek[3], Y. Roh[4], S. K. Sears[2], and T. J. Phelps[4]
[1]Department of Geological Sciences, University of Missouri, Columbia, MO 65211, zhangcl@missouri.edu,
[2]Electron Microscopy Center, McGill University, Montreal, Quebec H3A 2B2, Canada, [3]Savannah River Ecology Laboratory, University of Georgia, Aiken SC 29802, [4]Oak Ridge National Laboratory, Oak Ridge, TN 37831.

Introduction: The carbonate globules in the Martian meteorite ALH84001 play an important role in the interpretation of past biogenic activities retained in this meteorite. Discussions concerning the origin of the globules include the chemistry, formation temperature and texture of the carbonates [1]. Biogenic origin of the carbonates is based on observations of mineral formation in biological systems on Earth. Our understanding of biogenic iron-rich carbonates in terrestrial environments, however, is not well understood. For example, Pye et al. point out that the relationships between microbial activity, fluid chemistry, and authigenic mineral formation are not well delineated [2]. Research is also needed to more precisely define factors that influence the size and shape of biogenic iron-rich carbonates in natural terrestrial environments [3], [4]. In this study we present observation of siderite formation by a mesophilic (20-35°C) bacterium and a thermophilic (45-65°C) bacterium grown under laboratory conditions. We also discuss the implications for biological siderite formation in natural environments and for past biogenic activities in ALH84001.

Material and Methods: The mesophilic bacterium, *Shewanella* strain BrY, reduces iron when using H_2 or organic acids as the electron donors [5]. The thermophilic bacterium, strain TOR 39, ferments carbohydrates and produces single-domain magnetite when grown on glucose and amorphous ferric oxyhydroxide [6]. In this study, BrY and TOR 39 were grown using a medium buffered with 90 mM $NaHCO_3$ [6]. BrY used H_2 (balanced with 20% CO_2) as the electron donor; TOR 39 used glucose (10 mM) as the electron donor. Both strains used amorphous ferric oxyhydroxide (90 mM) as the electron acceptor. The pH of the medium was 7.0 for BrY and 8.7 for TOR 39. Experiments were performed at 25°C for BrY and 65°C for TOR 39. During bacterial growth, pH and Eh were measured by taking sequential subsamples from the cultures. The mineralogical characterization of the solids was performed by using X-ray diffraction patterns and by transmission electron microscopy (TEM) using electron diffraction patterns. A novel high-resolution replica technique was used to study the surface morphology of the siderite crystals by TEM. A magnet was used to detect the presence of magnetite during bacterial iron reduction. Experiments were terminated after 30 days incubation for BrY and after 22 days for TOR 39.

Results: During the growth of BrY, pH increased from 7.0 to 8.9 while Eh decreased from ~40 mV to <-450 mV. Color of the solids changed from reddish to brownish and to whitish, suggesting mineralogical transformation. During the experiment, weak magnetism was detected after two weeks of incubation but no magnetism was detected at the end of experiment. X-ray diffraction pattern of the final precipitate showed siderite as the only mineral formed by BrY (data not shown). The TEM replica showed that siderite particles were disk-like crystals having diameters between 2 and 3 μm and thicknesses <0.4 μm (Fig. 1). The electron diffraction pattern of the crystals showed well ordered lattice of pure siderite (data not shown).

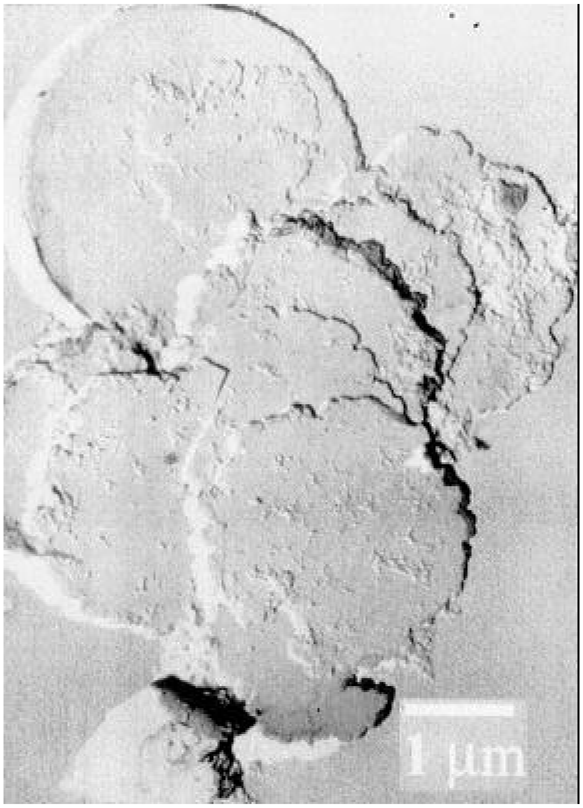

Fig. 1. Disk-like siderite crystals formed by mesophilic iron-reducing bacterium BrY.

During the growth of TOR 39, pH deceased from 8.7 to 7.5 and Eh decreased from ~40 mV to -300 mV. During mineral transformation, color of the solids changed from reddish to black; at the same time magnetic strength of the solids increased. The final black precipitate was strongly magnetic; the X-ray diffraction pattern showed that it contained both magnetite and siderite (data not shown). The TEM replica showed that siderite particles were globules with diameters between 3 and 5 µm (Fig. 2a). The magnetite particles that co-precipitated with siderite were octahedral crystals having edge lengths <0.3 µm (Fig. 2b).

Discussion: BrY and TOR 39 form iron minerals extracellularly through biologically induced processes. Results of this study showed that activities of BrY and TOR 39 had significant but different impacts on the chemical evolution of the fluids and the mineralogical transformation of the solids. Growth of BrY resulted in lower Eh and higher pH than TOR 39. The dominance of siderite and lack of magnetite in the BrY cultures indicated that greater iron reduction occurred under the influence of BrY than under the influence of TOR 39 because TOR 39 produced siderite and magnetite that still contains ferric iron.

Biomineralization may be controlled by solution chemistry [7] and bacterial enzymes [8], [9]. It is generally recognized that microorganisms produce metabolic products, create suitable microenvironments, or act as nucleation sites to facilitate biomineralization. Siderite formed by GS-15, a mesophilic iron-reducing bacterium, has rhombohedral shapes similar to siderite particles found in natural samples [10]. In this study, the disk-like siderite formed by BrY has not been reported in natural terrestrial environments. Interestingly, disk-shaped iron-rich carbonates were observed in ALH84001 and attributed to restricted growth of crystals in a fractured network [1]. At the present, the mechanisms of disk-like siderite formed by BrY can only be speculated. It is possible that BrY mediated the solution chemistry and protein-based mineralization to foster the formation of the disk-like siderite crystals in the biological system examined.

The siderite globules formed by TOR 39 were also different from siderite formed by GS-15. The unique feature of these globules is their surface structure which appeared to be composed of flakes of crystals (Fig. 2b) rather than a single rhombohedral crystal as in the case of GS-15 [10].

In summary, formation of siderite in this study was mediated by microbial activities in context with the fluid chemistry. Detailed examination of the fluid chemistry, mineralogy and microbiology in the biological system will help delineate the mechanisms of biomineralization in natural environments. Such information would be needed to further evaluate the origins of iron-rich carbonates in ALH84001.

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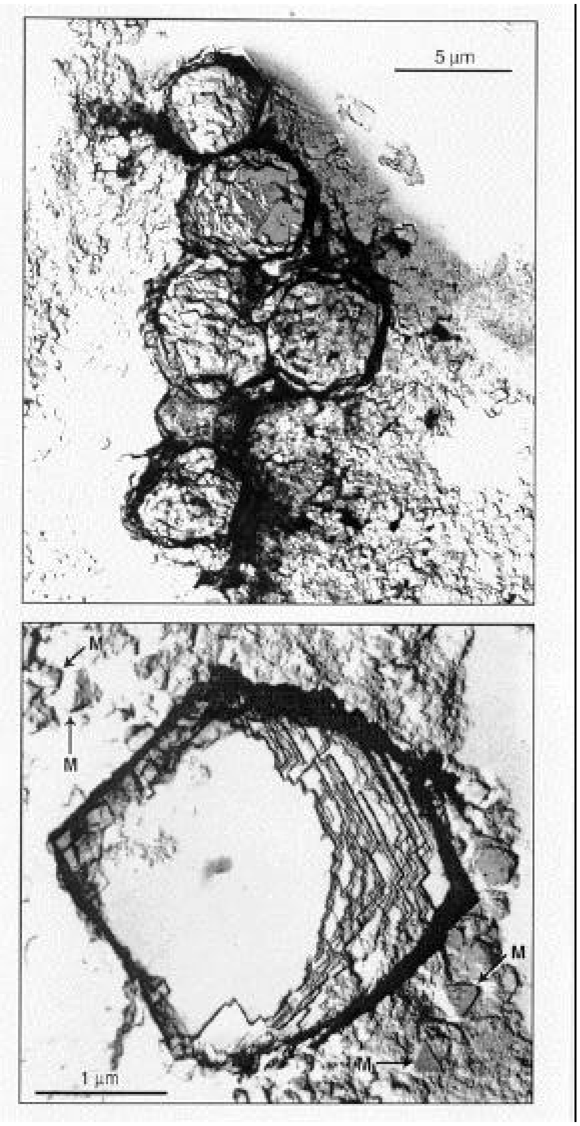

Fig. 2. (a) Upper. Siderite globules formed by thermophilic iron-reducing bacterium TOR 39. (b) Lower. Comparison of a siderite crystal with magnetite (M) crystals formed by TOR 39 in the same culture.