

Formation of Magnetite and Fe-rich Carbonates by Thermophilic Bacteria from Deep Terrestrial Subsurface: A Possible Mechanism for Biomineralization in ALH84001. H. Vali⁽¹⁾, C. Zhang⁽²⁾, S.K. Sears⁽¹⁾, S. Lin⁽²⁾, T.J. Phelps⁽²⁾, D. Cole⁽³⁾, T.C. Onstott⁽⁴⁾, J.L. Kirschvink⁽⁵⁾, A.E. Williams-Jones⁽¹⁾ and D.S. McKay⁽⁶⁾

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Understanding the biogenic formation of magnetite and Fe-rich carbonate by thermophilic bacteria is essential to the search for ancient biological activities in hydrothermal systems on Earth and Mars. Laboratory experiments were conducted to study the formation of magnetite and Fe-rich carbonates by unknown anaerobic, thermophilic (45-75° C) bacteria. The bacteria were obtained from deep subsurface sedimentary basins in the United States. Using amorphous iron as an electron acceptor and glucose, acetate or H₂ as an electron donor, these bacteria produced magnetite in a wide range of pH and Eh conditions. The measured pH values ranged from 6.2 to 8.7; low pH values (<7.0) were found mostly in glucose-enriched cultures whereas high pH values were found in H₂/CO₂-enriched cultures. Eh values decreased with increasing pH and ranged from -200 mV to -460 mV. In addition to magnetite, abundant siderite formed when pH was >7.0 and CO₂ concentration was >5% of the incubation atmosphere.

Run products from experiments incubated at 6, 30 and 72 days in a closed system were investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). TEM imaging of the magnetic separates revealed well-preserved, single domain (Butler and Banerjee, 1975) magnetite crystals embedded within a biomass consisting of both organic and inorganic components. After 6 days, a considerable amount of amorphous iron was still present in the sample (Fig. 1a). Concentrations of magnetite increased after 30 days with an apparent decrease in the concentration of the initial amorphous iron (Fig. 1b). After 72 days, magnetite showed dissolution features. There are large concentrations of euhedral, extremely fine-grained crystalline magnetite (superparamagnetic) in these samples (Fig.1c). Magnetite crystals produced by these bacteria resemble the diamond-shaped magnetosomes produced by *aquasperillum magnetotacticum* (Blakemore et al., 1979). However, the extracellular magnetite produced by thermophilic bacteria shows a wide range in size distribution (5 - 100nm) and a random arrangement of individual crystals. In contrast to the extracellular-precipitated superparamagnetic magnetite particles produced by the growth of anaerobic bacteria strain GS-15 (Lovley et al., 1987), the extremely fine-grained magnetite particles associated with thermophilic bacteria exhibit diamond-shaped crystals with defined edges. The magnetite described in this study (Figs. 1a -1d) is also different from the exclusively inorganically synthesized magnetite reported by Maher (1991). Similar single domain and superparamagnetic magnetite was also present in the sedimentary samples but was associated with Fe-rich clay minerals (Fig. 1d). Size distribution and morphological characteristics of the magnetite isolated from these samples resemble magnetite obtained from the culture after 72 day incubation (Figs.1c, 1d). The exact mechanism(s) of biomineralization by these unknown thermophilic bacteria is not well-understood. However, under the same experimental conditions, neither magnetite nor Fe-carbonate phases precipitated without the bacteria. Although well-preserved bacteria were not observed in this sample, the morphological features shown in figure 1a suggest a direct relationship between magnetite precipitation and the bacterial cell wall. The size and shape of the aggregates containing the magnetite particles resemble degraded bacteria.

The results of these laboratory experiments revealed that the concentration, size distribution and morphology of the magnetite depends strongly on the chemical composition and duration of the experiments. The size distribution and morphological characteristics of magnetic phases present within the carbonate globules in ALH84001 (McKay et al., 1996; Golden et al., 1997) are similar to the magnetic particles observed in these cultures. The formation of single domain magnetite associated with Fe-rich carbonate supports the hypothesis of biogenic formation of magnetite within the carbonate globules in ALH84001.

References: Blakemore R. P. et al., (1979) *J. Bacteriol.*, 140:720-729; Butler, R.F. and Banerjee, S.K. (1975) *J. Geophys. Res.* 80:4049-4058; Golden, D.C. et al. (1997) 28th LPSC Meeting, Houston (submitted); Lovley, D.R. et al. (1987) *Nature* 330:252-254; McKay, D.S. et al. (1996) *Science*, 273:924-930; Maher, B.A. (1991) *Iron Biominerals* (ed. R.B. Frankel and R.P. Blakemore) Plenum Press, NY.

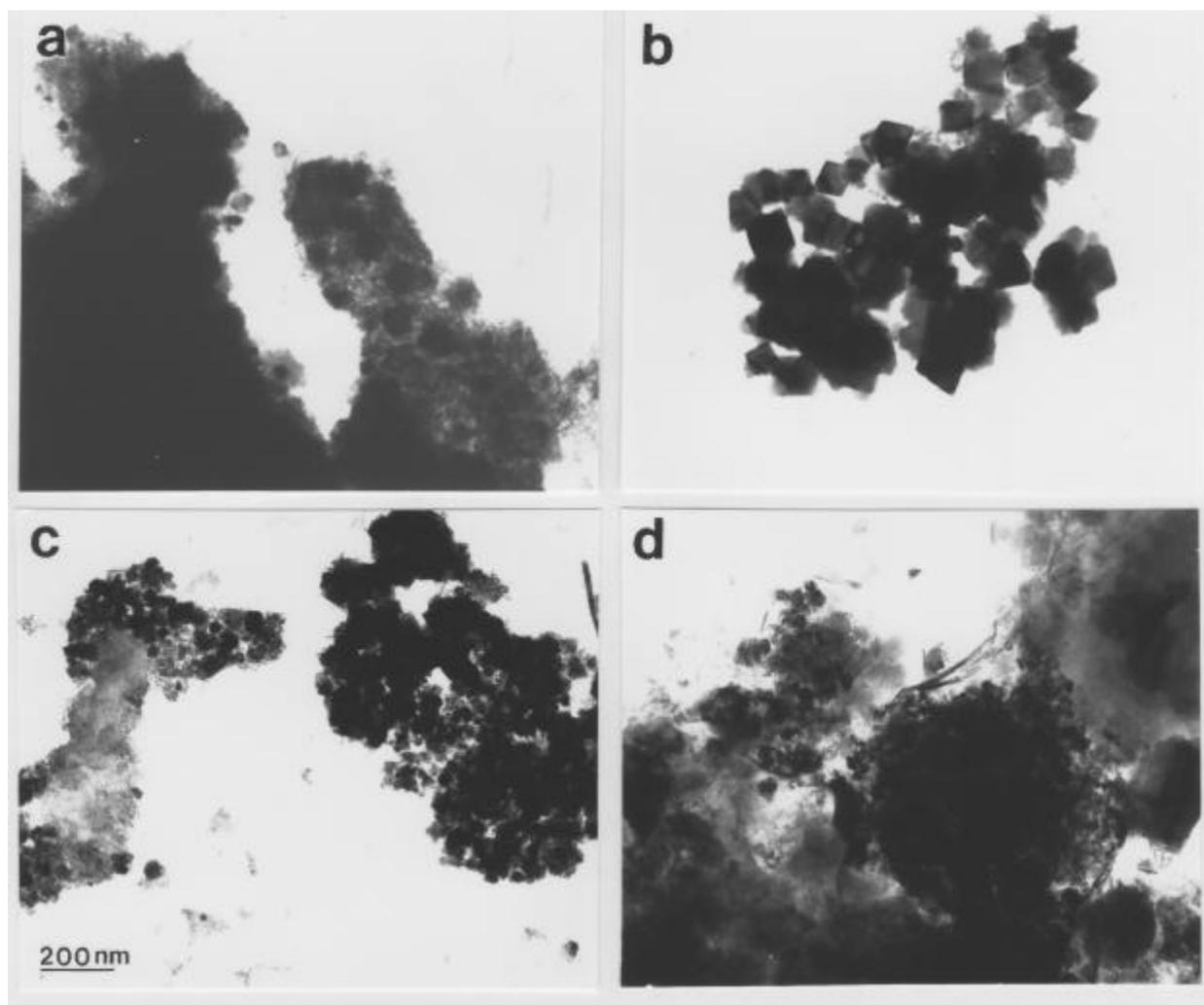


Figure 1. TEM images of magnetic separates from run products of laboratory experiments and a sediment sample. (A) Sample incubated at 6 days shows disorganised single domain magnetite crystals embedded in a mixture of amorphous iron and organic matter. The size and shape of the aggregates containing magnetite particles resemble degraded bacteria. (B) Sample incubated at 30 days shows well-preserved, euhedral magnetite crystals similar to those found in magnetic bacteria. (C) Sample incubated at 72 days shows a mixture of single domain and superparamagnetic magnetite crystals associated with an organic mass. (D) Magnetic separates of a sediment sample showing similar magnetic particles described in (C). Magnetic particles in this sample are associated with Fe-rich clay minerals. Same scale for all images.