Formation of Magnetite Nanoparticles by Thermal Decomposition of Iron Bearing Carbonates: Implications for the Evidence of Fossil Life on Mars

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Abstract:

The thermal decomposition of iron(Fe)-bearing carbonates to form magnetite nanoparticles was studied in order to better understand the parameters that control nanoparticle formation. Rates of decomposition were determined for natural siderite ($FeCO_3$) and ankerite ($Ca(Mg,Fe,Mn)(CO_3)_2$). An activation energy of 153 kJ/mol was determined for the decarbonation of siderite. Characterization of the magnetite nanoparticles using TEM, SEM, and EDS analysis showed a progressive increase in particle size and Mg/Mn contents as the reaction proceeded.

Introduction:

The origin of nanophase magnetite in Martian meteorite ALH84001 has fueled the debate as to whether there was ancient bacterial life on Mars. McKay [1] suggested that these 10-100 nm magnetite particles shared many of the characteristics of magnetite produced by magnetotactic bacteria on Earth, indicating a possible biogenic origin. An alternative, inorganic hypothesis (Brearley [2]) proposes thermal decomposition of Fe-bearing carbonates. To further explore the thermal decomposition mechanism, heating experiments have been carried out on siderite and ankerite to determine the reaction rates and characteristics of the products as a function of temperature and heating time.

Methods:

Heating experiments were performed by placing about 20 mg of uncrushed carbonate sample grains in a gold foil packet which was suspended in a Deltech furnace at the desired temperature and at 1 atm in a CO_2 environment. Reaction progress was measured by weight loss after completion of the experiment.

The starting materials and run products were characterized by x-ray diffraction (XRD), electron microprobe (JEOL 8200), scanning electron microscopy (SEM; JEOL 5800LV, Hitachi S-5200), transmission electron microscopy (TEM; JEOL 2010F) combined with energy dispersive spectroscopy (EDS). The percent Fe content (wt% Fe) of the ankerite determined by electron microprobe, was used to calculate maximum and minimum theoretical weight losses, assuming completed decomposition of the siderite component of the carbonate.

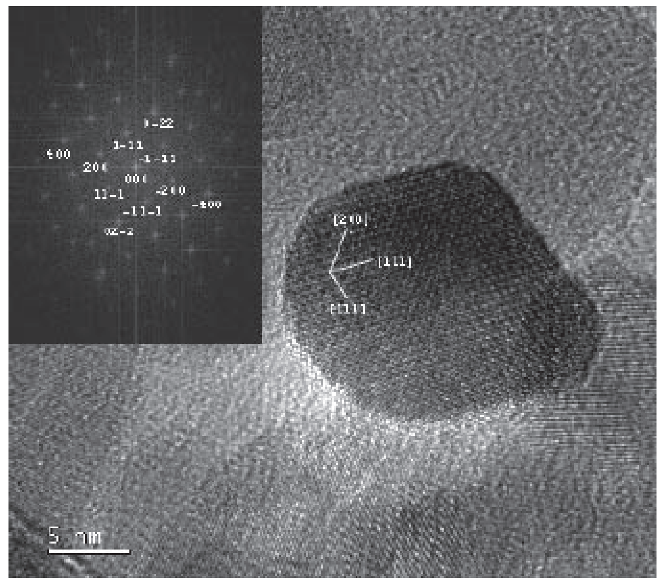

Figure 1: HRTEM image of magnetite reaction product (ankerite: 40 min, 700°C).

Results and Discussion:

The decomposition of siderite occurred in 30 seconds to 2.5 hours in the temperature range of 500°C to 700°C. The data followed a sigmoidal curve and were fitted to the Avrami-Erofeev rate equation. The rate constant at each temperature was determined to give an activation energy of 153 kJ/mol, comparable to the literature value of 183 kJ/mol for the decomposition of natural siderite [3].

The decomposition of ankerite was examined between 600°C and 800°C. At 600°C, weight loss did not change over time but at 650°C, significant weight loss occurred and the samples became magnetic. The predicted weight loss for the reaction was, however, only reached after 40 minutes at 700°C and 1 minute at 800°C.

For magnetite nanoparticles formed in the 700°C experiments, grain size was measured from TEM images. (Figure 1.) Thirty different grains were measured across the longest axis from each experiment. Grain size and distribution increased with heating duration to 20 min, but shrank after 40 min (Figure 2). Magnetite grain sizes were also measured from samples run for 20 min and 180 min at 650°C and have grain sizes and distributions comparable to those of the 700°C set of experiments.

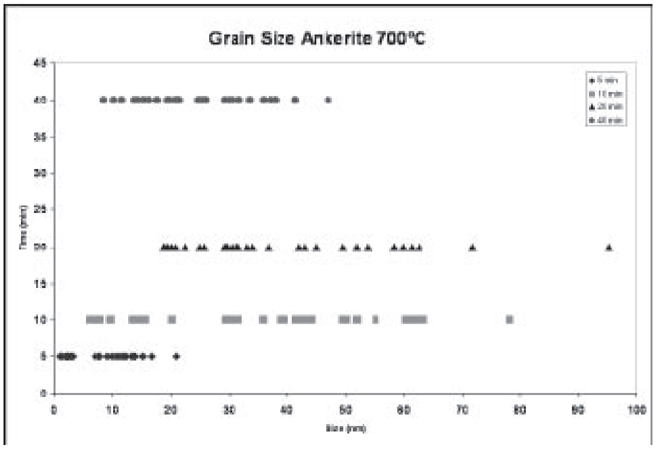

Figure 2: Magnetite grain size as a function of time at 700°C.

Magnetite compositions were determined by EDS analysis for samples from the 700°C series. The data show a progressive increase of Mg and Mn contents of magnetite with time, but reach a plateau after 20 min (Figure 3). This increase in Mg and Mn contents is probably the result of the progressive, but slower decomposition of Mg and Mn carbonates in the ankerite. The surface of one reacted ankerite (700°C for 40 min) was examined by FEGSEM. The surface appeared much rougher and had higher porosity compared to the smooth carbonate surfaces observed before heating (Figure 4).

Conclusion and Future Research:

The magnetite nanoparticles produced in these experiments support some aspects of the inorganic hypothesis, but there are still many unanswered questions. This study shows that thermal decomposition can reliably produce nanophase magnetite particles with grain sizes consistently < 100 nm, the maximum size of the nanoparticles observed by McKay in ALH84001 [1].

The magnetite found in ALH84001 and produced by bacteria is pure Fe_3O_4. However, in these experiments the magnetites contain significant amounts of Mn and Mg, whose concentrations increase in time. Nevertheless, the shortest ankerite heating experiments formed magnetite particles with high weight percent Fe contents. This result indicates that Fe-rich particles might be produced when complex carbonate decomposes rapidly such as during a shock event.

Our SEM observations revealed magnetite grains on the surface of the carbonate rather than embedded in the carbonate as occurs in the meteorite. Further TEM studies of cross sectional samples from carbonate grains are needed to establish whether magnetite has developed within the interior of the carbonate. In addition to variations of temperature and duration, more experiments should be done at different pressures to establish the possible effects of shock on the decomposition reaction.

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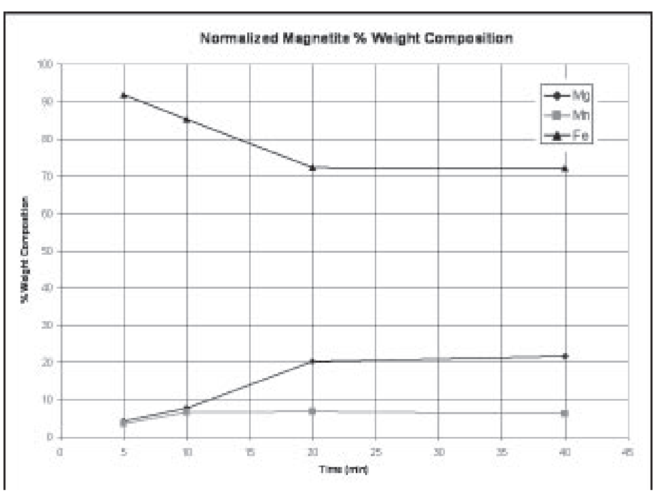

Figure 3: Fe-, Mg-, and Mn- % weight content of magnetite as a function of heating duration (ankerite, 700°C).

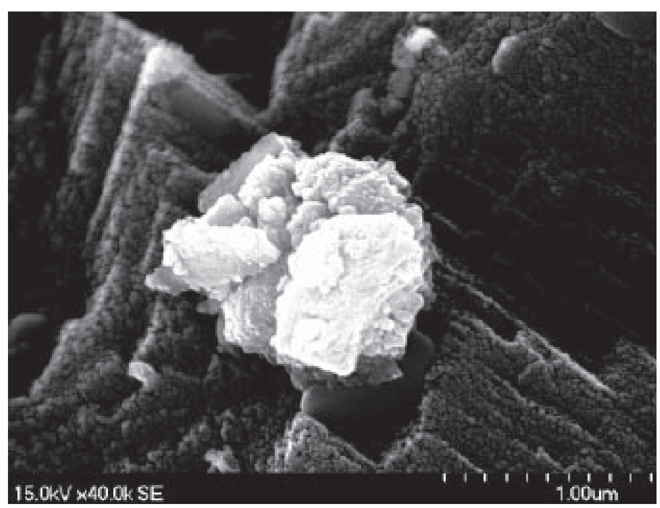

Figure 4: Cluster of magnetite particles on reacted ankerite. Secondary electron image (FE-SEM).