

**THERMAL CHARACTERIZATION OF Fe<sub>3</sub>O<sub>4</sub> NANOPARTICLES FORMED FROM POORLY CRYSTALLINE SIDERITE.** H. V. Lauer Jr.<sup>1</sup>, D. W. Ming<sup>2</sup>, and D. C. Golden<sup>3</sup>, <sup>1</sup>LMSO, 2400 NASA Rd1, Houston, TX 77058 (howard.v.lauer1@jsc.nasa.gov); <sup>2</sup>ARES NASA/JSC, Houston, TX 77058 (douglas.w.ming@nasa.gov); <sup>3</sup> and Hernandez Engineering Inc., Houston, TX 77058.

**Introduction:** Increasing interest in environmental geochemistry has led to the recognition that crystals with sizes in the nanometer range (e.g., colloids and nanoscale precipitates) and poorly crystalline compounds (e.g., ferrihydrites) may comprise the majority of reactive mineral surface area near the Earth's surface. When the diameters of individual particles are in the range of 100 nm or less, the surface energy contribution to the free energy modifies phase stability. This results in stabilization of polymorphs not normally encountered in the macrocrystal domain. These phases potentially have very different surface-site geometries, adsorptive properties, and growth mechanisms, and exhibit size-dependent kinetic behavior. Thus nanophases dramatically modify the physical and chemical properties of soils and sediments.

In a more general sense, the characteristics of nanocrystals are of intense technological interest because small particle size confers novel chemical, optical, and electronic properties. Thus, nanocrystalline materials are finding applications as catalytic substrates, gas phase separation materials, and even more importantly in the field of medicine. This is an opportune time for mineral physicists working on nanocrystalline materials to develop collaborative efforts with materials scientists, chemists, and others working on nanophase materials of technological interest (e.g., for magnetic memories).

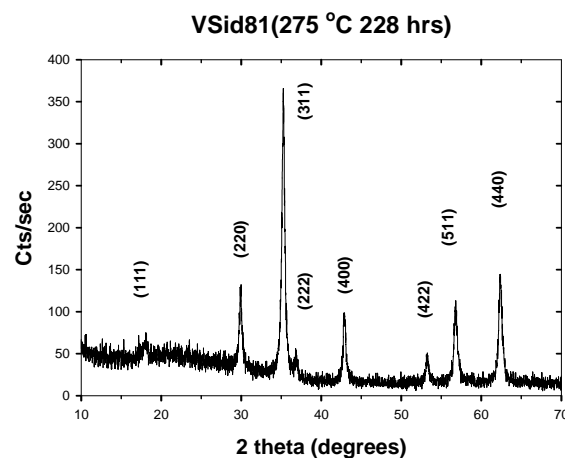
Our objective in this study was to synthesize submicron (<200 nm) magnetite and to study their thermal and particle size properties.

**Materials and Methods:** The starting material for these experiments was a synthetic very poorly crystalline, slightly hydrated iron carbonate, i.e. poorly crystalline siderite with adsorbed water [1], that was washed at least five times in deionised water to remove all of the salts etc. from the production of the starting material. After washing, the remaining material was freeze-dried and stored. Between 10 and 20 mg of the freeze-dried powder was then placed in a small open quartz crucible. In a second small open quartz crucible we added about 10 mg of dry CaO (lime that had been previously heated to 1000 °C for 24 hrs). Both of these small crucibles were then sealed under vacuum, one on top of the other, in a slightly larger quartz tube. The sealed tube was placed in an furnace at room temperature, slowly heated to a given temperature T<sub>MAX</sub> for at least 60 hrs and then cooled back down to ambient temperature. This process was repeated a number of ten times varying T<sub>MAX</sub> to give us a set of samples to study. The premise for the set of experiments was that at elevated temperatures in the evacuated environment, the hydrated poorly crystalline siderite will lose its water and the siderite will break down converting to magnetite. The lowest temperature sample (275 °C) was run for a longer time to obtain the optimal quality magnetite at the lowest temperature investigated. Siderite converts to magnetite according

to the following reaction:



In the experiments, the lime acts as a sink for the CO<sub>2</sub> liberated when the siderite breaks down. Without this sink, the partial pressure of CO<sub>2</sub> in the tube rises and eventually stops the siderite from breaking down. With the lime present, more and more siderite breaks down forming more CO driving down the *f*O<sub>2</sub> inside the tube. The lime also acts as a sink for any water that was in the original starting siderite forming calcium hydroxide (Portlandite). We have made a set of heated samples from the poorly crystalline siderite starting material varying T<sub>MAX</sub> from 275 to 700 °C.



**Figure 1:** XRD trace of the magnetic material heated at T<sub>MAX</sub> = 275 °C for 228 hrs. The magnetite peaks are labeled on the trace.

After heating and cooling back to ambient temperature, the sealed tubes were carefully cut open and the contents removed for analysis. The contents of the small crucibles containing the "heated-reacted siderite" were analyzed with a powder X-ray diffractometer. The XRD trace of the 275 °C sample is shown in Figure 1.

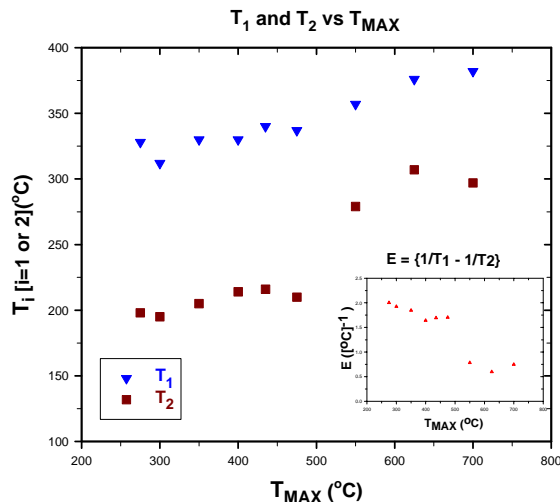
The XRD traces for the other samples, all run for only 60 hrs, also showed that the material was also magnetite. The half width at half max. of the 2.53 Å (311) peak systematically varied from 0.425 degrees for the 275 °C sample to 0.275 degrees for the 700 °C sample. XRD analysis of the heated CaO (lime) crucible in all cases showed that it contained a mixture of CaO (lime), CaCO<sub>3</sub> (calcite) and Ca(OH)<sub>2</sub> (Portlandite). Lime was observed in the final product because we purposely used excess amounts to insure that all of the CO<sub>2</sub> would be liberated from the siderite.

Thermal and mineralogical properties of the synthetically formed magnetite were characterized by differential

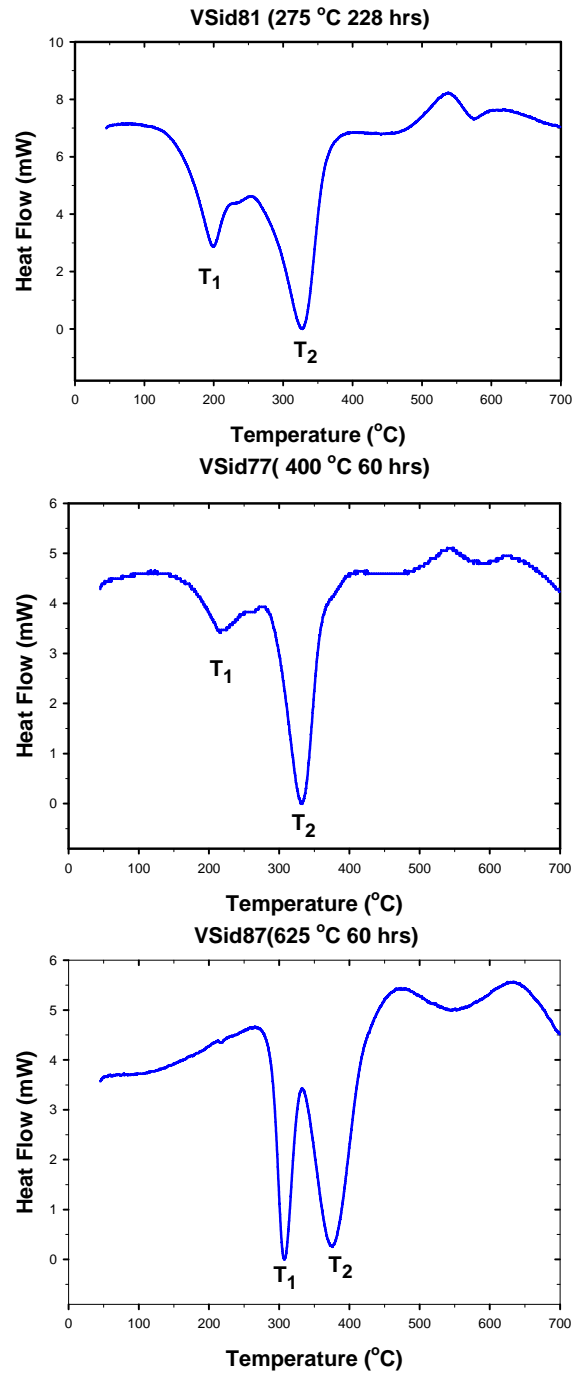
scanning calorimetry (DSC) and X-ray analysis. In order to oxidize the magnetite during the DSC runs, samples were heated in a pure O<sub>2</sub> carrier gas at atmospheric pressure (1 bar).

**Results and Discussion:** Formation temperature ( $T_{MAX}$ ) has a substantial effect on the thermal stability and particle size of the magnetite. Figure 2 shows the DSC heat flow curves for the magnetite samples formed at 275, 400 and 625 °C respectively. In each sample the broad exothermic transition defined by the two peaks labeled by  $T_1$  and  $T_2$  are both related to a magnetite to maghemite transition. The mineralogy of these phases, after each transition, was verified by XRD analysis (i.e. in separate experiments, runs were stopped after a transition and the product was characterized by XRD). In bulk large grain size magnetite, the magnetite to maghemite transition is defined by a single broad transition.[2,3] TEM analysis of magnetite samples formed under similar conditions indicate that the magnetite particles from our set are in the range of 100 nm or less.[4] Samples in this size range could be viewed as having a much larger surface to volume ratio than is found in normal bulk magnetite. One might then speculate that the  $T_1$  exothermic transition could be related to the energy required to convert the surface of the magnetite particles to maghemite. In a somewhat different context, Santucci [5] investigated calorimetry at a surface using high resolution core-level photoemission.

Figure 3 shows a plot of  $T_1$  and  $T_2$  for our set of magnetite as a function of  $T_{MAX}$ . The insert in the figure is a plot of the function  $E = [1/T_1 - 1/T_2]$  vs  $T_{MAX}$ . Note the discontinuity in  $T_2$  and also  $E$  for values of  $T_{MAX}$  between 475 and 550 °C. The half width at half max. of the 2.53 Å (311) peak decreased from 0.350 degrees for the 475 °C sample to 0.320 degrees for the 550 °C sample indicating an increase in grain size of the magnetite particles. At this point we don't know the significance of the discontinuity. It could be related to grain size or crystallinity or crystal defects. Whatever the reason, it will be to object of future study.



**Figure 3:** This figure shows a plot of  $T_1$  and  $T_2$  vs  $T_{MAX}$  for our set of magnetite.



**Figure 2:** This figure shows the DSC heat flow curves for 3 of the magnetite samples formed at 275, 400 and 625 respectively.

**References:** [1] Golden, D. C. et. al.,(2001) *American Mineralogist*, **86**, 370-375. [2] Lauer Jr., H. V.(2003) LPSC34, Abs#1341 CD-ROM. [3] Lauer Jr., H. V.(2001) LPSC32, Abs#2071 CD-ROM. [4] Golden, D. C. private communication. [5] Santucci, S. C. et. al.(2003) *Surfaces and Nanostructures*, 67-70.