

DIFFERENTIAL SCANNING CALORIMETRY MEASUREMENTS AND THE THERMAL ANNEALING OF AMORPHOUS SILICATES, Joseph A. Nuth III¹ and Frank Ferguson^{1, 2}, ¹Astrochemistry Laboratory, NASA's Goddard Space Flight Center, Greenbelt MD 20771 (Joseph.A.Nuth@NASA.gov) ²Chemistry Department, The Catholic University of America, Washington DC 20064 (ferguson@astrochem.gsfc.nasa.gov).

Introduction: Dust grains entering the primitive solar nebula are known to be amorphous [1-3] yet a large fraction of the solid materials observed around some comets [4] and returned by the STARDUST mission is crystalline material [5]. Observations of modern protostellar nebulae show that the grains of the innermost nebular regions can be crystalline while grains in the outer nebulae remain amorphous [6], thus suggesting that some annealing process operates in the higher density and higher temperature region closer to the forming star. This process might be simple thermal annealing in the hot innermost nebula [7] or annealing through shock processing in generally cooler but reasonably high-density environments out to about 10 AU from the central star [8]. Whatever the energy source for the annealing process, the temperature dependence of the annealing rate on composition is a poorly determined factor necessary to model the structural evolution of amorphous materials throughout the nebula.

We have previously measured the detailed spectral evolution of amorphous magnesium silicate smokes as a function of temperature and time [9,10] and used this information to develop a spectral evolution index that can be used to predict the spectrum of an amorphous magnesium silicate grain subjected to a specific temperature history [11]. Attempts to model the detailed spectral evolution of amorphous iron silicates failed because the temperatures required to anneal these grains within a reasonable timeframe (several hours to several months) was too high for the experimental system available at the time. Our preliminary measurements did show that the iron silicates could be annealed at roughly the same rate as the magnesium silicates if the temperature of the iron silicates was approximately 300K higher than the corresponding annealing temperature of the magnesium silicates [9]. This difference in temperature could be very important in explaining the presence of crystalline magnesium silicates in cometary materials with virtually no detectable crystalline iron silicates [12, 13]. Because of the potential importance in understanding the difference in thermal annealing rate as a function of temperature and composition we have investigated the use of differential scanning calorimetry (DSC) to compare the annealing profiles of smokes of different compositions. We will present the results of these investigations at the conference.

DSC Experiments: DSC measurements are conceptually simple: two identical crucibles are filled with material of identical thermal mass, one inert and the other potentially reactive. The paired crucibles are fitted with identical thermocouples to measure the interior temperature of the samples as shown in Figure 1 and the apparatus is placed inside a vacuum furnace. The temperature difference between the samples is recorded as the furnace is heated (or cooled) at a uniform rate. If an endothermic reaction occurs in the reac-

tive sample, its temperature will lag behind the reference during the reaction as some of the heat is absorbed to drive the chemical reaction. Similarly, if an exothermic reaction is triggered at a particular temperature then the temperature of the reactive sample will increase faster than the inert sample due to the energy released by the reactive sample.

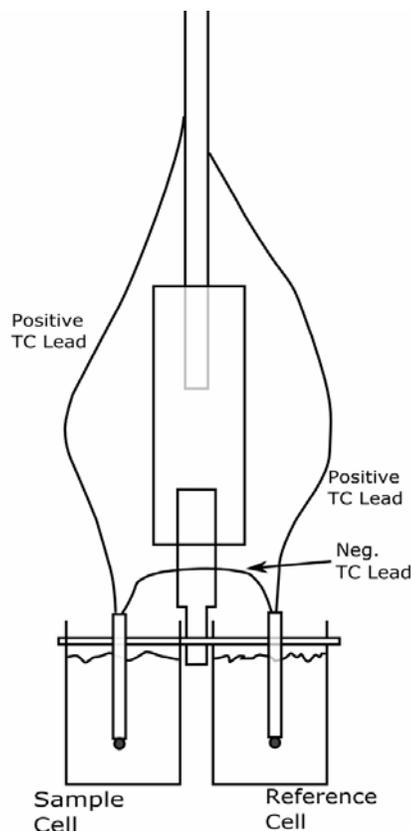


Figure 1: Schematic drawing of the Differential Scanning Calorimetry system that is inserted into a temperature programmable vacuum furnace to measure the energy released or absorbed in the sample cell due to specific chemical reactions.

Although conceptually simple, in practice we have found that DSC measurements are very sensitive to the heating rate chosen for the furnace and the specific form and mass of the reactive and reference samples used in the experiment. This is especially true when we try to extract quantitative measurements of the energy required to release bound water vapor from the samples or to measure the thermal energy released during annealing. Nevertheless, we have made considerable

progress since beginning this project as shown in Figure 2 below.

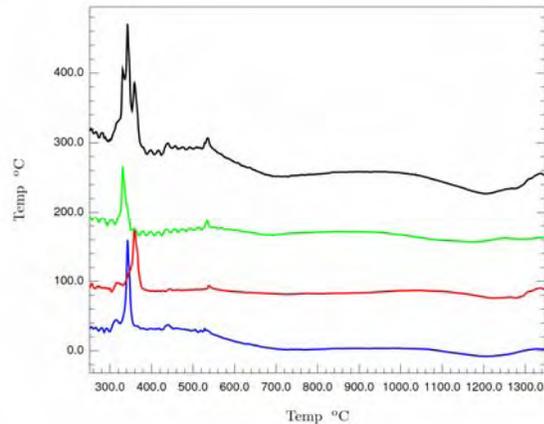


Figure 2: DSC data for three separate runs using amorphous magnesium silicate smokes (blue, red and green) as well as the summed data (black).

Results: There are several obvious features in the DSC spectra displayed in Figure 2 above. First, the large endothermic spike that occurs at about 350 C due to the evaporation of adsorbed water vapor in the sample. This appears to be followed by two more releases of small quantities of more tightly bound water at about 440 and 550 C. Finally we can see the broad exothermic peak associated with crystallization of the amorphous magnesium silicate starting at about 1000 C and continuing until about 1350 C. It is quite obvious that the exact temperatures where each “feature” begins and ends varies quite a bit from sample to sample, though the forms of these three different DSC spectra are similar. This is especially obvious in the summed spectrum (black) in Figure 2.

Discussion: The experiments shown in Figure 2 were done at a temperature ramp rate of 2 degrees per minute. At a temperature of 1000 C the amorphous magnesium silicate smokes should anneal to crystallinity (a spectral evolution index of ~100 [11]) almost instantaneously. We can therefore speculate that the initial deviation from uniform heating observed in these DSC runs does not occur when the sample reaches a temperature where the annealing rate is comparable to the timescale of the temperature ramp rate. It seems that the beginning of such a feature is a more complex function of the rate at which the sample is heated and the absorption or release of chemical energy that results in a noticeable difference in temperature between the sample and reference crucibles. Until the rate of reaction becomes sufficiently high, the amount of energy absorbed or released by the reaction has a negligible affect on the temperature of the sample, yet when sufficient energy is absorbed or released the heating or cooling effects can cause a runaway reaction that greatly magnifies such affects. The width of the feature observed in these spectra should be a rough measure of the heterogeneity of the sample. The most homogeneous samples will have the sharpest feature as all grains begin to react

simultaneously, and each releases the same amount of energy over the same time span.

We have used chromel-alumel (type K) thermocouples in these experiments. Type K thermocouples have a working temperature limit of about 1360 C before they melt. From our previous experiments [9,10] we have inferred that amorphous iron silicates require temperatures approximately 300 C above the annealing temperature of amorphous magnesium silicates to crystallize. As the beginning of the magnesium silicate annealing feature occurs near 1000C (range from ~1000-1100C), we have not been able to detect this transition using type K thermocouples before the thermocouples themselves melt. We have ordered higher temperature thermocouple wire (type B, Pt/Pt(Rh)) and hope to be able to report measurements of the annealing of amorphous iron silicates in Houston.

Summary: We have begun to utilize Differential Scanning Calorimetry to measure the temperatures at which amorphous magnesium silicates crystallize. We should soon be able to perform similar experiments on amorphous iron silicates to quantify the temperature difference in the annealing rates that we found previously using detailed spectroscopic measurements [9]. If these experiments prove to be successful we should be able to measure the temperature dependence of crystallization as a function of composition by making smokes of varying Fe/Mg ratio and then measuring the DSC spectrum of each smoke. We could also measure the DSC spectra of similar compositional mixtures of pure iron silicate and pure magnesium silicate smokes.

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