Condensation Processes in Astrophysical Environments

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1. Introduction

Astrophysical systems present an intriguing set of challenges for laboratory chemists. Chemistry occurs in regions considered an excellent vacuum by laboratory standards and at temperatures that would vaporize laboratory equipment. Outflows around Asymptotic Giant Branch (AGB) stars have timescales ranging from seconds to weeks depending on the distance of the region of interest from the star and, on the way significant changes in the state variables are defined. The atmospheres in normal stars may only change significantly on several billion-year timescales. Most laboratory experiments carried out to understand astrophysical processes are not done at conditions that perfectly match the natural suite of state variables or timescales appropriate for natural conditions. Experimenters must make use of simple analog experiments that place limits on the behavior of natural systems, often extrapolating to lower-pressure and/or higher-temperature environments.

Nevertheless, we argue that well-conceived experiments will often provide insights into astrophysical processes that are impossible to obtain through models or observations. This is especially true for complex chemical phenomena such as the formation and metamorphism of refractory grains under a range of astrophysical conditions. Data obtained in our laboratory has been surprising in numerous ways, ranging from the composition of the condensates to the thermal evolution of their spectral properties. None of this information could have been predicted from first principals and would not have been credible even if it had.

2. Dust Condensation Experiments

Our experiments were never intended to replicate the conditions that form grains in circumstellar shells. Such experiments are impractical for numerous reasons. Our apparatus is designed to make large quantities of highly amorphous condensate from a homogeneous vapor-phase. We needed highly amorphous solids, since the synthesis of grains with reproducible degrees of crystallinity is difficult and highly amorphous silicates are a logical starting point for annealing experiments that introduce increasing crystallinity as a function of time and temperature. We found that the infrared spectra of amorphous magnesium silicate grains produced in our laboratory matched those of grains in typical oxygen-rich circumstellar outflows after about 3 hours of vacuum annealing at 1027K. Had our analog grains initially been more crystalline than the natural materials there would have been no easy way to render them amorphous.

Grains are produced at a pressure of $\sim$ 90 torr in an atmosphere dominated by hydrogen at temperatures between $\sim$500K and 1500K. Condensable species are formed via combustion of gasphase precursors such as silane [SiH_4], iron pentacarbonyl [$Fe(CO)_5$], or trimethyl aluminum [$(CH_3)_3Al$)] and typically constitute less than 10% of the total gas input to the system. Oxygen is introduced separately, just before the furnace. A volatile metal such as magnesium can be placed into the furnace within a graphite crucible. Because the furnace temperature then controls the vapor pressure of this metal, only one metal is placed in the furnace during any given experiment. The total flow velocity through the furnace is $\sim$10 20 cm-s 1. A typical grain forms at the high-temperature flame front near the furnace entrance and spends much less than a second within the furnace. Hot gas and grains are rapidly quenched as they flow into a stainless steel chamber lined with an aluminum substrate that remains at $\sim$300 to 350K.

Condensation and growth are stochastic, kinetically controlled processes. Grains often form fluffy, open aggregates. Typical grains are $\sim$ 2030 nm in radius while aggregates frequently consist of thousands of individual grains; each connected to only two or three neighboring particles. The Dust Generator was designed to produce grains with chemical composition determined stochastically by the composition of the vapor. Though we expected some variation about the average composition we never expected any significant chemical processing during the rapid growth of the condensates. We were wrong. Chemical analyses of individual grains condensed from MgSiO vapors clustered around five distinct compositions: pure SiO_x and MgO grains, low- silica MgO grains and serpentine and smectite dehydroxylate grains at $Mg_3Si_2O_7$ and $Mg_3Si_4O_{11}$, respectively (1). In a similar fashion, analyses of FeSiO condensates also produced compositions clustered at the pure oxide end members and at intermediate compositions including the Fe-greenalite ($Fe_3Si_2O_7$) and Fe-saponite ($Fe_3Si_4O_{11}$) dehydroxylate compositions, and at a distinct low-Fe ferrosilica composition (2). Figure 1 is a ternary diagram of the composition of individual particles condensed from mixed Fe-MgSiO vapors. The dot is the average composition of the vapor as determined by SEM analysis of the smoke: this represents the average of many thousands of individual, mostly 20 nm-sized grains. Open squares represent individual grains determined by Analytical Election Microscopy. These cluster at the pure end-member compositions (FeO_y, MgO and SiO_x) and at mixed metastable eutectic grain compositions found in the Mg-SiO and Fe-SiO vapor condensates discussed above. However, what is most notable is that **there were no** *mixed* **FeMg silicate grains found anywhere** in this sample despite the very rapid nucleation and growth of the particles. There are no eutectic compositions possible in the FeOMgO binary phase diagram and therefore no metastable eutectics along this axis to direct the compositions of growing grains. Absent metastable eutectics along the MgOFeO axis, grain growth is confined to the pure FeOSiO and MgOSiO axes producing pure iron silicate and magnesium silicate grains and the oxides FeO_y, MgO and SiO_x.

The annealing rate for magnesium silicate smokes is a very steep function of temperature (3,4). Conversely, the time required to reach any given spectral stage is very temperature dependent. More crystalline grains are indicative of longer annealing times and/or higher temperatures. We did not measure the activation energy required to anneal iron silicate smokes, though we noted that temperatures on the order of 1300K were required in order to achieve spectral changes in the iron silicate smokes that evolved on timescales of days to weeks. This
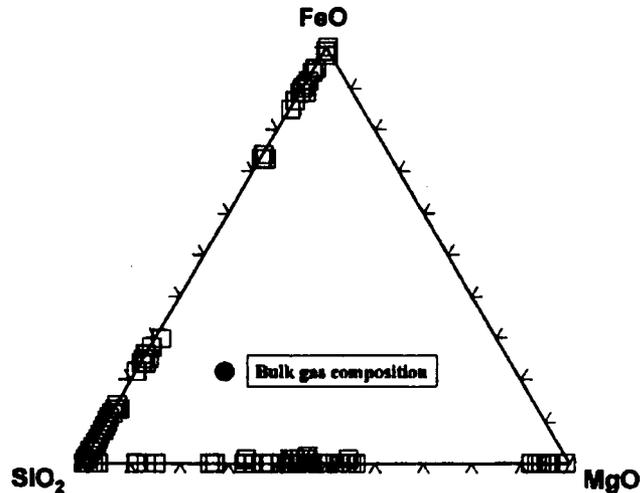
Fig. 1.— Ternary diagram showing the composition of individual 10-20 nm grains condensed from a mixed Fe-Mg-SiO-H$_2$-O$_2$ vapor. The large spot in the interior of the diagram represents the approximate composition of the vapor-phase as measured via TEM analysis of the bulk smoke. Modified after Rietmeijer (9).

is 250 to 300K higher than temperatures required for similar evolutionary timescales in magnesium silicates. At such temperatures iron silicates have an appreciable vapor pressure and small grains could easily vaporize before annealing. So for any amorphous grain there are both upper and lower time-temperature bounds to the conditions required to convert it to crystallinity without vaporization.

3. Astrophysical Application

In high mass-loss-rate circumstellar winds, features indicative of pure magnesium olivine and pyroxene were observed. No crystalline silicate minerals containing either aluminum or iron have yet been detected (4,5,6). We believe that the results discussed previously readily explain ISO observations of crystalline magnesium silicates. Our experiments yielded two unexpected conclusions: pure, amorphous, Mg-silicate and Fe-silicate grains condense from a mixed Fe-Mg- SiO vapor; and these Mg-silicate grains anneal at much lower temperatures than do Fe-silicates. Therefore we assume that the initial condensates are amorphous, though pure, iron and magnesium silicates. As the nucleation temperature increases with increasing massloss rate, pure Mg-rich silicates begin annealing just after formation, while iron silicates remain amorphous. The higher the stellar mass outflow rate, the larger the overall fraction of crystalline Mg-silicates. This is in agreement with ISO observations (6) although observational selection effects may obscure the true size of the crystalline mass fraction (8).

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