Condensation processes in astrophysical environments: 
The composition and structure of cometary grains

JOSEPH A. NUTH III1*, FRANS J. M. RIETMEIJER2 AND HUGH G. M. HILL1†

1Astrochemistry Branch, Code 691, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, USA
2Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131, USA
†NAS/NRC Resident Research Associate
*Correspondence author's e-mail address: nuth@gsfc.nasa.gov

(Received 2002 March 1; accepted in revised form 2002 July 10)
(Presented at "Laboratory Simulations of Circumstellar Dust Analogs: Expectations for Comet Nucleus Encounters", a special session of the 64th annual Meteoritical Society meeting, Vatican City, 2001 September 13)

Abstract—We review the results of our recent experimental studies of astrophysical dust analogs. We discuss the condensation of amorphous silicates from mixed metal vapors, including evidence that such condensates form with metastable eutectic compositions. We consider the spectral evolution of amorphous magnesium silicate condensates as a function of time and temperature. Magnesium silicate smokes anneal readily at temperatures of about 1000–1100 K. In contrast we find that iron silicates require much higher temperatures (~1300 K) to bring about similar changes on the same timescale (days to months). We first apply these results to infrared space observatory observations of crystalline magnesium silicate grains around high-mass-outflow asymptotic giant branch stars in order to demonstrate their general utility in a rather simple environment. Finally, we apply these experimental results to infrared observations of comets and protostars in order to derive some interesting conclusions regarding large-scale nebular dynamics, the natural production of organic molecules in protostellar nebulae, and the use of crystalline magnesium silicates as a relative indicator of a comet's formation age.

INTRODUCTION

Astrophysical systems present an intriguing set of challenges for laboratory chemists. Most chemistry occurs in atmospheric regions that would be considered an excellent vacuum by terrestrial laboratory standards and at temperatures that would quickly vaporize normal laboratory equipment. Timescales for changes in state variables such as temperature, pressure and composition range from milliseconds to minutes for rapid events like collisions or electrical discharges. 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. "Steady state" protostellar systems evolve on timescales ranging from centuries to millions of years, while the atmospheres in normal stars may only change significantly on several billion year timescales. Needless to say, most laboratory experiments carried out to understand astrophysical processes are not carried out under conditions that perfectly match the natural suite of state variables or the timescales appropriate for changes under natural conditions. Experimenters must of necessity make appropriate use of simple analog experiments that seek to place limits on the behavior of natural systems, often extrapolating the knowledge gained from such experiments to lower pressure and/or higher temperature environments.

Having admitted that few laboratory experiments can be done under natural astrophysical conditions, we will nevertheless argue below that well-conceived experimental data will often provide insights into astrophysical processes that are impossible to obtain through models, or even through observations, of natural systems. This is not to diminish the importance of either modeling or observation as vital components contributing to our understanding of natural phenomena but, rather, to emphasize the fact that experiments provide practical information that is otherwise unavailable. This is especially true for complex chemical phenomena such as the formation and metamorphism of refractory grains under a wide range of astrophysical conditions. Experimental data obtained in our laboratories have been quite surprising in a number of areas, ranging from the chemical composition of the condensates themselves to the evolution of their spectral properties as a function of temperature and time. None of this information could have been predicted from first principles and would not have been deemed credible even if it had been.
It should be noted that there are several other groups engaged in the experimental study of astrophysical grains and their simple (or more complex) analogs. An excellent summary of the work of the research group at Naples, Italy can be found in the review by Brucato et al. (2002). This group forms grains via laser vaporization of natural minerals and synthetic chemical mixtures pressed into pellets. They record the infrared spectra of their condensates as a function of composition and degree of thermal annealing, as a function of both temperature and time (see, for example, Brucato et al., 1999). The research group at Jena, Germany has measured the optical constants of a wide range of natural minerals and synthetic glasses. They have also studied the infrared spectral evolution of glassy silicates (e.g., Fabian et al., 2000) and have applied their measurements of crystalline spectra to observations obtained by the infrared space observatory (ISO) satellite (Jäger et al., 1998). This is a very rapidly developing field of study and the interpretations of our separate experiments are not always in agreement.

For example, Rietmeijer et al. (2002a) found that a stall phase that occurred during thermal annealing of an ultrafine-grained, porous "MgSiO" smoke (see Hallenbeck et al., 1998) defined a stage in the textural evolution of the sample. The stall phase was characterized by fusion of the adjacent, <20 nm sized, non-stoichiometric condensate grains into annular structures larger than ∼50 nm in diameter. They had Mg/Si ratios to support the formation of coarse-grained enstatite instead of the assemblage forsterite plus tridymite, which is also critically dependent on the tridymite grain size (Rietmeijer et al., 1986). Fabian et al. (2000) reported condensed spherical MgSiO grains 10–50 nm in diameter with non-stoichiometric Mg/Si ratios and a central void but they did not find a stall phase during thermal annealing of amorphous smokes produced by laser ablation. The faster rate at which crystalline materials developed in the study reported by Fabian et al. (2000) suggests that the agglomeration and fusion processes might have already begun during the initial laser ablation experiments. When the original nanometer-sized condensates were preserved in the original experiments as in the study reported by Rietmeijer et al. (2002a) mineralogical evolution requires textural coarsening. This example highlights our observation that different results among laboratories can be explored more readily when detailed petrological characterizations are available to allow assessments of different experiments in terms of differences in the dissipation of thermal energy during the condensation experiment proper or differences in vapor-production methods.

Such differences should not come as a great surprise, since we noted above that each experiment must deviate from the natural conditions found in astrophysical sources for practical reasons. Given the extent of some of these variations, and the degree of importance accorded to each by the various researchers engaged in this effort, some differences of opinion regarding the interpretation of the results of individual experiments are inevitable. As one example, we can look at the initial structure of our starting materials. Our smokes form from SiO, AIO, metallic magnesium and iron on timescales of milliseconds in a mixture rich in hydrogen. They are therefore both highly reduced and defect-rich. Few silicon atoms in these amorphous smokes are tetrahedrally coordinated with oxygen. Laser vaporization can produce similarly amorphous materials (quenched on a microsecond timescale), but also produces mineral grain fragments and glasses via shock interactions with the target. Finally, gel desiccation techniques (Thompson and Tang, 2001) start with tetrahedrally coordinated silicate ions in solution, and precipitate a gel with no longer range order. Each of these materials might be expected to behave somewhat differently. In particular, we believe that the extremely high degree of disorder found in our smokes is responsible for the higher activation energy required for their annealing. Although we naturally believe that our grains, results and interpretations are more reasonable than those from other laboratories, the reader is urged to view all experimental results and their applications with some caution. All experiments are flawed to some degree.

In what follows, we will describe our experimental apparatus and argue that the conditions within this simple system are comparable, in overall terms, to the natural environments in both circumstellar outflows and grain-forming regions within the primitive solar nebula. We will then present data detailing the composition of particulates formed from several different vapors and outline a model consistent with these results. Based upon these experimental observations and on measurements of the spectral evolution of simple silicates, we will then proceed to derive some constraints on the conditions under which silicate grains must have formed both in the outflows of AGB stars and in protostellar nebulae. Finally, based upon the above considerations we will present a model for circulation in protostellar nebulae that has interesting consequences for understanding the organic content of comets and meteorites. However, before discussing specific experimental results, we will first present a few very general rules concerning vapor-phase condensates that are usually applicable to solids in astrophysical systems.

**RULES FOR ASTROPHYSICAL CONDENSATES**

Astrophysical grains fall into two broad classes: materials that have achieved chemical equilibrium at a particular set of state variables and materials that have never reached chemical equilibrium. Examples of condensates that achieved equilibrium and are familiar to the meteoritic community include presolar graphite, silicon carbide (SiC), diamond, corundum and spinel grains. Although these grains once achieved equilibrium, most probably in the stellar atmosphere in which they initially condensed and grew, they did not remain in equilibrium with their environment throughout their entire existence. Indeed, the carbonaceous minerals cited above are highly unstable within the oxygen-rich meteorite matrix in
which they are found and are destroyed in thermally metamorphosed meteorite parent bodies (Huss and Lewis, 1995). Survival of these grains indicates that the primitive matrices in which they are found were never heated for a prolonged period of time to a sufficiently high temperature to overcome the kinetic barrier inhibiting the system from achieving a new equilibrium state. It is therefore possible to place specific experimental constraints upon the time-temperature history of this matrix (Huss, 1997). Similarly, one can derive limits to conditions in the bulk solar nebula based on the survival of presolar materials such as SiC (Mendybaev et al., 2002).

Many condensates never achieve equilibrium under any set of state variables. Ostwald (1896) proposed that the thermodynamically stable form of the bulk condensate never nucleated directly from the vapor phase. Indeed the surface energies of very tiny particles can potentially change the relative stabilities of specific mineral assemblages including forsterite, silica and enstatite (Rietmeijer et al., 1986) or graphite and diamond (Nuth, 1987a,b). Very high surface energies can ensure that condensates nucleate as amorphous liquids at very high levels of supersaturation and relatively low temperatures. However, the internal chemistry of such amorphous condensates might still be controlled to some degree by kinetic or thermodynamic factors, and is always subject to thermal annealing at some later time to convert these amorphous grains to crystalline mineral assemblages. In fact, the survival of amorphous or non-equilibrium mineral assemblages also provides time-temperature limits to the maximum conditions the system could have experienced while still remaining amorphous (see Hallenbeck et al., 2000). The higher the surface energy of the phase and the smaller the particle size, the more stringent are the limits placed on the severity of the environmental conditions experienced by the system since its formation.

As a general rule we can assert that the presence of well-formed crystalline grains indicates that such materials were subjected to high temperatures for at least a minimum, material-specific, time at some point either during or subsequent to their formation. Conversely, the presence of amorphous material sets strict time-temperature limits on the maximum stress level experienced by those grains, just as the presence of a non-equilibrium crystalline mineral assemblage sets limits on the environmental conditions experienced by the system since its formation. Crystalline grains usually signify extended periods at high temperatures such as in stellar atmospheres, whereas amorphous materials are often products of rapidly changing, lower temperature environments as might be found in the outflows around AGB stars or in vapor plumes generated by high-speed collisions.

**DUST CONDENSATION EXPERIMENTS**

As noted in the "Introduction", our experiments were never intended to replicate the precise conditions that form solid condensates in either circumstellar shells or in protostellar nebulae. Such experiments are extremely impractical for numerous reasons. Our experimental apparatus is designed to make reasonably large quantities of highly amorphous condensates from a very well-mixed, homogeneous vapor-phase. We deliberately designed our condensation experiments to yield highly amorphous solids, since the synthesis of grains with reproducible degrees of crystallinity is difficult. In addition, highly amorphous silicates are a logical starting point for annealing experiments that introduce increasing crystallinity as a function of time and temperature. Naturally, a goal of the exercise is to reproduce, as closely as possible, the crystallinity that one observes (telescopically) in a variety of astrophysical objects. Amorphous materials are much more useful in these studies than are materials that begin more ordered than those found in nature. By carefully annealing the amorphous magnesium silicate grains produced in our laboratory, we found that their infrared spectra matched those of grains in typical oxygen-rich circumstellar outflows after ~3 h of vacuum annealing at 1027 K (Fig. 1). Had our analog grains initially been more crystalline than the natural materials there would have been no easy way to render them amorphous, though it is possible that radiation damage could have produced appropriate starting materials (Demyk et al., 2001).

Grains are produced in the apparatus shown in Fig. 2 at a total pressure of ~90 Torr in an atmosphere dominated by hydrogen at temperatures between ~500 and 1500 K. The condensable species are formed via combustion from gas-phase precursors such as silane (SiH₄), iron pentacarbonyl (Fe(CO)₅), trimethyl aluminum ((CH₃)₃Al) or titanium tetrachloride (TiCl₄). These species typically constitute <10% of the total gas input to the system. The oxidant is introduced separately, just before the furnace, and is typically pure molecular oxygen, though nitrous oxide has been used on several occasions. Finally, it is possible to place a volatile metal into the heated furnace section of the system within a graphite crucible. Because the furnace temperature then controls the vapor pressure of this metal vapor, only one metal can be placed in the furnace during any given experiment. Metals that can be used in this system include magnesium, calcium, sodium and potassium. The total flow velocity through the furnace is typically on the order of 10–20 cm s⁻¹. A typical grain formed at the high-temperature flame front near the furnace entrance will therefore spend much less than a second within the furnace following nucleation and growth. The hot gas and fresh grains are rapidly quenched as they flow into a larger stainless steel chamber lined with an aluminum substrate that remains at a temperature of ~300 to 350 K.

Condensation and growth is a stochastic, kinetically controlled process. Grains formed in these experiments are often fluffy, open aggregates. Typical grains are on the order of 20–30 nm in radius while aggregates frequently consist of hundreds to thousands of individual grains; each connected to only two or three neighboring particles. The dust generator
was designed to condense amorphous grains with chemical composition determined stochastically by the composition of the vapor from which they formed. Though we expected some variation about the average grain composition we never expected that any significant chemical processing could occur during the extremely rapid growth of the condensates. We were wrong.

ANALYTICAL AND TRANSMISSION ELECTRON MICROSCOPY

Images, crystallographic, and chemical analyses of a wide range of astrophysical grain analogs are available in the literature. These include FeO-Fe₂O₃-SiO₂ smokes (Rietmeijer et al., 1999a); Mg-Fe-SiO condensates (Rietmeijer et al., 1999b); Mg-SiO condensates (Rietmeijer et al., 2002b), annealed Mg-SiO condensates (Rietmeijer et al., 2002a); Al₂O₃-SiO₂ condensates (Rietmeijer and Karner, 1999), and Al₂O₃-Fe₃O₄-SiO₂ vapors (Rietmeijer et al., 1999c; Nuth et al., 2000a). In each of the systems above, we found evidence for the operation of complex chemical processes during the extremely short duration of the vapor-growth phase. This is in stark contrast to our initial expectation that, due to the rapid condensation and growth of the grains, their compositions would cluster about the average vapor-phase condensible composition. Some of the most striking evidence for chemical control of particle growth comes from experiments on Mg-SiO, Fe-SiO and Mg-Fe-SiO smokes.

Chemical analyses of individual grains condensed from Mg-SiO vapors clustered around five distinct compositions: pure SiO₂ (the pure grains are always tridymite, SiO₂) and MgO grains, low-silica MgO grains as well as serpentine and smectite dehydroxylate grains at Mg₃Si₂O₇ and Mg₃Si₄O₁₁, respectively (Rietmeijer et al., 2002b). In a similar fashion, analyses of Fe-SiO condensates also found condensate compositions clustered at the pure oxide (FeOₓ, SiOₓ) end members and at intermediate compositions including the greenalite (Fe₃Si₂O₇)
and Fe-saponite (Fe$_3$Si$_4$O$_{11}$) dehydroxylate compositions, and a distinct clustering at a low-Fe ferrosilica composition (Rietmeijer et al., 1999a).

To the extent that all experiments are somewhat flawed, the finding of pure oxide grains may well be, at least in part, an experimental artifact due to incomplete vapor mixing at the time scale of the experiment and silicon saturation of the vapor. The critical result of these experiments is that kinetically controlled condensation of silicate vapors leads to apparent chemical ordering in the condensed solids. Although fundamentally identical arguments will apply to the other binary systems that are discussed in this paper, below we offer a few words on metastable eutectic solids using the MgO-SiO$_2$ phase diagram (Ehlers, 1972) as an example.

If condensation had proceeded at thermodynamic equilibrium, the compositions of the condensed Mg-SiO$_2$ solids would have been (1) MgO = 2 wt% and SiO$_2$ = 98 wt% at 1986 K, (2) MgO = 36 wt% and SiO$_2$ = 64 wt% at 1816 K, and (3) MgO = 63 wt% and SiO$_2$ = 37 wt% at 2123 K. These compositions are at the three stable eutectics in this phase diagram. But, that is not what we found when we analyzed the compositions of the individual Mg-SiO$_2$ grains that condensed from the Mg-SiO-H$_2$O$_2$ vapor (Rietmeijer et al., 2002b). The observed compositions were (a) MgO ≈ 25 wt%, (b) MgO ≈ 45 wt% and (c) MgO ≈ 85 wt%. Composition (a) is between the eutectic compositions (1) and (2) while composition (b) lies between eutectic compositions (2) and (3). The third condensate's composition (c) was not constrained by the existing phase diagram. Thus, Rietmeijer et al. (2002b) proposed a revision in the MgO-rich part of this diagram that was never experimentally defined.

The observed grain compositions (a–c) are defined by the intersections of metastable extensions of the liquidus from two adjacent eutectic points (see Rietmeijer and Nuth, 2000). Such
an intersection is a metastable eutectic. (A common example of such extensions would be superheated or supercooled water, that is, still-liquid water at 1 bar and 400 K or 1 bar and 265 K, as might occasionally be found in a microwave or a freezer, respectively.) In our diagrams we plot the observed metastable eutectic compositions at the nominal quench temperature of our experiments. (Note that this is incorrect, and is only done for presentation purposes, because a metastable eutectic point can not be fixed at a particular temperature.) Based on these observed compositions (a–c) we argued that the vapor-phase growth seemed to be controlled by processes that formed metastable eutectic compositions (Rietmeijer and Nuth, 2000) and that these compositions can be found in many diverse natural environments (Rietmeijer et al., 2000). However, even more convincing evidence for the operation of metastable eutectic growth was provided by analysis of individual grains condensed from Fe-Mg-SiO vapors.

Figure 3 is a ternary diagram showing the compositions of individual particles condensed from mixed Fe-Mg-SiO vapors. The dot is the average composition of the condensible vapor phase as determined by scanning electron microscope analysis of the smoke found on the collector: this represents the average of many thousands of individual, mostly 20 nm sized grains. The open squares represent the individual grain compositions determined by analytical electron microscopy. Note that these grains roughly cluster at the pure endmember compositions (FeO, MgO and SiO₂) and at the mixed metastable eutectic grain compositions that were found in the Mg-SiO and Fe-SiO vapor condensates discussed above. However, what is most noticeable is that there were no mixed Fe-Mg-silicate grains found anywhere in this sample despite the very rapid nucleation and growth of the particles. We note that there are no eutectic compositions possible in the FeO–MgO binary phase diagram and therefore there are no metastable eutectics along this axis to direct the compositions of growing grains. Absent metastable eutectics along the MgO–FeO axis, grain growth is confined to the pure FeO–SiO and MgO–SiO axes producing pure iron silicate and magnesium silicate grains as well as the endmember

![Figure 3](image-url)

**Fig. 3.** Ternary diagram showing the composition of individual 10–20 nm grains condensed from a mixed Fe-Mg-SiO-H₂-O₂ 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 (2002).
oxides FeO$_x$, MgO and SiO$_x$. The observation that kinetically controlled vapor phase condensation alone does not lead to the formation of Mg-Fe-silicates places important constraints on the common presence of such silicates in interplanetary dust particles (IDPs). However, agglomeration of the solid condensates in the Mg-Fe-Si system shown in Fig. 3 will lead to the formation of the small (~100 nm sized), initially amorphous, Mg-rich ferromagnesiosilica units in the matrix of aggregate IDPs (Rietmeijer et al., 1999b). Thermal processing of these units will produce the pure-Mg and Mg-Fe-silicates seen in IDPs (Rietmeijer, 2002).

**THERMAL ANNEALING OF MAGNESIUM-AND IRON-SILICATE SMOKEs**

Infrared spectroscopy is the primary technique available for the comparison of laboratory-made analogs to the natural grains formed in astrophysical environments, including circumstellar outflows. In these outflows, the primary environmental influence that could change the spectra of freshly condensed silicates is thermal annealing. As noted above, our initial goal is to make silicate condensates that are more primitive, that is, amorphous, than those seen in the natural environment. However, since these initial condensates are unlikely to survive in nature, the only way to tell if we have been successful is to anneal the material at reasonable temperatures while carefully monitoring its infrared spectra. Success will be based on comparison of the analog spectra with the morphology of the well-known "10-μm" and "20-μm" infrared features in astronomical silicates. If annealing brings the spectrum of the laboratory-made material into agreement with that of the natural silicates within a reasonable time period, then we have achieved our objective.

Figure 4 shows the spectrum of silicate dust observed in comet Halley (Hanner et al., 1994) and of our laboratory-produced magnesium silicate analog as a function of vacuum annealing. This can be compared to Fig. 1, which shows the evolution of the infrared (2.5–25 μm) spectrum of an amorphous magnesium silicate condensate annealed at 1027 K for varying times. Note that the infrared spectrum of the initial synthetic condensate originally peaks near 9.3 μm, but quickly evolves to the "natural" 9.7–9.8 μm position after only a few hours of annealing. Circumstellar silicates also generally peak in the 9.7–9.8 μm range, as do most interstellar and molecular cloud silicates. The spectra of silicate dust in many comets (Hanner, 1999), and in older Herbig Ae and Be stars (Grady et al., 2000), show a second feature developing near 10.8–11.2 μm that is similar to the feature easily seen in our analog grains after 10.5 h of annealing (Fig. 1). One should note that the spectral evolution of the analog silicates beyond this stage of annealing is characterized by a sharpening of the individual spectral subcomponents that make up the 10 μm feature (Figs. 1 and 4). It would therefore be very difficult to distinguish a mixture of well-annealed and amorphous grains from a population of moderately annealed silicates based on the shape of the 10 μm region alone. Even using both the 10 and 20 μm features together does not resolve this ambiguity. We will come back to this problem below.

At Goddard Space Flight Center we homogenized the products of many separate experimental runs carried out under identical conditions wherein we synthesized amorphous magnesium silicate smokes. This homogenized sample then served as a reservoir for many separate annealing runs carried out at 1000, 1027, 1038, and 1048 K. For each of these runs we calculated their progression into and out of the "stall" phase (see Fig. 1, between 10.5 and 48 h) which appears to be a natural pause in the evolution of the infrared spectrum of the porous smoke samples (Hallenbeck et al., 1998). Based on the annealing time required to enter and to exit the stall phase at 1000, 1027 and 1038 K we were able to calculate the activation energy required for annealing the synthetic material. Based on this activation energy and our previously measured annealing rates at specific temperatures, we can now predict the infrared spectrum for any of our magnesium silicate smokes annealed for any specified time-temperature history (Hallenbeck et al., 2000).

The measured annealing rate for magnesium silicate smokes is a very steep function of annealing temperature. Conversely, the time required to reach any given spectral stage is also very temperature dependent. To reach the "stall" phase requires a few minutes at 1067 K, 23 days at 1000 K, 39 centuries at 900 K and roughly 6000× the age of the universe (taken here to be ~20 × 10⁹ years) at 800 K (Hallenbeck et al., 2000). 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 1300 K were required in order to reach spectral changes in the iron silicate smoke samples that evolved on timescales of days to weeks. This is 250 to 300 K higher than the temperatures required to achieve similar evolutionary timescales in the porous magnesium silicates. We note that at such high temperatures iron silicates begin to have an appreciable vapor pressure, such that small grains (e.g., <0.1 μm) could easily vaporize before annealing to crystallinity. This implies that for any particular sized amorphous grain there are both upper and lower time-temperature bounds to the environmental conditions required to convert the grain to crystallinity without vaporizing it. Vapor condensates usually begin as amorphous "quenched liquid" drops and would therefore require an additional round of heating and thermal annealing for crystallization.

The corollary of this and the preceding sections is that we have experimental constraints on the thermal annealing of Mg- and Fe-silicates that form via kinetically controlled vapor phase condensation, but not on the thermal evolution of mixed Mg-Fe-silicates. But, since the latter require post-condensation processing, they are not yet part of our laboratory experiments. When the ISO data show evidence for pure Mg-silicates, it
follows from our results that the post-condensation processing required to create Mg-Fe-olivines and -pyroxenes has not yet occurred. The Mg-rich ferromagnesiosilica units in aggregate IDPs show that thermal processing of amorphous Mg-Fe-silicates will indeed yield crystalline Mg-Fe-silicates (Rietmeijer, 2002; Rietmeijer et al., 1999b). Our results do not rule out the possibility that amorphous ferromagnesiosilica materials exist in ISO environments (Rietmeijer, 2002) but such amorphous aggregates are undetectable by infrared spectroscopy.

**APPLICATION OF LABORATORY STUDIES TO ASTROPHYSICAL PROCESSES**

The ISO satellite carried two high-resolution spectrometers operating at a combined wavelength range of 2 to 200 μm (Kessler et al., 1996). With these instruments, for the first time at wavelengths inaccessible for ground-based observations, many narrow solid-state infrared features could be resolved that are diagnostic for well-ordered solids, that is, minerals (e.g., Waters et al., 1996). In very high mass-loss-rate circumstellar winds, features indicative of pure magnesium olivine (forsterite) and pyroxene (enstatite) were observed. No crystalline silicate minerals containing either aluminum or iron have yet been observed (Waters et al., 1996; Molster, 2000; Molster et al., 1999). Similarly ISO observed crystalline forsterite but not enstatite in several comets and in various protostellar nebulae. We believe that the experimental results discussed previously readily explain the ISO observations of the crystalline magnesium silicates.

We will start with the ISO observations of circumstellar grains, most of which are characterized by the typical 9.75 μm
"amorphous silicate" feature. In such systems we assume that both iron and magnesium silicate grains form, though there is no reliable, diagnostic observation to confirm this hypothesis. In very high mass-loss-rate outflows the concentration of condensable species is higher than in lower mass-loss-rate outflows and therefore grains will nucleate at higher temperatures (Draine, 1979; Nuth and Ferguson, 1993). Our experiments yielded two unexpected conclusions: (1) pure, amorphous, Mg-silicate and Fe-silicate grains condense from a mixed Fe-Mg-SiO vapor; and (2) these Mg-silicate grains anneal at much lower temperatures than do the Fe-silicates. Therefore we will assume that the initial circumstellar condensates are amorphous, though pure, iron and magnesium silicates. As the nucleation temperature of the grains increases with increasing mass-loss rate, the pure Mg-rich silicates will begin annealing to crystallinity just after their formation, while the iron silicates remain amorphous. The higher the mass outflow rate of the star, the larger the overall fraction of crystalline Mg-silicates will be. This appears to be in agreement with ISO observations (Molster, 2000) although observational selection effects may obscure the true size of the crystalline mass fraction (Kemper et al., 2001).

Applications of our results to the solar nebula are both complex and intriguing as we require a very distinct change in the "standard" nebular model (see, for example, Woolum and Cassen, 1999). In what we call the "standard" model, material falls onto the accretion disk and gradually works its way inward, eventually falling onto the growing protosun. A very small fraction of infalling matter manages to avoid this fiery fate by growing into planetesimal-scale objects that orbit the sun. Although most material in the disk moves monotonically towards the central star, some turbulent mixing between nearby adjacent regions does occur (Morfill et al., 1985) and this can mix materials processed at somewhat higher and lower temperatures. Our results, when combined with observations of crystalline magnesium silicates in recent comets, demand that there be some level of dust and gas circulation that carries material from the innermost regions of the nebula (e.g., <1 AU) out to several hundred astronomical units (Nuth et al., 2000b; Hill et al., 2001).

Previous wisdom held that comets could be simple agglomerates of interstellar dust and ice (Greenberg, 1983). The observation that comet Halley dust was consistent with crystalline olivine (Campins and Ryan, 1989) implies that comets could contain additional materials that may have been processed to some degree in the solar nebula. However, ISO observations of the prevalence of Mg-rich olivine grains in comets Hyakutake and Hale-Bopp are difficult to explain as randomly annealed grains preserved in largely interstellar ices. In addition, observations of modern, higher mass, protostellar systems (Herbig Ae/Be stars) show a very interesting trend. "Young" Herbig Ae/Be stars—those just beginning to show ultraviolet emission as they break out of their natal cocoons—contain amorphous silicate dust comparable to our laboratory analogs. On the other hand, "old" Herbig Ae/Be stars contain a significant fraction of crystalline magnesium silicate mineral grains. Intermediate age stars lie somewhere in between these two extremes (Grady et al., 2000). Unfortunately, it appears that the spectral evolution of the dust in such systems is not a simple function of stellar age but might also depend on additional factors that would affect the disk itself, such as the presence or absence of a companion star (Carol Grady, pers. comm.). These observations imply that some fraction of the amorphous silicate dust inherited from the interstellar medium must be processed to crystallinity during the star formation process (Bouwman, 2001; Bouwman et al., 2001; Meeus et al., 1997; Waelkens et al., 1996). We note that dust, vaporized near the protostar and re-condensed in an expanding wind, will most likely resemble grains condensed in oxygen-rich circumstellar outflows. Except in highly unusual circumstances (e.g., very high mass outflow rates), such dust is amorphous.

The easiest way to process amorphous dust to yield crystalline silicates is by thermal annealing. The environment most conducive to the thermal annealing of amorphous silicates (T > 1000 K) is in the innermost regions of the protostellar nebula (<1 AU). The ices that characterize comets are not stable in such environments and the annealed dust must, in our opinion, be transported out to well beyond the nebular snow line (at ~5 AU in the solar nebula) in order to be accreted into an icy planetesimal. The mechanism by which this occurs is not yet clear (e.g., Prinn, 1990), but could be quite important in understanding the overall chemistry of protostellar nebulae and the chemistry of comets. This is especially interesting because of the potential for synthesis of biogenic molecules required for the origin of life at the higher pressure–temperature conditions of the inner nebula, from the predominantly H2, CO, N2 and water that dominates interstellar molecular chemistry. This material could then also be transported out to several hundred astronomical units together with the annealed silicates.

**CATALYTIC CHEMISTRY AND COMETARY AGES**

If annealed grains from within ~1 AU of the protosun can be transported to the region of comet formation by some, as yet unrecognized mechanism (e.g., Prinn, 1990), then gas from this same high-pressure, high-temperature environment is likely to make the trip as well. Models of the volatile components released by comets require that some fraction of these materials were processed in higher temperature–pressure environments than is possible in the outer solar nebula (Prinn and Fegley, 1989; Fegley, 1993, 1999). It was previously hypothesized that giant gaseous protoplanetary subnebulae could have provided such environments, yet there is little observational evidence that suggests that these subnebulae even exist in modern protostellar systems. While there is no doubt that the inner solar nebula would provide the required thermodynamic
environment needed to synthesize complex organic molecules, to date we have little evidence that such materials could have been transported to the outer nebular regions (>100 AU) where comet formation might actually begin (Weidenschilling, 1997). For the moment we will simply assume that a suitable transport mechanism exists and examine its consequences.

We have recently demonstrated that amorphous iron silicates are very efficient catalysts (Ferrante et al., 2000; Hill et al., 2001). These silicates convert molecular nitrogen, carbon monoxide and hydrogen into a variety of volatile organic compounds while depositing a carbonaceous residue on the catalyst itself (Gilmour et al., 2002). More recent experiments indicate that both amorphous magnesium silicate smokes and amorphous SiO₂ smokes also act as excellent methanation and Fischer–Tropsch catalysts. Neither the amorphous Mg-rich nor SiO₂ rich smokes were able to catalyze the conversion of molecular nitrogen and hydrogen into ammonia: only the Fe-rich silicate smoke was observed to catalyze this reaction. However, when molecular nitrogen, hydrogen and carbon monoxide were used as the starting gas mixture, all three smokes produced a volatile product with an infrared feature at 950 cm⁻¹ identified as N-methyl methylene imine, as well as a suite of other organic molecules. These studies imply that much of the amorphous dust in the innermost regions of the solar nebula will efficiently catalyze the formation of complex hydrocarbons and C–N bonded molecules. Given the higher pressures and temperatures in this region, considerable quantities of organic materials could have been synthesized over the lifetime of the warm, inner nebula.

In the earliest stages of nebular history, everything falls into the protostar. At some later stage we believe that an outward flowing wind begins to carry processed gas and annealed dust into the outer nebula (Nuth et al., 2000b; Hill et al., 2001). Comets formed prior to the presence of the wind could only form from interstellar dust and ices. Comets formed at later times would incorporate larger fractions of complex organics and crystalline magnesium silicate grains from among the accreted dust and pebbles. Comets formed at the end of the nebular phase should contain the highest amount of both crystalline magnesium silicate grains and complex hydrocarbons. Based on this scenario we predicted both that the levels of crystalline silicate and complex organic molecules should be correlated and that these species should increase to a maximum in the youngest comets. The oldest comets should contain mostly interstellar ices and grains; the youngest will contain complex nebular organics and annealed magnesium silicates (Nuth et al., 2000b). The fraction of crystalline silicate dust contained within a comet might therefore be used as a rudimentary indicator of its relative age. This said, we appreciate that attempting to quantitatively calibrate such an indicator would be difficult. However, in overall terms, we believe that this method has value as it permits one to think of an evolutionary relationship between the nebula and distinct cometary histories and compositions.

SUMMARY

Individual amorphous grains condensed from several different vapor phases form at predictable metastable eutectic compositions. Lacking metastable eutectics along the MgO–FeO join, condensates from a Mg-Fe-SiO vapour form smokes consisting of only pure magnesium silicate, iron silicate and metal oxide grains. The proportions of grains at individual compositions are determined by the overall composition of the initial mixed metal vapor. Experimental studies of the spectroscopic evolution of magnesium silicate grains as a function of time at various temperatures, indicate that temperatures of about 1100–1000 K are required to anneal such materials to crystallinity on reasonable (hour-to-month) timescales. Annealing typically forms forsterite plus tridymite instead of the more thermochemically stable, but rarely observed, enstatite. Iron silicates require much higher temperatures (temperature greater than ~1300 K) to bring about similar rates of change in their infrared spectra.

Observations of relatively large quantities of crystalline magnesium silicate grains in comets and in older Herbig Ae/Be stars indicate that crystallization naturally occurs within protostellar nebulae. When such observations are combined with the experimental results discussed above, we infer that there must be a mechanism to circulate annealed grains from the inner nebula (<1 AU) out to several hundred astronomical units where grains begin to accrete into icy cometary solids. Such winds would also naturally carry gas, rich in organic molecules, freshly synthesized in the inner nebula, out beyond the nebular snowline where they could easily be incorporated into growing planetesimals. Our experiments show that amorphous metastable silicates readily catalyze the conversion of H₂, N₂ and CO into organic species. We therefore expect that the innermost regions of protostellar nebulae will be potent factories for the production of essential prebiotic molecules necessary for the origin of simple living organisms in most young stellar systems. Whether these prebiotic molecules get the chance to evolve to more complex forms will depend, in part, on the nature of the environment where they are deposited within the system and the timescales over which such conditions persist. The research summarized here makes predictions about the nature of condensed grains, the products after thermal annealing and the efficiency of catalytic conversion in circumstellar and protoplanetary environments. These predictions should be testable by astronomical observations. In this respect, there is a natural fusion with several observing projects, especially in the infrared. In addition to telescopic projects, our predictions are also intimately related to laboratory analyses of IDPs, meteorites and materials retrieved by sample return missions.

Acknowledgments—We like to thank Cornelia Jäger and Jeroen Bouwman for constructive reviews. F. J. M. R. was supported by NASA grant NAG5-11762. H. G. M. H. acknowledges funding from the NAS/NRC Resident Research Associateship Program. J. A. N.
is grateful to NASA's Cosmochemistry Research and Analysis Program for its generous support.

**Editorial handling:** P. Cassen

**REFERENCES**


RIETMEIJER F. J. M. (2002) The earliest chemical dust evolution in
the solar nebula. *Chemie der Erde* 62, 1–45.
in the Al$_2$O$_3$–SiO$_2$ system explored by vapor phase condensation.
equilibrium brought down to Earth. *EOS* 81, 409 + 414–415.
Analytical electron microscopy of Mg-SiO smokes: A
comparison with infrared and XRD studies. *Icarus* 66, 211–222.
Metastable eutectic, gas-to-solid, condensation in the FeO–
Metastable eutectic condensation in a Mg-Fe-SiO-H$_2$O$_2$ vapor:
RIETMEIJER F. J. M., KARNER J. M., NUTH J. A. AND WASILEWSKI
P. J. (1999c) Nanoscale phase equilibrium in a triggered lightning
RIETMEIJER F. J. M., NUTH J. A., III, JABLONSKA M. AND KARNER
environments: Recent developments and research opportunities.
*Res. Trends Geochem.* 1, 30–51.

RIETMEIJER F. J. M., HALLENBECK S. L., NUTH J. A. AND KARNER
J. M. (2002a) Amorphous magnesiosilicate smokes annealed in
vacuum: The evolution of magnesium silicates in circumstellar
and cometary dust. *Icarus* 156, 269–286.
S. L. (2002b) Gas-to-solid condensation in a Mg-SiO-H$_2$O$_2$
vapor: Metastable eutectics in the MgO–SiO$_2$ phase diagram.
THOMPSON S. P. AND TANG C. C. (2001) Laboratory Investigation of
crystallization in annealed amorphous MgSiO$_3$. *Astron.
Astrophys.* 368, 721–729.
WAEKENS C. ET AL. (1996) SWS observations of young main-
sequence stars with dusty circumstellar disks. *Astron. Astrophys.*
WEIDENSCHILLING S. J. (1997) The origin of comets in the solar
nebular temperatures: Implications for planetesimal formation.