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Crystalline silicates in comets: How did they form?

Joseph A. Nuth III [a,*], Natasha M. Johnson [a,b]

[a] Astrochemistry Lab, NASA's Goddard Space Flight Center, Code 691, Greenbelt, MD 20771, USA
[b] NAS/NRC Resident Research Associate, NASA's Goddard Space Flight Center, Greenbelt, MD 20771, USA

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Abstract

Two processes have been proposed to explain observations of crystalline silicate minerals in comets and in protostellar sources, both of which rely on the thermal annealing of amorphous grains. First, high temperatures generated by nebular shock processes can rapidly produce crystalline magnesium silicate grains and will simultaneously produce a population of crystalline iron silicates whose average grain size is ∼10–15% that of the magnesium silicate minerals. Second, exposure of amorphous silicate grains to hot nebular environments can produce crystalline magnesium silicates that might then be transported outward to regions of comet formation. At the higher temperatures required for annealing amorphous iron silicates to crystallinity the evaporative lifetime of the grains is much shorter than a single orbital period where such temperatures are found in the nebula. Thermal annealing is therefore unable to produce crystalline iron silicate grains for inclusion into comets unless such grains are very quickly transported away from the hot inner nebula. It follows that observation of pure crystalline magnesium silicate minerals in comets or protostars is a direct measure of the importance of simple thermal annealing of grains in the innermost regions of protostellar nebulae followed by dust and gas transport to the outer nebula. The presence of crystalline iron silicates would signal the action of transient processes such as shock heating that can produce crystalline iron, magnesium and mixed iron–magnesium silicate minerals. These different scenarios result in very different predictions for the organic content of protostellar systems.

Keywords: Comets; Comets, origin; Solar nebula processes; Silicate grains; Interplanetary dust

1. Introduction

Campins and Ryan (1989; Ryan and Campins, 1991) first proposed the presence of crystalline silicates in Comet Halley, based on the presence of an 11.2-micron shoulder within the broad 10-micron silicate-stretching mode. This shoulder seemed consistent with the presence of the mineral forsterite (Mg_2SiO_4). Until that time, silicates in comets were thought to be primarily unprocessed, amorphous interstellar grains coated by water ice containing various impurities (Greenberg, 1983). The Infrared Space Observatory (ISO) was used to observe crystalline silicates in the dust around Comet Hale–Bopp (e.g., Crovisier et al., 1997, 2000). As the peaks observed near 33 and 69 microns are due to phonon transitions in the crystalline silicate lattice, the ISO observations are an unambiguous indication of the presence of crystalline silicates in cometary dust. More recently, crystalline olivine and orthopyroxene have been identified in Comet C/2001 Q4 (NEAT) via 10-micron observations (Wooden et al., 2004). There is considerable controversy concerning the origin of these crystalline grains.

As much as 5% of the interstellar silicate grain population could be crystalline, yet still lie below our current limits of detection (Li and Draine, 2001). It could equally well be true that any crystalline silicates injected into the interstellar medium become amorphous after long exposure to galactic cosmic rays (Krätschmer and Huffman, 1979; Day, 1977; Demyk et al., 2001; Brucato et al., 2004). Based on the structure of the 10-micron silicate feature measured along a single line of sight towards the galactic center, Kemper et al. (2004) calculated an upper limit on the fraction of crystalline silicates along that very long path to be $0.2 \pm 0.2\%$. Finally, observations of the spectral evolution of silicate grains in Herbig Ae/Be Stars appear to indicate that the degree of crystallinity increases as a function of the age of the protostellar nebula (Grady et al.,

* Corresponding author. Fax: +1 301 286 1683.
E-mail address: joseph.a.nuth@nasa.gov (J.A. Nuth III).

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1999) provided that no stellar companions are present to complicate nebular evolution. These observations, based on a very small sample of stars, argue that processes within the protostellar nebula itself are responsible for the production of crystalline silicates. It should now be possible to test this trend for a much larger sample of protostars using Spitzer (previously known as the Space Infrared Telescope Facility, SIRTF) observations.

One of us (Nuth, 1999) previously argued that the presence of crystalline silicate grains in comets must be the result of thermal annealing of amorphous silicates within the inner regions of the primitive solar nebula, followed by transport of the new crystalline solids out beyond the nebular snow line in winds flowing well above and below the disk out to distances where the grains and ices they carried could be incorporated into newly forming comets (Nuth et al., 2000a, 2000b; Hill et al., 2001). One source of such winds might be the magneto-hydrodynamic interactions that Shu has proposed to produce chondrules in the primitive nebula (Shu et al., 1996), or they may be driven by interactions between such forces and nebular turbulence, or even by terms typically left out of model calculations for simplicity (Prinn, 1990; Stevenson, 1990). A new model of transport in the solar nebula (Boss, 2004) actually shows that materials readily move both inwards and outwards in the nebula prior to the formation of the giant planets. No matter the source, no observational evidence for the existence of such transport processes yet exists. In contrast, Harker and Desch (2002) have suggested that shock waves in the outer solar nebula could anneal the amorphous silicates to crystallinity in situ prior to their incorporation into comets, thereby eliminating the need for large-scale nebular transport processes. Similarly, there is yet no observational evidence for the existence of such shocks.

Observational tests to distinguish between thermal annealing in the inner nebula and shock heating in the outer nebula have previously been proposed (Hill et al., 2001; Harker and Desch, 2002), but all such tests involve long-term cometary observation programs. Here we propose a direct and definitive observational test to distinguish between the relative importance of the two models for the origin of crystallinity in cometary grains: namely, the presence or absence of crystalline iron-bearing silicates in the grain population.

2. Nebular processing

2.1. Grain properties

For these calculations we maintain that there exist separate populations of amorphous magnesium silicate and amorphous iron silicate grains that either survive from their formation in circumstellar outflows (Rietmeijer et al., 1999) or are formed via the evaporation and recondensation of presolar silicates (Nuth et al., 2002). These separate grain populations then follow the Mathis et al. (1977) size distribution. For simplicity we do not include mixed amorphous iron–magnesium silicate grains. Such grains have not been observed though, in principle, there seem to be no reasons why small, amorphous iron and magnesium silicate grains could not coagulate, then anneal to produce mixed iron–magnesium silicate crystals. Perhaps shocks tend to disrupt grain aggregates before ambient temperatures can become sufficiently high to either weld small grains together or cause such grains to anneal. Or perhaps aggregates simply tend to anneal closer to their high temperature end member. No matter the reason, mixed iron–magnesium silicate crystals have not yet been observed and are not included in these calculations.

2.2. Shock heating

Harker and Desch (2002) calculated that it was possible for shocks to heat silicate grains to sufficiently high temperatures to produce magnesium silicate crystals using the Silicate Evolution Index of Hallenbeck et al. (2000). Hallenbeck et al. (1998) noted that iron silicates [i.e., amorphous ferrosilica smokes consisting of maghemite (γ-Fe_2O_3) and silica (Rietmeijer and Nuth, 1991)] appear to anneal on the same timescale as magnesium silicates, provided that their ambient temperature is at least 300 K higher than that of the magnesium silicates. We note here that 300 K is a very rough estimate for the difference in annealing temperature between magnesium and iron silicates, but will argue later that this estimate is of sufficient accuracy for our purposes. Moreover, the calculations done by Harker and Desch (2002) used a 50/50 Fe/Mg silicate grain: magnesium silicate grains would therefore get a bit hotter while iron silicate grains would remain cooler than the values calculated by Harker and Desch based on grain density and heat capacity considerations for similar sized grains.

Alternatively, as iron is often considered to be the constituent that renders both circumstellar and interstellar grains "dirty" (Jones and Merrill, 1976; Ossenkopf et al., 1992) and since radiatively heated dirty grains become hotter than clean grains, estimates of grain temperatures in shocks based upon a 50/50 mix of magnesium and iron in a silicate could potentially underestimate the temperatures of the pure iron silicates while overestimating the temperatures of the pure magnesium silicates of the same grain size in an optically thick environment. In an optically thin region of the nebula the greater emissivity of the iron silicate grains could result in lower peak temperatures. Measurements of the rate of annealing and spectral evolution of amorphous iron silicate condensates, or of mixed iron–magnesium silicate condensates, as a function of temperature do not currently exist but would be quite useful.

Table 1 is based on the results provided by Harker and Desch (2002) for 50/50 Fe/Mg silicate grains and shows the maximum temperature reached by specific diameter grains during a shock event that occurs in a medium of specific density. Values marked with an asterisk ($*$) represent our interpolations or extrapolations, as appropriate, for this maximum (calculated using a simple cubic polynomial) based on the values originally tabulated by Harker and Desch (2002). Fig. 1 graphically presents the temperature data in Table 1.

A quick look at Table 1 reveals that 1 micron-diameter (0.5 μm radius) silicate grains can reach temperatures in excess of ∼1100 K. These grains will therefore easily anneal on timescales of a few seconds if they are pure magnesium sili-

Table 1
Peak temperatures for different grain sizes of $(Mg_{0.5}Fe_{0.5})SiO_3$ heated by an accretion shock

Ambient gas density, ρ (g cm^{-3})	0.01 μm (K)	0.10 μm (K)	0.25 μm (K)	0.50 μm (K)	1.0 μm (K)
0.3×10^{-10}	*1301**	1100	*895**	*794**	670
1.0×10^{-10}	*1508**	1305	1095	990	920
2.0×10^{-10}	*1593**	1405	1210	1110	1035
3.0×10^{-10}	*1648**	*1467**	*1277**	1175	1110
5.0×10^{-10}	*1718**	*1546**	*1362**	1255	1200
10.0×10^{-10}	*1810**	1650	*1477**	*1371**	1300

* Extrapolated and interpolated values are based on peak temperatures obtained from the shock models of Harker and Desch (2002).

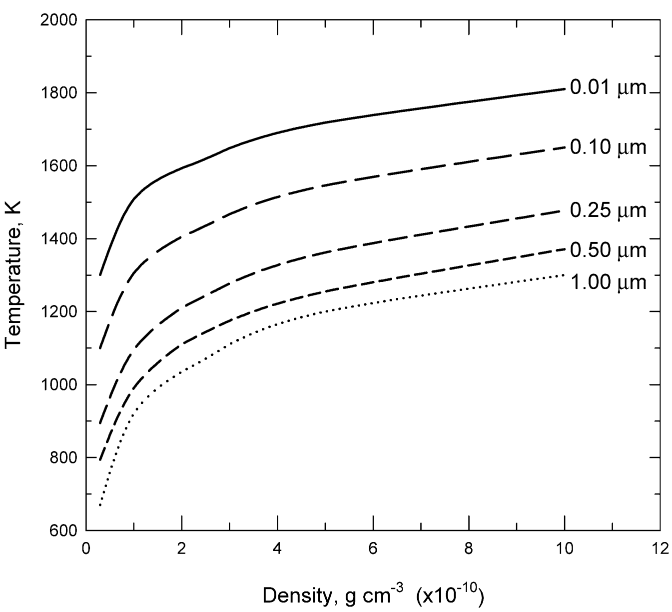

Fig. 1. Peak temperatures reached during a shock event for different sized radius 50/50 Fe/Mg silicate grains in a medium of a specific density (see Table 1).

cates (Hallenbeck et al., 2000). One can also see that for shocks at the same density, 0.1 micron radius grains reach temperatures in excess of 1400 K while grains only 0.01 micron in radius are heated to nearly 1600 K. Even amorphous iron silicates will anneal to crystallinity on timescales of a few seconds at 1400 K, though at much higher temperatures the smaller radius grains might evaporate. For slightly higher densities even a 0.25 micron-diameter (0.125 μm radius) amorphous iron silicate grain should become crystalline, while at densities slightly in excess of 10×10^{-10} g cm^{-3} even 0.5 micron-diameter iron silicate grains can be shock heated to temperatures in excess of 1400 K, and thus become crystalline, though smaller grains will surely lose mass as they both evaporate and anneal.

One product of shock heating events in the primitive solar nebula will therefore be a population of crystalline magnesium silicate grains extending up to a specific size range, while larger silicates remain amorphous. Shocks will also produce crystalline, iron silicate grains (of smaller diameter than the crystalline magnesium silicates) while a population of larger, amorphous iron silicates remains unannealed. Note that even iron silicate grains that have been irradiated in the ISM to the point where iron–silica phase separation has occurred (Bradley, 1994) could react at 1400–1500 K to produce crystalline iron silicate minerals provided that these small grains begin to achieve chemical equilibrium (Brucato et al., 2004).

As smaller cometary grains are typically heated to higher temperatures in the ambient solar radiation field, the population of smaller, iron silicate crystals should be readily observable in cometary comae if the population of larger magnesium silicate crystals is seen.

2.3. Thermal annealing

The temperature gradient in the solar nebula is reasonably well defined (e.g., Woolum and Cassen, 1999) and increases slowly from ∼150 K near the Jupiter–Saturn formation region to ∼1000 K near 1 AU. The temperature continues to climb as one approaches the early Sun, though the profile here begins to depend on the details of how the dust disk interacts with the protostar. We follow a monotonic temperature increase as the grains move inward. The grains move inward due to gas drag on loose aggregates in Keplerian orbits or due to the slow migration of gas and dust through the disk on its way to accretion in the protostar. Such inward migration occurs over many orbital periods. Grains exposed to high temperatures (e.g., 1300–1400 K) in this scenario have already spent many years at slightly lower temperatures (e.g., 1100–1200 K). This slow migration through successively hotter layers of the nebula adds an extra dimension to thermal annealing and the production of crystalline minerals: grain survival.

The lifetime of an individual grain at a given temperature is inversely proportional to its vapor pressure [$P(T)$], surface area [$4\pi r^2$], the rate at which the vapor expands from the vaporizing grain [$(2\pi RT/M)^{-1/2}$] and roughly proportional to its mass [$4/3\rho\pi r^3$]. Combining these terms, a rough estimate for the grain lifetime (t) is given by

$$t = r\rho[2\pi RT/M]^{1/2} \big/ \big[3P(T)\big], \tag{1}$$

where ρ is the grain density, r is the grain radius, R is the ideal gas constant, M is the mass of the vaporizing species [here SiO at 44 amu], T is temperature and $P(T)$ is the effective vapor pressure of the grain material. For this set of calculations we use the vapor pressure of SiO over silica obtained from the work of Shornikov et al. (1998, 1999, 2000) as a proxy for the vapor pressures of both amorphous iron silicate and amorphous magnesium silicate. Because these measurements were obtained under somewhat oxidizing conditions and in the presence of SiO_2 solid, we consider them to represent effective lower limits to the actual vapor pressure of SiO in the low pressure environment of the solar nebula. Note that we have not accounted for the decreasing mass flux from the grains as they evaporate, due to decreasing surface area. This effect will be most serious in estimates of the lifetimes of the largest grains.

For these calculations we will ignore the fact that some of the vaporizing species can recondense onto the grain surface, even though this process can reduce the effective vapor pressure—and thus extend the grain lifetime—by as much as a factor of

Table 2
Log(seconds) of grain lifetime vs temperature and radius

	1000 K	1100 K	1200 K	1300 K	1400 K	1500 K
10,000 nm	13.48	11.23	9.35	7.76	6.4	5.24
1000 nm	12.48	10.23	8.35	6.76	5.4	4.24
100 nm	11.48	9.23	7.35	5.7	4.4	3.24
10 nm	10.48	8.23	6.35	4.76	3.4	2.24

Note. 1 hour = 3.56, 1 day = 4.94, 1 month = 6.43, 1 year = 7.50.

fifty. The exact value of this factor (the accommodation coefficient) is the subject of considerable debate (Schaefer and Fegley, 2004) and is intimately connected to measured values of the SiO vapor pressure. However, the accommodation coefficient is likely to decrease at lower pressures and could therefore be relatively insignificant in the solar nebula. It is sufficient for our purposes here to acknowledge that the grain lifetimes that are calculated based on the use of Eq. (1) could be considerably longer in the unlikely scenario where the appropriate value of the accommodation coefficient for vaporization of SiO in the solar nebula is nearer to 50 than to 1. Alternatively, under more reducing conditions the vapor pressure of SiO could be more than four orders of magnitude higher than the values we use here (Schick, 1960). Although high values of the accommodation coefficient would offset the effects of this higher vapor pressure to some degree, there is little doubt that under reducing conditions, the lifetimes of grains would be considerably shorter than we have shown in Table 2. In this study we have chosen to err on the side of grain survival and have therefore potentially overestimated the lifetimes of hot iron silicates.

To balance this uncertainty, we note that our simple calculation of an evaporative lifetime does not account for the integrated effect of the grains' long exposure to lower nebular temperatures prior to reaching the specific temperature of interest. In addition, we do not know how long grains remain exposed to such high temperatures once they are annealed before they are transported out to cooler temperatures. At a minimum we suggest that grains are exposed to the highest temperatures experienced for a length of time that is comparable to that of an orbital period. Thus, we assume that grains exposed to nebular temperatures of ~1000–1100 K must be able to survive for ~1 year, while grains heated to ~1300–1400 K need only survive for a few months before they are transported to a cooler environment. Of course if the average time required for an annealed grain to be transported outward is on the order of 10 to 20 orbital periods, then the grain must survive that much longer. Such longer timescales might be achieved by using a more realistic value for the accommodation coefficient for SiO vaporization; if an accurate value for this constant were available and more accurate estimates of grain lifetimes were warranted.

In the calculations above we had assumed that the annealing took place near the nebular mid-plane where frictional turbulence provides the energy for heating the disk. However, it has been suggested that the vertical structure of the nebula could be affected by heating of the top and bottom of a flared disk by the protostar: in the most extreme cases, the disk would be stabilized against thermal convection because the top and bottom could be hotter than the mid-plane. Under these circumstances

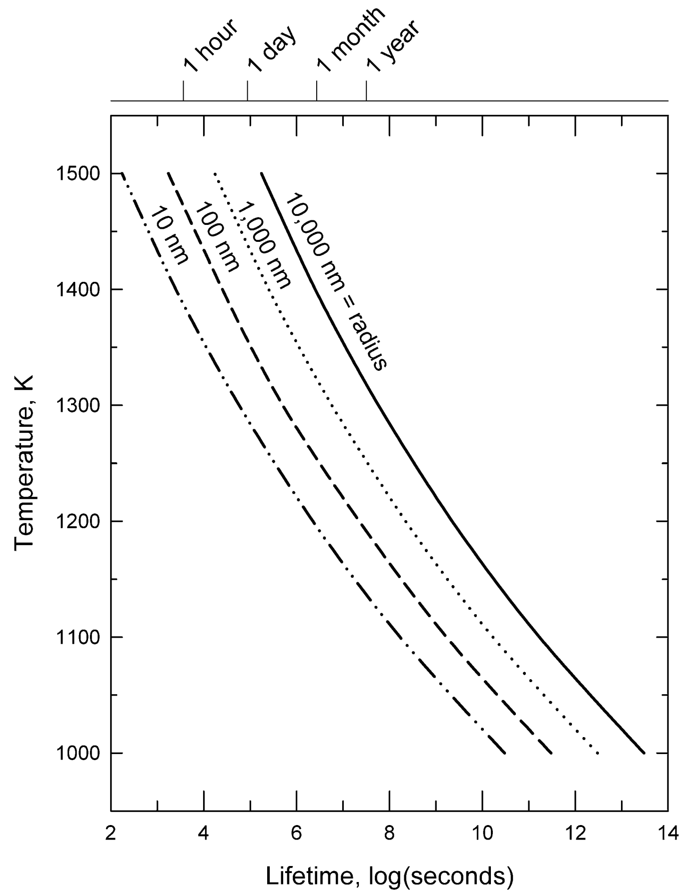

Fig. 2. Grain lifetime in log(seconds)—grain radius indicated on plot (see Table 2).

it is unclear how long grains might be exposed to the highest temperatures at the outer surface of the nebula before falling back to the midplane: alternatively, it is not really clear how they would be lofted either above or below the nebular midplane in such a scenario. If it is possible to expose grains to the hot surface for only very brief periods, then it should certainly be possible to form both crystalline magnesium silicates as well as crystalline iron silicates by this mechanism. Again, it is unclear how grains would be rapidly exposed to such an environment that would, by nature, be relatively stagnant: if stagnant, then one would expect that regions that were hot enough to produce iron silicate minerals, would also vaporize them in rather short order.

2.4. Comet formation

Weidenschilling (1997) has modeled the formation of comets using the minimum mass solar nebula as his starting point. In this model, icy grains begin to stick together into larger aggregates at nebular radii out to about 200 AU. As these aggregates accrete more ice and dust, gas drag gradually slows them down and they begin a very long process (up to ~100,000 years) of spiraling in towards the protosun until they are either ejected from the system or placed into the Oort cloud by gravitational interaction with a gas giant planet. One other option is that they might grow sufficiently large that they break free of the gas out beyond the orbit of Pluto and take up permanent residence in the Kuiper belt. The minimum mass solar nebula is, of course, a lower limit and in more massive nebulae comets will certainly grow faster and their greater mass will more readily free them from gas drag at greater orbital radii. Nevertheless, even in a fairly massive nebula the original grain aggregates for comets in the Oort cloud could begin to form out at distances approaching 20–50 AU.

Crystalline minerals observed in comets most likely come from multiple jets originating from vents of various depths as well as surface regions. If crystalline minerals were produced preferentially in the highest density regions of the nebula, near the giant planets, then one might expect that these minerals would be distributed on the surfaces of cometesimals that had aggregated much further out in the nebula and finished growing near the regions of the giant planets at approximately 5 to 10 AU. This distribution of crystalline material on such comets would be much like sugar on the outside of a doughnut. Once these comets had made several passes around the Sun, much of this outermost material should have been lost. Yet it appears that the crystalline grains are distributed throughout the comets whenever they are observed. This implies that crystalline grains must either be transported outwards from near 10 AU to become incorporated into the smallest cometary accretion units, or that shock processes must still produce such materials even at very low densities in the far reaches of the outer nebula. As models of shock heating (Harker and Desch, 2002) demonstrate that the latter scenario is unlikely, we are left to conclude that a transport mechanism must exist to bring crystalline materials out to the region where the first cometary aggregates formed. If a mechanism exists to transport grains from ∼10 out to ∼50 AU, then such a mechanism may also transport grains from inside 1 AU to similar or even greater distances (e.g., Boss, 2004).

3. Results

Table 2 shows the logarithm of the grain lifetime in seconds as a function of the grain radius in nanometers and the nebular temperature. Note that laboratory-produced grain condensates are often on the order of 10 to 20 nm in radius (Nuth et al., 2002) while the “average” interstellar grain has a radius of ∼100 nm (Mathis et al., 1977). It is possible that “average” interstellar grains are simply aggregates of the smaller condensates (Mathis, 1996) from circumstellar environments that coagulate either in the stellar outflow or in the interstellar medium. One to ten micron-sized grains become increasingly rare in the interstellar medium (Mathis, 1996; Mathis and Wallenhorst, 1981), but are certainly present in meteorite matrix (Scott et al., 1988). Of course Solar System aggregates could also contain materials that have been significantly processed in the nebula as well, including both fresh condensates as well as metals and annealed grains (Molster et al., 2002; Bradley et al., 1999).

The composition of individual 10–20 nm grains is a bit more problematic than the size distributions of the aggregates. In a series of publications, Rietmeijer and colleagues (e.g., Nuth et al., 2000a, 2000b) have argued that the compositions of vapor-phase condensates lie at metastable eutectics in the appropriate binary or ternary phase diagrams (Rietmeijer and Nuth, 2000). These results are consistent with both astrophysical observations (Rietmeijer et al., 1999) and with the analyses of more down to earth materials such as coal fly ash (Rietmeijer et al., 2000). The implications of such studies are that oxygen-rich stellar or nebular condensates would be pure, amorphous, iron- or magnesium-silicates: no mixed iron–magnesium silicate grains condense directly from the vapor (Nuth et al., 2002). More complex compositions could result from grain aggregation followed by thermal annealing of the aggregate. However, these would be much larger grains than are found in the original condensate population and we do not yet know how the thermal annealing rate depends on the Fe/Mg ratio or overall composition of the grains.

One final complication is that crystalline iron and magnesium silicate minerals are known products of parent body processes and are certainly present in a large number of meteorites. Disruption of parent bodies could therefore provide a source of crystalline iron silicate, crystalline magnesium silicate and mixed iron–magnesium silicate minerals that might have been incorporated into comets, provided that outward transport of such debris is possible.

From Table 2 it is clear that even the smallest grains survive for many years, even centuries, at the temperatures (∼1100 K) required to produce crystalline magnesium silicate grains from amorphous precursors via thermal annealing at the mid-plane. These same grains survive much less than a day at the temperatures required to thermally anneal amorphous iron silicates to crystallinity (1300–1400 K). Even the largest grains (10 microns in radius) only survive for a few months at such high temperatures, though the evaporated cores of these grains might produce crystalline iron silicates containing large quantities of refractory impurities.

These results demonstrate that simple thermal annealing in the mid-plane of the solar nebula cannot easily produce crystalline iron silicate minerals, though this process is perfectly capable of producing crystalline magnesium silicate grains. From Section 2.2, we recall that shock–induced annealing produces both crystalline magnesium silicates plus a smaller grain-size population of crystalline iron silicates. As noted above, parent body processing could also produce crystalline iron- and magnesium-silicate minerals. We therefore suggest that the fraction of crystalline magnesium silicate grains observed in comets, or in protostellar nebulae, can serve as a direct measure of the relative importance of simple thermal annealing followed by outward transport of grains and gas in winds flowing high above and below the plane of the disk, while the detection of crystalline iron silicates would indicate the importance of other processes such as shocks, in making crystalline grains.

4. Discussion

As noted above, there may be many different ways to produce crystalline iron-bearing silicates, such as pure fayalite or an iron–magnesium olivine. If only amorphous iron- and magnesium-silicate grains exist in the nebula then shock heating will produce both crystalline iron- and magnesium-silicate grains. Similarly, grains heated for brief periods at the top of the nebula or grains produced in a parent body then released by collision will also consist of both iron- and magnesium-silicate minerals. Though little is known concerning the conditions required to anneal mixed iron-silicate, magnesium-silicate aggregates to crystallinity, one might suppose that it would depend to some extent on the iron/magnesium ratio of the aggregate and should to first approximation fall between the temperatures required to form crystalline magnesium silicates ($\sim$1100 K) and those required to form crystalline iron silicates ($\sim$1400 K).

Although there appear to be several potential processes that could produce mixed populations of both crystalline iron and magnesium silicate grains, there appears to be only one scenario that will produce pure magnesium silicate crystals while leaving all other grains amorphous. Magnesium silicate grains in Keplerian orbits around the protostar can be annealed to crystallinity and still survive for reasonably long times, whereas amorphous iron silicates that get hot enough to crystallize also vaporize on very short timescales. If a small fraction of the dust in the disk can be transported outward (to $\gg$50 AU and possibly even much farther out) in winds that flow above and below the mid-plane, then newly forming comets could be supplied with crystalline magnesium silicate minerals plus amorphous dust, consistent with astrophysical observations.

When one considers all of the processes that might produce mixed populations of crystalline iron- and magnesium-silicate minerals, or olivines and enstatites of intermediate composition, it is indeed remarkable that the infrared spectrum of Comet Hale–Bopp is consistent with a crystalline dust population that is more than 90% magnesium silicate minerals—with no evidence at all for the presence of crystalline iron silicates (Molster et al., 2003; Wooden et al., 2004). Of course the spectrum of one or two comets alone do not prove the hypothesis that thermal annealing of dust in the inner nebula, coupled with an unidentified transport mechanism, seeded the outer nebula with crystalline magnesium silicates. Many more observations both of modern protostellar systems and of comets in our own Solar System will be needed before the case is settled. Luckily, Spitzer results should soon be able to either confirm or refute such a hypothesis by placing an upper limit on the iron content of crystalline dust in these objects using far-infrared spectroscopy.

Shock-induced grain annealing occurs at orbital frequency whenever gravitational instabilities form clumps or nonaxisymmetric density structures in the disk (Boss, 2000, 2001a, 2001b), or randomly as the result of other disk processes (Harker and Desch, 2002). Simple thermal annealing is a nearly continuous low-level process that occurs to material in the inner regions of the nebula throughout the lifetime of the disk. However, it is important to recognize that the chemistry of protostellar disks can be vastly different under these two scenarios for making crystalline silicates. In shock events, species formed in the dark cloud phase of the interstellar medium would be only slightly modified by the very short duration temperature increase they experience in the disk as they migrate inward to $\sim$5 or 10 AU. A brief period of elevated nebular temperatures only slightly modifies the gas phase chemistry and evaporates ices condensed on grains (that are then annealed). Many constituents of these ices would remain unchanged by the shock (e.g., the bulk of the H_2O and simple hydrocarbons) and would recondense on the surfaces of grains following passage of the shock. These grains would then aggregate into cometesimals that already contain unprocessed interstellar materials accreted prior to the shock. Materials produced in the interstellar medium (Greenberg, 1983) would therefore dominate the organic chemistry of comets, with only a modest contribution from chemical processes in the nebula unless shocks occurred at very high frequency.

Alternatively, if thermal annealing inside $\sim$1 AU produces the crystalline silicates observed in comets, then both grains and gas must be transported outward in order to be incorporated into comets (Hill et al., 2001). The rates of chemical reactions are often exponentially dependent on increasing temperature and at least linearly dependent on increasing pressure. More often, reaction rates increase as the second or third power of the total pressure. The chemistry of the inner nebula is therefore much more complex than that of the cold, low-density outer nebula. The high temperatures and higher pressures of the inner nebula are sufficient to drive Fischer Tropsch-type surface-mediated reactions (Kress and Tielens, 2001) on grains that can convert ambient CO, N_2, and H_2 into high molecular weight hydrocarbons, including alkanes, alcohols, poly-aromatic hydrocarbons, amines, amides, and organic acids (Hill and Nuth, 2003).

The conversion of a significant fraction of nebular CO and N_2 into complex hydrocarbons could vastly increase the organic content of protostellar systems compared to scenarios where such species are produced exclusively in the ISM and may even be destroyed by nebular processes. The transport of such materials out to the $\sim$100 AU regions (e.g., Boss, 2004) where comet formation begins (Weidenschilling, 1997) would, in turn, seed high concentrations of complex organics throughout the nebula. Complex organic materials would certainly be accreted into comets, but would also be found in the moons around giant planets as well as in the asteroids and terrestrial planets of the inner nebula. This latter scenario is very conducive to Solar System-wide chemical evolution leading to the origin of life, both in the primitive solar nebula and in more modern protostellar systems that most likely form by similar mechanisms.

5. Conclusions

Shock-induced grain annealing should produce different grain-size populations of both crystalline iron silicate minerals and crystalline magnesium silicate minerals and there may be additional nebular processes that could produce both iron and magnesium silicate crystals. Simple thermal annealing due to high ambient temperatures in a protostellar nebula can only produce crystalline magnesium silicate minerals. At ambient temperatures high enough to crystallize iron silicates, the lifetime against grain evaporation is so short that it is highly unlikely that such annealed grains would survive long enough to be transported to the outer nebula. Crystalline iron silicate minerals therefore are unlikely products of simple thermal annealing near nebular mid-planes. This suggests that there might be an observational test to determine the relative importance of thermal annealing and shock-heating for the production of the crystalline silicate grains observed in comets.

The detection of crystalline iron silicate minerals in either comets or in protostellar nebulae would confirm the operation of shock-induced annealing, or more complex annealing scenarios, in such systems. The absence of crystalline iron silicate minerals would suggest that simple thermal annealing and the outward transport of gas and grains from the innermost regions of protostellar systems to significant distances away from the central star is the dominant mechanism for the production of crystalline silicates in protostellar systems and in comets. In the former case, products made in the ISM would dominate the organic chemistry of the nebula; while in the latter, organic chemistry would be dominated by nebular products.

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References

Boss, A.P., 2000. Possible rapid gas giant planet formation in the solar nebula and other protoplanetary disks. Astrophys. J. 536, L101–L104.

Boss, A.P., 2001a. Gas giant protoplanet formation: Disk instability models with detailed thermodynamics and radiative transfer. Lunar Planet. Sci. XXXII. Abstract 1193.

Boss, A.P., 2001b. Preservation of isotopic heterogeneity in the solar nebula. Meteor. Planet. Sci. Suppl. 36. Abstract A26.

Boss, A.P., 2004. Evolution of the solar nebula. VI. Mixing and transport of isotopic heterogeneity. Astrophys. J. 616, 1265–1277.

Bradley, J.P., 1994. Chemically anomalous, preaccretionally irradiated grains in interplanetary dust from comets. Science 265, 925–929.

Bradley, J.P., Keller, L.P., Snow, T.P., Hanner, M.S., Flynn, G.J., Gezo, J.C., Clemett, S.J., Brownlee, D.E., Bowey, J.E., 1999. An infrared spectral match between GEMS and interstellar grains. Science 285, 1716–1718.

Brucato, J.R., Strazzulla, G., Baratta, G., Colangeli, L., 2004. Forsterite amorphisation by ion irradiation: Monitoring by infrared spectroscopy. Astron. Astrophys. 413, 395–401.

Campins, H., Ryan, E.V., 1989. The identification of crystalline olivine in cometary silicates. Astrophys. J. 341, 1059–1066.

Crovisier, J., Leech, K., Bockelée-Morvan, D., Brooke, T.Y., Hanner, M.S., Altieri, B., Keller, H.U., Lellouch, E., 1997. The spectrum of Comet Hale–Bopp (C/1995 01) observed with the Infrared Space Observatory at 2.9 AU from the Sun. Science 275, 1904–1907.

Crovisier, J., and 14 colleagues, 2000. The thermal infrared spectra of Comets Hale–Bopp and 103P/Hartley 2 observed with the Infrared Space Observatory. In: Sitko, M.L., Sprague, A.L., Lynch, D.K. (Eds.), Thermal Emission Spectroscopy and Analysis of Dust, Disks and Regolith. Astron. Soc. Pac., San Francisco, pp. 109–117.

Day, K.L., 1977. Irradiation of magnesium silicates with MeV protons. Mon. Not. R. Astron. Soc. 178, 49P–51P.

Demyk, K., Carrez, Ph., Leroux, H., Cordier, P., Jones, A.P., Borg, J., Quirico, E., Raynal, P.I., d'Hendecourt, L., 2001. Structural and chemical alteration of crystalline olivine under low energy He^+ irradiation. Astron. Astrophys. 368, L38–L41.

Grady, C.A., Sitko, M., Russell, R.W., Lynch, D.K., Hannes, M.S., Percz, M.R., Bjorkman, K.S., DeWinter, W., 1999. Infalling planetesimals in pre-main-sequence stellar systems. In: Mannings, V., Boss, A.P., Russell, S.S. (Eds.), Protostars and Planets, vol. 4. Univ. Arizona Press, Tucson, pp. 613–638.

Greenberg, J.M., 1983. The largest molecules in space—Interstellar dust. In: Ponnemperama, C. (Ed.), Cosmochemistry and the Origin of Life. Reidel, Dordrecht, pp. 71–112.

Hallenbeck, S.L., Nuth, J.A., Daukantas, P.L., 1998. Mid-infrared spectral evolution of amorphous magnesium silicate smokes annealed in vacuum: Comparison to cometary spectra. Icarus 131, 198–209.

Hallenbeck, S.L., Nuth, J.A., Nelson, N., 2000. Evolving optical properties of annealing silicate grains: From amorphous condensate to crystalline mineral. Astrophys. J. 535, 247–255.

Harker, D.E., Desch, S.J., 2002. Annealing of silicate dust by nebular shocks at 10 AU. Astrophys. J. 565, L109–L112.

Hill, H.G.M., Nuth, J.A., 2003. The catalytic potential of cosmic dust: Implications for prebiotic chemistry in the solar nebula and other protoplanetary systems. Astrobiology 3, 291–304.

Hill, H.G.M., Grady, C.A., Nuth, J.A., Hallenbeck, S.L., Sitko, M.L., 2001. Constraints on nebular dynamics and chemistry based on observations of annealed magnesium silicate grains in comets and in disks surrounding Herbig Ae/Be stars. Proc. Nat. Acad. Sci. 98, 2182–2187.

Jones, T.W., Merrill, K.M., 1976. Model dust envelopes around late-type stars. Astrophys. J. 209, 509–524.

Kemper, F., Vriend, W.J., Tielens, A.G.G.M., 2004. The absence of crystalline silicates in the diffuse interstellar medium. Astrophys. J. 609, 826–837.

Krätschmer, W., Huffman, D.R., 1979. Infrared extinction of heavy ion irradiated and amorphous olivine, with applications to interstellar dust. Astrophys. Space Sci. 61, 195–203.

Kress, M., Tielens, A.G.G.M., 2001. The role of Fischer–Tropsch catalysis in solar nebula chemistry. Meteorit. Planet. Sci. 36, 75–91.

Li, A., Draine, B.T., 2001. On ultrasmall silicate grains in the diffuse interstellar medium. Astrophys. J. 550, L213–L217.

Mathis, J.S., 1996. Dust models with tight abundance constraints. Astrophys. J. 472, 643–655.

Mathis, J.S., Rumpl, W., Nordsieck, K.H., 1977. The size distribution of interstellar grains. Astrophys. J. 217, 425–433.

Mathis, J.S., Wallenhorst, S.G., 1981. The size distribution of interstellar particles. III. Peculiar extinctions and normal infrared extinction. Astrophys. J. 244, 483–492.

Molster, F.J., Bradley, J.P., Sitko, M.L., 2002. The origin of the crystalline silicates in our Solar System. Lunar Planet. Sci. XXXIII. Abstract 1471.

Molster, F., Demyk, A., d'Hendecourt, L., Bradley, J.P., Bonal, L., Borg, J., 2003. The first 2–50 μm infrared spectrum of an interplanetary dust particle (IDP). Lunar Planet. Sci. XXXIV. Abstract 1148.

Nuth, J.A., 1999. Constraints on nebular dynamics based on observations of annealed magnesium silicate grains in comets and in disks around Herbig AE and Be stars. Lunar Planet. Sci. XXX. Abstract 1726.

Nuth, J.A., Hallenbeck, S.L., Rietmeijer, F.J.M., 2000a. Laboratory studies of silicate smokes: Analog studies of circumstellar materials. J. Geophys. Res. Space Phys. 105, 10387–10396.

Nuth, J.A., Hill, H.G.M., Kletetschke, G., 2000b. Determining the ages of comets from the fraction of crystalline dust. Nature 406, 275–276.

Nuth, J.A., Rietmeijer, F.J.M., Hill, H.G.M., 2002. Condensation processes in astrophysical environments: The composition and structure of cometary grains. Meteorit. Planet. Sci. 37, 1579–1590.

Ossenkopf, V., Henning, Th., Mathis, J.S., 1992. Constraints on cosmic silicates. Astron. Astrophys. 261, 567–578.

Prinn, R.G., 1990. On neglect of nonlinear momentum terms in solar nebula accretion disk models. Astrophys. J. 348, 725–729.

Rietmeijer, F.J.M., Nuth, J.A., 1991. Tridymite and maghemite formation in an Fe–SiO smoke. Proc. Lunar Sci. Conf. 21, 591–599.

Rietmeijer, F.J.M., Nuth, J.A., 2000. Metastable eutectic equilibrium brought down to Earth. EOS 81, 414–415.

Rietmeijer, F.J.M., Nuth, J.A., Karner, J.M., 1999. Metastable eutectic condensation in a Mg–Fe–SiO–H_2–O_2 vapor: Analogs to circumstellar dust. Astrophys. J. 527, 395–404.

Rietmeijer, F.J.M., Nuth, J.A., Jablonska, M., Karner, J.M., 2000. Metastable eutectic equilibrium in natural environments: Recent developments and research opportunities. Res. Trends Geochem. 1, 30–51.

Ryan, E.V., Campins, H., 1991. Comet Halley: Spatial and temporal variability of the silicate emission feature. Astron. J. 101, 695–705.

Schaefer, L., Fegley, B., 2004. A thermodynamic model of high temperature lava vaporization on Io. Icarus 169, 216–241.

Schick, H.L., 1960. A thermodynamic analysis of the high-temperature vaporization properties of silica. Chem. Rev. 60, 331–362.

Scott, E.R.D., Barber, D.J., Alexander, C.M., Hitchinson, R., Peck, J.A., 1988. Primitive material surviving in chondrites: Matrix. In: Kerridge, J.F., Matthews, M.S. (Eds.), Meteorites and the Early Solar System. Univ. Arizona Press, Tucson, pp. 718–745.

Shornikov, S.I., Archakov, I.Yu., Shul'ts, M.M., 1998. Mass spectrometric study of vaporization and thermodynamic properties of silicon dioxide. I. Composition of the gas phase and partial vapor pressures of the molecular forms over silicon dioxide. Russ. J. Gen. Chem. 68, 1171–1177.

Shornikov, S.I., Archakov, I.Yu., Shul'ts, M.M., 1999. Mass spectrometric study of vaporization and thermodynamic properties of silicon dioxide. II. Determination of partial vaporization coefficients of silicon dioxide. Russ. J. Gen. Chem. 69, 187–197.

Shornikov, S.I., Archakov, I.Yu., Shul'ts, M.M., 2000. Mass-spectrometric study of evaporation and thermodynamic properties of silica. III. Equilibrium reactions of molecules occurring in the gas phase over silica. Russ. J. Gen. Chem. 70, 360–369.

Shu, F., Shang, H., Lee, T., 1996. Toward an astrophysical theory of chondrites. Science 271, 1545–1552.

Stevenson, D., 1990. Chemical heterogeneity and imperfect mixing in the solar nebula. Astrophys. J. 348, 730–737.

Weidenschilling, S.J., 1997. The origin of comets in the solar nebula: A unified model. Icarus 127, 290–306.

Wooden, D.H., Woodward, C.E., Harker, D.E., 2004. Discovery of crystalline silicates in Comet C/2001 Q4 (NEAT). Astrophys. J. 612, L77–L80.

Woolum, D.S., Cassen, P., 1999. Astronomical constraints on nebular temperatures: Implications for planetesimal formation. Meteor. Planet. Sci. 34, 897–907.