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Laboratory Studies of Simple Dust Analogs in Astrophysical Environments

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Abstract Laboratory techniques seek to understand and to place limits upon chemical and physical processes that occur in space. Dust can be modified by long-term exposure to high-energy cosmic rays, thus rendering crystalline material amorphous. It can be heated to high temperatures, thus making amorphous material crystalline. Dust may be coated by organic molecules, changing its spectral properties, or may act as a catalyst in the synthesis of both simple and complex molecules. We describe experimental studies to understand such processes and report studies that focus on the properties of simple oxide grains. We give an overview of the synthesis and characterization techniques most often utilized to study the properties of solids in the laboratory and have concentrated on those techniques that have been most useful for the interpretation of astrophysical data. We also discuss silicate catalysis as an important mechanism that may drive the formation of complex molecular compounds relevant for prebiotic chemistry.

5.1 Introduction

Laboratory Astrophysics is not an oxymoron. Laboratory studies are one of the very few means to understand the chemical and physical processes that occur in the outlandish environments (by terrestrial standards) observed by astronomers. Such processes often occur under conditions that are far removed from what is considered normal by most chemists and physicists, and the application of a terrestrially honed chemical intuition to processes in astrophysical systems is likely to yield incorrect interpretations of the observations unless the environmental effects are carefully considered. The design of experiments that address processes active in astrophysical environ-

ments must also account for differences between the laboratory and reality. Often one finds that it is neither necessary or even desirable to carry out experiments under typical astrophysical conditions. Few funding agencies will support experiments lasting ten million (or even ten!) years to duplicate processes in the interstellar medium, and few institutions will hire or promote a researcher who must wait tens of years before the publication of their next paper. However, by carrying out the experiment at higher pressure or by irradiating at higher fluxes, it is often possible to reduce the timescale of experiments from several million years to several days or weeks without changing the final product. Nevertheless, laboratory experiments do not necessitate the exact replication of all the possible chemical and physical processes that occur in complex astrophysical environments. Usually, laboratory studies are performed to understand processes occurring at atomic or molecular scale or to determine basic physical and chemical quantities (e.g. activation energies, reaction cross-sections, etc.) that are universally applicable.

The first decade of the 21st century is a revolutionary period in the study of extraterrestrial material. On 15th January 2006 samples of dust collected from the Wild 2 cometary coma by NASA's Stardust mission were successfully delivered to Earth. Thousands of particles originally in the protosolar nebula have been collected from a Kuiper belt comet and are at the disposal of analysts worldwide. Beside these very special samples, extraterrestrial material is continuously collected from the near-Earth environment both as interplanetary dust particles (IDPs) and meteorites. Wide ranging analytical investigations performed directly on these extraterrestrial samples, carrying information on the origin and evolution of the Solar System, have important advantages over analogs. However, a stringent limitation exists due to the relatively small amount of material collected and the lack of precise information regarding their actual physical or thermal history. Furthermore, IDPs, micrometeorites and samples returned from Solar System bodies require dedicated collection efforts or even space missions, with severe time and economic constraints.

IDPs occur in space as more or less fluffy aggregates with variable proportions of silicate, oxide, pure metal, pure carbon and organic components, which could be amorphous or crystalline; they are structurally-mixed, and complex. Furthermore, recent laboratory examination of cometary dust samples collected by the Stardust mission, showed that cometary dust is highly heterogeneous and very fluffy, consisting of silicate fragments, organic and possibly volatile-rich particles that represent an unequilibrated assortment of solar and pre-solar materials (Sandford et al. 2006; Keller

et al. 2006; Brownlee et al. 2006). The presence of high-temperature minerals (forsterite and CAIs), that formed in the hottest regions of the solar nebula (Zolensky et al. 2006; McKeegan et al. 2006), provided dramatic evidence confirming predictions of extensive radial mixing at early stages of the solar nebula (Nuth 1999; Nuth et al. 2000; Hill et al. 2001; Bockelée-Morvan et al. 2002). Astro-materials have complex natures that are the outcome of various astronomical environments they crossed. Thus, we are very interested in the formation and properties of solid particles that form in the outflows of stars, spend hundreds of millions of years in the interstellar medium, become part of a newly forming star or planetary system and possibly undergo moderate to severe metamorphic reactions due to heating or reactions with water or ambient nebular gas.

The use of dust analogues offers several advantages with respect to the use of actual extraterrestrial materials: a) there are no constraints to the type of measurements to be performed, so that characterization of such materials can be as thorough as required; b) there is no limitation in the available abundance, so that tests can be repeated and destructive processes can be applied on subsets of the same material. Finally, since analog materials are generally simpler, and their chemical compositions are constrained by the initial choices of reactant, they can serve to ensure that the analytical technique in question is performing nominally. Having acknowledged 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.

There are several groups engaged in the experimental study of astrophysical grains and their simple (or more complex) analogs. A 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 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). The group at Goddard Space Flight Center makes smokes via evaporation/condensation and by combustion, then either follows the spectral changes of these materials during annealing or hydration (Nuth et al. 2002) or uses these materials as catalysts for the production of organics from H_2 , N_2 and CO (Hill & Nuth 2003). There are also several collaborative research groups in Japan that measure the spectra of minerals in the far infrared (Koike et al. 1993), study the isotopic fractionation during evaporation of minerals (Nagahara et al. 1988) and observe the transformation of amorphous grains and grain mixtures into more highly ordered systems using state-of-the-art transmission electron microscopes (Kaito et al. 2003).

This is a very rapidly developing field of study and the interpretations of our separate experiments are not always in agreement. Most of the analog studies reported to date are attempts to understand the properties of oxide grains. This is both because there is considerable data already available in the literature on the properties of carbonaceous materials (Mennella 2005; Mennella et al. 1999; Dartois et al. 2004, 2005) and because it is difficult to carry out appropriate analog experiments on carbonaceous grains that add new information to this extensive database. We have not covered all of the laboratory techniques that have been used to study the properties of solids, but we have focused on those that have been most useful for the interpretation of astrophysical data.

5.2 Dust Analogue Synthesis

To experimentally model the formation and properties of solid particles that form in the outflows of stars under realistic conditions appropriate to a circumstellar outflow, we would need a system large enough that the walls of the chamber are unimportant and the chamber itself needs to be pumped down to pressures that are several orders of magnitude less than the partial pressure of the least abundant reactant. In a typical stellar outflow SiO is present at $\sim 10^{-6}$ the abundance of hydrogen, while hydrogen is present at

10^{10} particles per cm^3 . In practical terms, this means that the experimental system must be capable of achieving a vacuum better than 10^{-15} atm. and operate at about 10^{-9} atm. or less. These conditions are barely achievable in terrestrial laboratories. However, for wall effects to be unimportant, the chamber radius must be several times the mean free path of the gas: at 10^{-9} atm. the mean free path is ~ 100 meters.

A spherical vacuum chamber several hundred meters in radius, capable of achieving a vacuum less than 10^{-15} atm. and operating at 10^{-9} atm. might be possible, but would be very expensive. Heating the system to more than 2,000 K only adds spice to the problem. If the system were built and, in the 1-meter cube center, SiO molecules were introduced at 10^4 cm^{-3} , then condensed to make 10 nm grains ($\sim 10^5$ SiO molecules/grain) that are allowed to settle onto a 10 m square collection plate, and if this experiment were repeated 10 times, then the collector would be covered with 10 nm scale grains at a concentration of 1 grain per cm^{-2} . Collecting this sample, measuring its spectral properties and using such materials as the starting point for additional experiments would be somewhat challenging. As a matter of fact, conditions in the relatively high pressure environment of a circumstellar outflow are easier to duplicate in the laboratory than many higher temperature and much lower pressure astrophysical environments such as the regions surrounding Eta Carinae or the Red Rectangle, where laboratory experiments under ambient natural conditions would be nearly impossible using today's technology.

5.2.1 Vapor condensation, electrical discharge and laser pyrolysis

Solid grains form in circumstellar outflows via condensation from a high temperature gas. It is therefore not surprising that many analog experiments start with simple grains condensed from a high temperature vapor. Vapors are produced in a variety of ways, ranging from the evaporation of simple metals from hot crucibles at controlled temperatures (Day & Donn 1978; Nuth & Donn 1981), to condensation in high energy, but less controlled environments such as in laser plumes (Stephens & Rusell 1979; Brucato et al. 2002) or plasmas produced via microwave discharge (Tanabé et al. 1988; Kimura & Nuth 2007) or electron bombardment (Meyer 1971). Each of these techniques produces interesting analog materials, but only in very small (milligram) quantities. The combustion of refractory precursors such as silane and pentacarbonyl iron highly diluted in hydrogen and mixed with oxygen or nitrous oxide at controlled temperatures in a tube furnace can

produce gram quantities of analog oxides that are useful for many additional studies (Nuth & Hill 2004). The results from these studies will be discussed below.

High-voltage discharges in gases, driven by Tesla coils or microwave discharges, create a high-energy plasma that can break bonds and initiate reactions to produce solids from appropriate precursor molecules such as silane, siloxanes or various volatile hydrocarbons. Grains produced in electrical discharges are a subset of vapor-phase condensates discussed above. While SiO molecules are produced in electrical discharges containing silane (Kimura & Nuth 2007) or various siloxanes (Tanabé et al. 1988), the effects of the ions or transient molecules such as ozone are poorly understood. As an example, it is likely that oxygen transfer from the non-mass dependently fractionated ozone to the growing silicate grains results in the production of similarly fractionated solid oxide grains (Kimura & Nuth 2007). However, the solids themselves are quite similar in their infrared spectra to grains produced via other vapor condensation techniques (Kimura & Nuth 2007). A wide range of carbonaceous morphologies can be produced in these discharges depending on the input gas and the characteristics of the discharge, though the technique has not been widely used to produce astrophysical analogs.

Laser pyrolysis is based on the interaction of a high-power laser beam with the target surface. It is basically a vapor deposition process where condensation occurs in an expanding plasma plume caused by laser vaporization of the target. The physical processes involved in the vaporization of solids depend both on the laser and material properties. Laser power density, the absorption properties of the target material at the laser wavelength and the target's thermal properties all drive the vaporization process. Materials with low thermal diffusivity and high absorbance reach a very high local thermal energy and, thus, high peak temperatures are achieved in a small area on the target surface. When temperatures rise sufficiently above the boiling point, evaporation occurs and material is removed as both vapor and solid/liquid ejecta. The interaction of the laser beam with the expanding material in the plume or a higher powered laser with a sample surface can generate more energetic species to form a plasma. The plasma close to the surface emits radiation, which is more efficiently absorbed by the solid. At high power density (above 10^7 W cm^{-2}) the vapor becomes ionized and absorbs a fraction of the laser energy. The temperature conditions for evaporation are usually reached in a short time, which depends on the laser power density, thermal diffusivity and heat of sublimation of the material. Generally, these quantities vary with temperature. One of the advantages of

laser pyrolysis is the homogeneous evaporation of the target material. Since atomic diffusivities are several orders of magnitude smaller than thermal diffusivities, during the vaporization process fractionation of the material is usually not observed. For this reason the technique is useful for congruent evaporation. This generally results in a condensed sample with the same chemical composition as the target, even if segregation of a small fraction of the product is sometimes observed (Brucato et al. 1999).

A Nd-YAG solid-state pulsed laser has its fundamental laser wavelength output at 1064 nm. Laser beam energy may vary according to the instrument's technical configuration. However, the power emitted per laser pulse is typically of the order of 10^{8-10} W cm⁻². Sets of doubling crystals are frequently used to get the II and IV laser harmonics at 532 and 266 nm, respectively, and a typical optical set-up allows one or more of these wavelengths to reach the target. The optical properties of silicates used as target materials typically vary with wavelength in such a way that the absorption coefficient of the bulk target is lower by orders of magnitude at 1064 nm with respect to 266 nm. Therefore, a laser wavelength in the UV, rather than in the IR, will vaporize silicates more efficiently. Targets may be bulk, flat polished slices or pressed powder. The flat surface optimizes the interaction between the incident laser beam and the target, having high output during the first part of the vaporization process. In order to produce condensates, a target is mounted inside a vaporization chamber, designed to work in different gas environments. The pressure inside the chamber is usually maintained at a few millibar and the gas used depends on the experimental conditions required. Quick quenching of the hot atoms by multiple collisions with cold atoms or molecules of gas present inside the evaporation chamber results in rapid energy loss that favors supersaturation of the vapor. These conditions result in condensation. The rapid freezing of the mutual interatomic positions, which are chaotic at the very high evaporation temperature, causes the formation of amorphous material, even if a few crystalline particles are produced simultaneously. In order to prevent the formation of pure iron grains during the vaporization of Fe-bearing silicates and to ensure that the chemical composition of the condensed grains is maintained similar to that of the target, an oxygen atmosphere is required. Finally, the condensates are collected on different types of substrates depending on the analyses to be performed and on the type of sample processing planned.

5.2.2 Melt solidification, sol-gel reactions, Czochralski and floating-zone methods

It is well known that a liquid can be cooled below its equilibrium freezing temperature. Crystallization during melt solidification is hampered due to an activation barrier caused by the surface energy of the crystal nuclei (surface energy is due to the unfilled or distorted chemical bonds on a solid surface). High cooling rates are usually needed to produce glasses, notably cooling rates of the order of thousands of K s^{-1} might be needed. The supercooled liquid passes through a transition to a glass at a temperature that is typically $2/3$ of the melting temperature. At this transition some degrees of freedom are frozen in. Since the transition is out-of-equilibrium, the properties of the resulting glass depend on its thermal history. Supercooled liquid below the melting point therefore becomes metastable with respect to the crystalline solid state. Glasses are, thus, out of equilibrium solids with many of the liquid's degrees of freedom frozen in. Solidification from a melt is often too fast to produce crystals and amorphous silicates usually result (Dorschner et al. 1995). Slower cooling allows some crystals to grow. Crystals can be achieved, for example, by immersing the sample container in a larger volume of liquid in a dewar, or by wrapping it in thermal insulating material. A variation of the simple cooling method uses thermal convection. Where applicable, it can be used to cool from a high-temperature melt to room temperature, or from a room-temperature liquid to a lower temperature. The latter is a specialized technique, usually carried out in situ on a diffractometer, with monitoring of the crystal growth by optical and X-ray methods; the sample is contained in a sealed capillary tube, and selective heating may be applied by an infra-red laser to develop a single crystal. A more complete discussion of these topics can be found in (Byrne 1965).

Sol-gel reactions were developed in the 1950s as a method to synthesize pure silicate mineral grains such as forsterite or clinopyroxene. These techniques begin with sodium metasilicate or sodium orthosilicate, both of which are highly soluble in water. Adding magnesium chloride or iron (ii) chloride to such a solution forms precipitates such as magnesium metasilicate or iron-orthosilicate gels, respectively. Freeze drying such gels yields amorphous powders that can be annealed to form fine-grained crystalline materials. Whereas making magnesium silicate grains is relatively easy, iron-bearing silicates are very sensitive to oxidation, requiring careful handling to prevent the formation of Fe(III) during the freeze drying. The major difference between grains produced via the sol-gel technique and vapor phase condensation is that sol-gel grains contain fully-oxidized SiO_4^{-4} or $(\text{SiO}_3^{-2})_n$ struc-

tural units whereas many vapor phase condensates form from SiO molecules and contain both under-oxidized metal and silicon atoms. Thompson et al. (2003) used the sol-gel technique to produce starting materials for a series of detailed thermal annealing experiments using x-ray diffraction to follow the changes in structure from amorphous grains to crystalline minerals (Thompson & Tang 2001).

Synthesis in laboratory of large crystal minerals is often used not only to produce dust by grinding methods, but also to measure their optical constants in wide spectral range (from UV to far-infrared). The Czochralski technique is mainly used to prepare large single crystals of silicon, which are subsequently sliced into wafers for use in electronic devices. Single crystals up to a few inches in diameter may be prepared from a melt by this technique, which involves contacting the melt with a seed crystal under an inert atmosphere and controlled conditions of temperature and withdrawal of the crystal from the melt. This technique has also been used to prepare in the laboratory highly pure synthetic crystals of forsterite and enstatite (Takei & Kobayashi 1974). The sizes of the bulk silicate crystals range from a few up to tens of millimeters.

Silicate crystals may also be prepared by a floating-zone technique (e.g. as can metals of high melting point, Takei 1978). A pure polycrystalline rod is gripped at the top and bottom in water-cooled grips and rotated in an inert gas or vacuum. A small melt zone, produced by either a water-cooled radio-frequency coil or by electron bombardment from a circular filament, is passed up its length. High purity is possible because the specimen has no contact with any source of contamination and also because there is a zone-refining action. Methods involving grain growth in the solid state depend upon the annealing of deformed samples. In the strain-anneal technique, a fine-grained polycrystalline metal is critically strained, approximately 1-2% elongation in tension, and then annealed in a moving gradient furnace with a peak temperature set below the melting point or transformation temperature. Light straining produces very few nuclei for crystallization; during annealing, one favored nucleus grows more rapidly than the other potential nuclei, which the growing crystal consumes.

5.3 Characterization techniques

5.3.1 Spectroscopy

Spectroscopic measurement is a particularly favored analytical technique because spectra can be compared in a direct way to interpret the chemical and mineralogical composition of dust in various astronomical environments.

Depending upon the different spectral regions under analysis and depending on the optical properties of the material, one must use different techniques. In regions of strong absorption, such as in the phonon band range (mid-IR) or the ultraviolet, direct absorption measurements require very low column densities of material, which can only be achieved with thin films or diluted powder samples.

The resolution of the spectroscopic technique applied should be comparable to the resolution of the astrophysical observations, since artificial degradation of high spectroscopic resolution datasets are somewhat model dependent. However, higher resolution data is also useful in that future missions could be designed to specifically discriminate between alternative materials whose high resolution spectra are distinct, but whose lower resolution spectra are virtually identical. This is a common problem for many silicate minerals and is also the case for some carbonaceous grains. It is always useful to cover as wide a range in wavelength as possible for each analog material characterized.

Although the emission spectra of some analog silicate grains have been published (Lynch et al. 1989) the most typical form of such data is the transmission or absorption spectrum of the analog grains embedded in KBr, CsI, polyethylene or other materials. There has been some controversy in the past over the effect of the neutral medium in which the samples are embedded on the detailed spectrum of SiC crystals. However, as a general rule, there has been little controversy over the use of KBr, CsI or polyethylene as embedding materials for silicates or metal oxides. Once samples are embedded in a matrix (or deposited onto a transparent surface such as a window) the spectra are recorded using normal spectroscopic techniques and instrumentation.

Thin films of silicates have been produced by pressing powders in a diamond anvil cell (Hofmeister 1997), by cutting grain samples to sub-micron thick slices with an ultra-microtome (Bradley et al. 1999), by electron-beam evaporation (Djouadi et al. 2005) and by laser deposition in vacuum (Brucato et al. 2004). On one hand, powders produced in a laboratory are directly measured in transmittance when they are embedded in a matrix of transparent materials (e.g. KBr or Polyethylene). On the other hand, reflectance measurements do not require the use of matrices; powders of selected size grains are directly measured with an appropriate optical accessory. Through measurements in both transmittance and reflectance, it is possible to evaluate the optical constants of a material. These are certainly the physical parameters that best describe the nature of the interactions between electromagnetic waves and matter. In astronomical applications it

is a very demanding task to construct models that use spectra and/or optical constants obtained in appropriate geometries. Even if this procedure is not straightforward, theoretical models such as those by Hapke (1993) or Shkuratov et al. (1999) have achieved a satisfactory degree of confidence and are widely used for astronomical spectral interpretations.

Raman spectroscopy can provide valuable information on the chemical species present in a sample and can probe the structural properties of materials; in particular, the structure of carbonaceous materials. Carbonaceous materials can vary widely in chemical composition and structure (diamond, graphite, glassy carbon, hydrogenated amorphous carbon, etc.). Depending on the degree of order of graphitic (sp^2 hybridization) materials, one or two first-order Raman bands are observed. According to the momentum conservation selection rule, the first-order Raman band at about 1582 cm^{-1} is known as the G (Graphitic) line (Tuinstra & Koenig 1970). Spectra of micro-crystalline graphite and disordered carbon show an additional band at 1360 cm^{-1} . This D (Disordered) line is attributed to phonons active in small crystallites or on the boundaries of larger crystallites (Fig. 5.1). In amorphous carbon and hydrogenated amorphous carbon, both G and D bands are present. These bands are quite a bit broader than those observed in disordered graphite: the broader the bands, the more disordered the amorphous carbon is. In amorphous carbon obtained by sputtering and deposition, the two bands cannot be distinguished; the G line is usually found at lower Raman shifts (1560 cm^{-1}) and the D line becomes a shoulder of the G line. The widths of the G and D bands are related to the bond angle disorder and to the relative fraction of crystallites versus the amorphous matrix. Annealing experiments carried out on very disordered hydrogenated amorphous carbon films have indeed shown that the I_D/I_G line intensity ratio vs. the annealing temperature initially increases, then develops a maximum at some temperature between 800 and 900 °C, and finally decreases down to zero at high annealing temperature when graphitisation occurs (Dillon et al. 1984). Under the hypothesis that annealing induces a monotonic increase in the average size of the sp^2 cluster, the initial increase of the I_D/I_G ratio can be interpreted as evidence that the sp^2 clusters grow in size and/or in number. When effects of momentum conservation become important (momentum is conserved in large crystals), the I_D/I_G ratio starts to decrease. A similar evolution of I_D/I_G has been observed during annealing of hydrogenated amorphous carbon grains (Baratta et al. 2004; Dartois et al. 2005).

In situ Raman spectra of amorphous carbon grains irradiated with 3 keV He ions at different fluences are reported in Fig. 5.1 The amorphous carbon grains have been produced by arc discharge between two amorphous car-

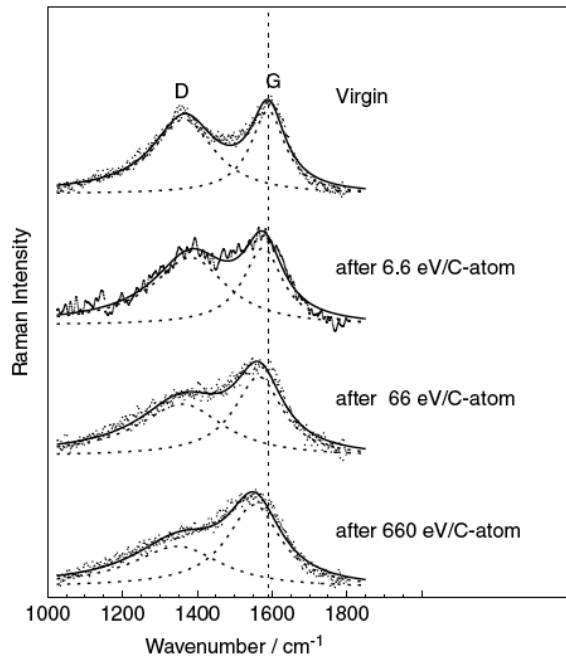


Fig. 5.1. Raman spectra of amorphous carbon grains produced by arc discharge and deposited on an LiF substrate before and after irradiation at different fluences with 3 keV He^+ ions. The continuous lines are theoretical fits to the data given by the sum of two line profiles (dashed lines) representing the G and D lines (Baratta et al. 2004).

bon electrodes in an inert argon atmosphere. TEM studies show that they are made up of spheroids with average radii of 5 nm arranged in a fluffy structure. Infrared spectroscopy has shown that amorphous carbon grains contain hydrogen (CH_3 and CH_2 , $\text{H}/\text{C} \sim 4\%$) and a small amount of oxygen (CO , $\text{O}/\text{C} \leq 0.5\%$). The decrease in the I_D/I_G line intensity ratio versus the ion fluence is due to progressive disorder induced by ion irradiation (Baratta et al. 2004).

5.3.2 *Electron microscopy*

Most primary condensates are extremely small, ranging from 5 nm to 50 nm in diameter. Adequate characterization of such grains must rely on very high spatial resolution techniques such as transmission electron microscopy (TEM) or analytical electron microscopy (AEM). In the former technique, the emphasis is on obtaining very clear pictures of the morphology, homogeneity, elemental and mineralogical composition, shape, size and degree of

coagulation of the grains at nearly atomic level resolution. The method allows for the direct imaging of the sample by which one is able to distinguish between amorphous, partly amorphous, and crystalline (mono- or poly-crystalline) phases. TEM observations of carbon soot samples reveal the presence of complex mixed structures such as amorphous grains organized in chain-like aggregates, minor amounts of poorly graphitized carbon and graphitic carbon ribbons, multi-walled onions and fullerenes (Rotundi et al. 2006).

In the AEM technique, the emphasis is on obtaining chemical and/or structural information at the highest spatial resolution possible. Electron diffraction is used to determine the crystal structure of grains under the beam, and X-ray fluorescence to obtain their composition. However, AEM strives to analyze each separate grain independent from interference from any other. This can be especially difficult for small grains in epoxy mounts where the mount thickness could allow grains to lie below one another and the electron beam can produce signal from any particle in its path. Eliminating such interferences can be extremely important in understanding the properties of the samples. An example of this will be discussed below. Scanning electron microscopy (SEM) is a much lower spatial resolution technique than TEM or AEM and is generally suitable either for determination of the properties of large grains (micron-scale) or to determine the average chemical and structural composition of large aggregates of very small grains. SEM is also a useful preliminary technique to characterize the properties of samples and to select portions of samples for characterization by TEM or AEM as necessary, or to characterize the success of specific sample preparation techniques. We have found SEM to be very useful in determining the average chemical composition of specific experimental runs producing gram level quantities of 10 to 20 nm scale grains. SEM shows that synthetic samples produced by vapor condensation have a very fluffy chain-like texture, formed by grains with spheroidal shapes. The size distributions of the condensed grains for a variety of chemical compositions (olivine, pyroxene and SiC) follow a log-normal law, with a tail at sizes larger than the mean grain size, which is of the order of few tens of nanometers. This tail consists of both single grains that have grown faster than most as well as of grains that have first coagulated then fused (or partially fused) into single particles. While the condensed carbon-based samples synthesized by the arc discharge technique form a complex mixture of solid carbon phases, the analogues produced at the same pressure and atmospheric composition using laser ablation consist only of carbon with a chain-like texture. This confirms that chain-like carbon is the only texture strictly related to the

condensation process and that it is not affected by auto-annealing (Rotundi et al. 1998, 2002).

5.4 Dust processing

5.4.1 *Thermal annealing*

If grains condense in a stellar outflow they should also be annealed to some extent since they remain in close proximity to the star and can be heated directly by absorption of energetic stellar photons or by contact with the hot gas. While tiny grains (nanometer scale) can be heated to quite high temperatures for short times (tens of seconds) by single UV photons, the effect on larger grains will be modest, heating them to temperatures just above the ambient gas kinetic temperature. However, even modest heating can have an effect on the structure of newly condensed grains. Laboratory studies of the annealing process have been carried out by several research groups, most commonly by placing samples of freshly condensed grain materials into a furnace under vacuum for carefully controlled times at specific temperatures. Although quantitative measurement of specific changes in the grains as a function of annealing time and temperature can be tricky, several different techniques have been used for such studies ranging from Fourier-transform infrared (FTIR) spectroscopy to X-ray diffraction, to simply imaging the grains as they annealed on a hot stage in a transmission electron microscope.

Hallenbeck et al. (1998) carried out a study of the spectral changes that occurred during the thermal annealing of amorphous magnesium silicate smokes (condensates) over a relatively narrow temperature range ($1,026 \text{ K} \leq T \leq 1,053 \text{ K}$) and obtained two interesting results. First, they observed a continuous change in the spectral properties of the grains as a function of annealing time up to a point that they identified as the stall (see Figure 5.2). When the stall was reached, the spectral properties of the grains stopped changing for a period of time on the order of the total time that the grains had been annealed to that point. After this hiatus, the grains again began to exhibit roughly continuous changes in their spectral properties until they became crystalline. The stall spectrum is seen in Figure 5.2 at 10.5 and 48 hours and is quite different from the 9.7 micron astronomical silicate feature seen in the interstellar medium: it is both broader and has peaks at 9.8 microns and at 10.8 - 11 microns. The stall spectrum is very similar to that of the crystalline olivine observed in Comets P/Halley (Bregman et al. 1987; Campins & Ryan 1989), Bradfield 1987 XXIX (Hanner et al. 1990), Levy 1990 XX (Lynch et al. 1992), Mueller 1993a (Hanner et al. 1994a). An

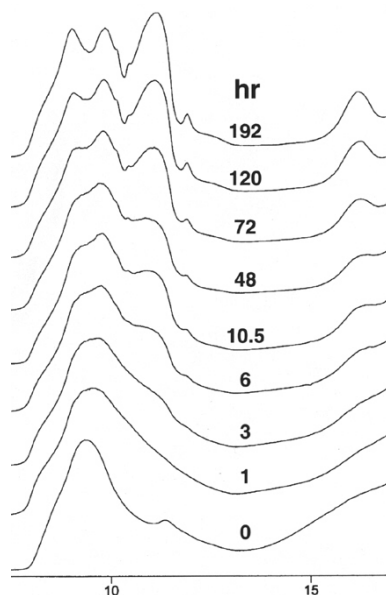


Fig. 5.2. Infrared spectra from 8-15 μm of magnesium silicate smoke samples annealed in vacuum at 1027 K. Spectra of grains annealed for ~ 10.5 hours are mainly identical to those annealed for up to 48 hours (Hallenbeck et al. 1998). These represent the “Stall” spectrum.

excellent review of the 8 to 13 micron region of cometary spectra is provided by Hanner et al. (1994b) and is also discussed in Chapters 6 and 8.

Thompson and Tang (2001) started with amorphous magnesium silicate samples made by the sol-gel technique and used very high resolution x-ray diffraction to study the change in silicate structure as a function of annealing time and temperature. They confirmed the presence of the stall in their samples which is interesting because sol gel samples are more highly ordered than are condensates. While grains prepared via the sol-gel technique begin with each silicon atom fully coordinated by 4 oxygen atoms (using Na orthosilicate as the starting material), condensates begin with many unsaturated silicon atoms as condensation begins with SiO molecules as well as atomic Mg or Fe (See Figure 5.3). Confirmation of a stall in sol-gel produced grains proved that this phenomenon was not the result of some chemical rearrangement of the silicon oxidation state, but must have some other cause such as the formation of small polycrystalline regions.

Kaito et al. (2003) performed a very simple, yet elegant experiment. They placed amorphous magnesium silicate condensates onto a heated stage in a transmission electron microscope and recorded the changes in the physical

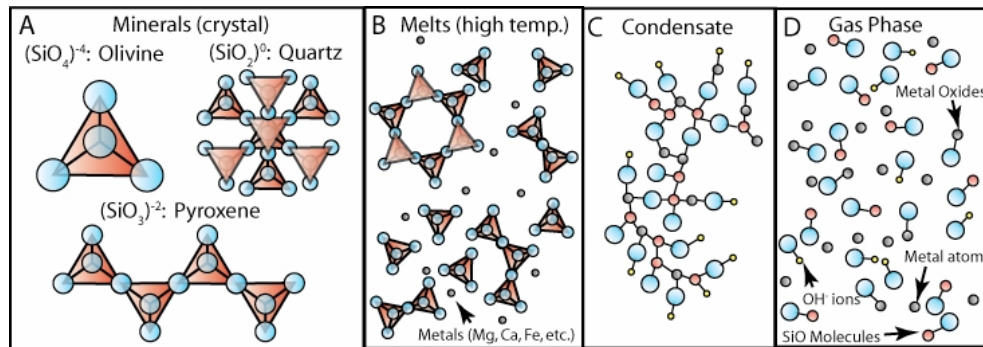


Fig. 5.3. The amount of order in silicates can vary dramatically. A. The crystalline backbone structures for olivine, pyroxene and quartz. The charge of the silicon tetrahedra is neutralized by metal cations in olivine and pyroxene. B. Silicate melts contain a mix of unaligned crystalline structures with metal cations randomly distributed in the melt. C. Chaotic condensates have not formed silicate tetrahedra; rather, they appear more like a frozen gas state. These materials are typically under-oxygenated and contain more metals than a glass. Annealing supplies the chaotic silicate with the energy needed to rearrange into the more stable silicate tetrahedra. D. The gas phase largely consists of SiO. Metals are typically present as atoms or simple monoxides while excess oxygen can be found as OH (Nuth et al. 2002)

structure of the grain as a function of temperature and time. They found that the initial stage of annealing produced a layer of polycrystalline material on the grain surface. The polycrystalline layer completely covered the surface at a time commensurate with the beginning of the stall. During the stall phase, no crystals were observed in the interiors of the grains, though the tiny crystals on the grain surfaces were growing due to a process called Ostwald ripening where smaller grains lose mass to larger ones powered by an overall reduction in the surface energy of the system that results in an overall increase in the size of the crystals (Ostwald 1896). At the end of the stall phase the crystallization began to penetrate to the centers of the grains and the average size of the crystals in the interiors began to increase. Based on these studies, we can conclude that grains in comets and protoplanetary disks exhibiting a stall spectrum probably consist of an amorphous magnesium silicate core covered by a polycrystalline crust. Further annealing will slowly reduce the number of individual crystals, increasing their average size, until a single crystal is eventually produced.

Hallenbeck et al. (2000) used the spectral changes they had measured for thermally annealed amorphous magnesium silicate grains to construct a Silicate Evolution Index (SEI) that can be used to calculate the spectral

properties of such materials based on an assumed thermal history. As an example, if a model predicted that a grain condensed at a particular temperature in an outflow and the grains remained in the gas as it flowed outward and cooled, then the final spectrum of the grains could be predicted by first calculating the SEI, then matching this to the appropriate standard spectrum. Harker & Desch (2002) used the SEI to demonstrate that small grains heated by strong shocks in the primitive solar nebula could be annealed to crystallinity on very short timescales out to nebular distances of about 10 to 12 AU.

5.4.2 *Ion irradiation*

Stars belonging to the asymptotic branch (AGB, Gehrz et al. 1989) and supernovae (SNe, Jones et al. 1996) are considered the principal sites of cosmic dust formation and, once formed, particles are injected into the interstellar medium (ISM) by expanding stellar winds. AGB stars are considered to be ubiquitous in our Galaxy (Habing 1996) and they account for 50% of the total stellar mass-loss. Crystalline silicates are observed in the outflows around high mass loss rate AGB stars (see Chapter 2). It was estimated that AGB stars could inject about 10–20% of the observed crystalline silicates into the ISM (Suh 2002). Contrary to what might be expected, spectroscopic analysis showed that an upper limit of only a few percent of crystals are present in the dense and the diffuse ISM (Li & Draine 2001; Demyk et al. 1999). Selective destruction, low production rates or interstellar dust dilution mechanisms have been suggested to justify the absence or non-observation of crystalline silicates in the ISM (about 2.2% of crystalline silicates was estimated as the upper limit present in the ISM by Kemper et al. 2005).

An efficient way to produce amorphous grains from crystalline silicates is ion irradiation by energetic particles. Laboratory irradiation experiments on natural silicates were first performed by Day (1977). Protons with an energy of 1.5 MeV and fluences similar to those expected for cosmic rays were used in his laboratory. Day did not find evidence of structural modifications for crystalline forsterite, but the spectrum changed dramatically, most likely due to changes in the structure of the surface layers of the crystal. More recently, low energy (4–400 keV) ions (H, He, C, Ar) at similar fluences were used in experiments that demonstrated that the ion irradiation of crystalline silicates rather efficiently leads to their amorphization (Demyk et al. 2001; Carrez et al. 2002; Jäger et al. 2003, Brucato et al. 2004, Demyk et al. 2004, Davoisne et al. 2008). Further laboratory experiments have shown that single-crystal synthetic forsterite (Mg_2SiO_4) is amorphized when irradiated

by heavy ions at high energy (10 MeV Xe ions) and at sufficiently high fluences (10^{13} ions cm^{-2} , Bringa et al. 2007). This process thus explains the absence of crystalline silicates in the ISM and it argues that the crystal-to-amorphous transition is affected significantly by various physical parameters of the impinging ions, as e.g. the mass, charge and the kinetic energy.

5.5 Grain growth studies

5.5.1 *Efficiency of crystalline grain growth in stars*

The interstellar grain population is overwhelmingly amorphous; no evidence for the presence of crystalline materials has ever been detected (Kemper et al. 2005). Some primitive meteorites contain grains that unambiguously formed prior to the formation of the Solar System in astrophysical environments such as the stellar winds from dying stars, in novae and even in supernovae (see Chapter 2). Interestingly enough, the largest species of pre-solar material consists of crystalline graphite and SiC grains that can range up to 25 microns in diameter. In addition, corundum (Al_2O_3) and spinel (MgAl_2O_4) crystals, formed in oxygen-rich systems are also present, though these grains are generally smaller in size (~ 1 micron or so in diameter). These materials are presumably present in the interstellar medium as well, but are too rare to detect. A more intriguing question is, however, how did such large crystalline grains ever form?

Bernatowicz et al. (1996) and Sharp & Wasserburg (1995) both demonstrated that large graphite grains probably formed under near-equilibrium conditions in the atmospheres of low-mass AGB stars. Both studies calculated that, even if every appropriate atom that struck the growing grain actually stuck to its surface and became incorporated into the growing crystal, the largest graphite crystals would still require nearly a full year to reach their observed diameters. A new study on the efficiency of crystalline grain growth from a metallic vapor (Michael et al. 2003) has shown that only a few atoms of every 10^5 that strike a growing crystalline surface from the ambient gas phase will actually become incorporated into the crystal. Taken together, these studies imply that the growth of large graphite and SiC crystals, and of the smaller corundum and spinel crystals must have occurred under near-equilibrium conditions that persisted for at least many years, if not for hundreds of thousands of years. The next big question is, “How does a growing grain stay suspended under near-equilibrium conditions in a stellar atmosphere for such long times?”

Nuth et al. (2006) showed that for particle sizes ranging from a few hundred Ångströms up to several tens of microns in diameter the force exerted

by radiation pressure in some red giant and AGB stars exceeds the force of gravity and thus offers the potential for graphite, SiC, corundum and spinel grains to grow to the size range observed in primitive meteorites (e.g., up to ~ 25 microns). In the highest-mass AGB stars radiation pressure on growing grains greatly exceeds the force of gravity and thus ejects a grain from the star before it can grow larger than a few tens of nanometers. Only in very low mass AGB stars (less than 3 solar masses) does the radiative force balance the gravitational force to such a fine degree that the net acceleration on individual particles ranging from a few nanometers up to about 25 microns produces particle velocities that are comparable to atmospheric turbulence. Their analysis shows that the large graphite, SiC, corundum and spinel crystals found in primitive meteorites can only have formed in atmospheres of the lowest-mass red giant and AGB stars, where particle growth is able to occur on timescales of a hundred thousand years under near equilibrium conditions. We note that this suggestion is contrary to the standard assumption that grains can only form in stellar winds and implies that there is a class of grains that can form in chemical equilibrium deep within a stellar atmosphere, just above the photosphere.

5.5.2 Metastable eutectic condensation and magnesium-rich minerals in astrophysics

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. 1999); Mg-Fe-SiO condensates (Rietmeijer et al. 1999); Mg-SiO condensates (Nuth et al. 2002), annealed Mg-SiO condensates (Rietmeijer et al. 2002); Al₂O₃-SiO₂ condensates (Rietmeijer & Karner 1999), and Al₂O₃-Fe₃O₄-SiO₂ vapors (Rietmeijer et al. 2008). 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 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 condensable 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. Elemental analyses of individual grains condensed from Mg-SiO vapors clustered around five distinct compositions: pure SiO_x (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 (Nuth et al. 2002). In a similar fashion, analyses of Fe-SiO condensates also found con-

densate compositions clustered at the pure oxide (FeO_y , SiO_x) end members and at intermediate compositions including the greenalite ($\text{Fe}_3\text{Si}_2\text{O}_7$) and Fe-saponite ($\text{Fe}_3\text{Si}_4\text{O}_{11}$) dehydroxylate compositions, and a distinct clustering at a low-Fe ferrosilica composition (Rietmeijer et al. 1999). For a more detailed discussion of metastable eutectics see Rietmeijer & Nuth (2000).

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 section, below we offer a few words on metastable eutectic solids using the MgO-SiO₂ phase diagram (Ehlers, 1972) as an example. If condensation had proceeded at thermodynamic equilibrium, the compositions of the condensed Mg-SiO solids would have been (1) MgO = 2 wt % and SiO₂ = 98 wt % at 1,986 K, (2) MgO = 36 wt % and SiO₂ = 64 wt % at 1,816 K, and (3) MgO = 63 wt % and SiO₂ = 37 wt % at 2,123 K. These compositions are at the three stable eutectics in this phase diagram. But, that is not what was found when the compositions of the individual Mg-SiO grains that condensed from the Mg-SiO-H₂-O₂ vapor were analyzed (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. (2002) 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 & 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. From an astrophysical perspective, a more interesting system is what was observed following the condensation of Fe-Mg-SiO vapor.

Figure 5.4 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 condensable 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

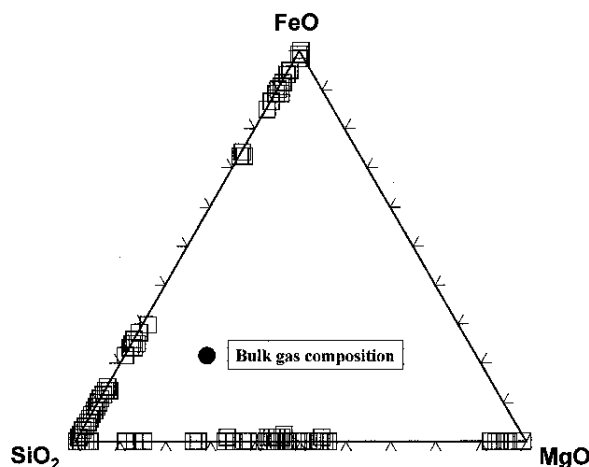


Fig. 5.4. Ternary diagram showing the composition of individual 10-20 nm grains condensed from a mixed Fe–Mg–SiO–H₂–O₂ vapor. The large spot in the interior of the diagram represents the approximate composition of the vapor-phase as measured via SEM analysis of the bulk smoke (modified after Rietmeijer et al. 1999).

grains. The open squares represent the individual grain compositions determined by analytical electron microscopy. Note that these grains roughly cluster at the pure end member compositions (FeO_y, MgO and SiO_x) 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 end member oxides FeO_y, 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) and has interesting consequences when one notes that only pure magnesium silicate minerals have been observed in comets and stellar sources.

Condensation produces separate populations of amorphous iron silicate and magnesium silicate grains. Hallenbeck et al. (1998) demonstrated that

magnesium silicates anneal at the same rate as iron silicates if the iron silicates are approximately 300 K hotter than the magnesium silicates. Nuth & Johnson (2006) thereby argued that shocks could produce both crystalline magnesium and crystalline iron silicates whereas thermal annealing of a mixed small grain population might produce crystalline iron silicates, but would do so on a timescale sufficiently long that all of the grains would evaporate. At temperatures sufficiently high to produce crystalline magnesium silicates while still leaving the iron silicates as amorphous dust, the lifetimes of the grains against evaporation are more than long enough to ensure survival of the bulk of the grain population. They therefore conclude that the crystalline magnesium silicate minerals observed in comets and protostars are the products of thermally annealing a population of pure amorphous magnesium and iron silicate condensates. A similar process would account for the production of crystalline magnesium silicate minerals observed in the winds of high-mass-loss giant branch stars.

5.5.3 Prediction of large scale nebular circulation

Campins & Ryan (1989) 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 2 to 5% of the interstellar silicate grain population could be crystalline, yet still lie below our current limits of detection (Li & Draine 2001; Kemper et al. 2005). As said before, it could equally well be true that any crystalline silicates injected into the interstellar medium become amorphous after long exposure to galactic cosmic rays. Finally, studies on the spectral evolution of silicate grains in protoplanetary disks indicate that the degree of crystallinity is not simply correlated with age (see Chapter

8 for more details). These observations, argue that processes within the protostellar nebula itself are responsible for the production of crystalline silicates.

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. 2000; 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). Earlier models of transport in the solar nebula (Bockelée-Morvan et al. 2002; Boss 2004; Ciesla 2007; Dullemond et al. 2006) actually show that materials readily move both inwards and outwards in the nebula prior to the formation of the giant planets. In contrast to simple thermal annealing, Harker & Desch (2002) have suggested that shock waves in the outer solar nebula could anneal the amorphous silicates to crystalline *in situ* prior to their incorporation into comets, thereby eliminating the need for large-scale nebular transport processes. However, if the Weidenschilling (1997) model for comet formation is correct, most comets began to form at distances much greater than 10 AU from the Sun. Therefore, grains annealed by shocks would still need to be transported out to distances where comets begin to form (as shown in Figure 5.5 in Nuth 2001). This hypothesis, based solely on observations of crystalline magnesium-rich minerals in comets and laboratory studies of their production, was spectacularly confirmed by the Stardust mission to comet Wild 2 (Zolensky et al. 2006). Grains from this comet, which should never have been inside the orbit of Jupiter during its formative stages, contain fragments of calcium aluminum inclusions (CAIs) and chondrules that could only form at the very high temperatures possible in the innermost regions of the solar nebula. If comet Wild 2 was never inside the orbit of Jupiter as it formed, then such materials must have been transported out to the growing comet. As noted below, such large scale circulation can have a major influence on the organic chemistry of protostellar nebulae, including the solar nebula.

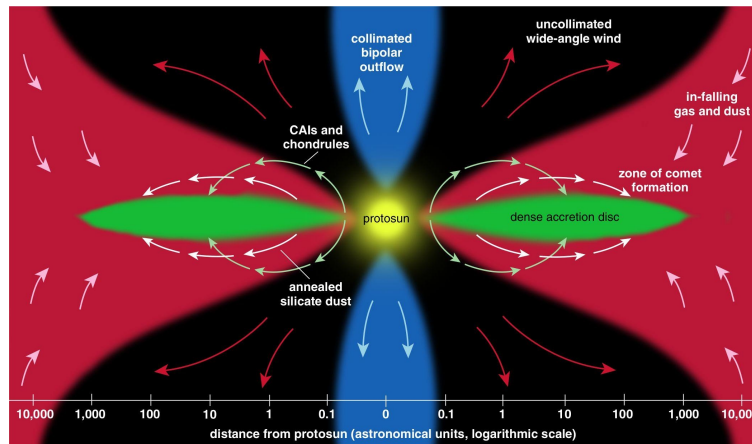


Fig. 5.5. Winds in the solar nebula might be one of the possible processes responsible for the mixing of “hot” and “cold” components found in both meteorites and comets. Meteorites contain calcium–aluminum–rich inclusions (CAIs, formed at about 2,000 K) and chondrules (formed at about 1,650 K), which may have been created near the protosun and then blown (gray arrows) several astronomical units away, into the region of the asteroids between Mars and Jupiter, where they were embedded in a matrix of temperature–sensitive, carbon–based “cold” components. The hot component in comets, tiny grains of annealed silicate dust (olivine) is vaporized at about 1,600 K, suggesting that it never reached the innermost region of the disk before it was transported (white arrows) out beyond the orbit of Pluto, where it was mixed with ices and some unheated silicate dust (“cold” components). Vigorous convection in the accretion disk may have contributed to the transport of many materials and has been dramatically confirmed by the Stardust Mission (Nuth 2001).

5.6 Grain catalysis studies

5.6.1 Amorphous dust grains as catalysts for the reduction of CO and N₂

Llorca & Casanova (2000) demonstrated that Fischer-Tropsch Type (FTT) catalytic reactions (see Fig. 5.6) occur under low pressures typical of the primitive solar nebula, converting CO and H₂ into hydrocarbons. The Haber-Bosch Type (HBT) reaction converts N₂ and H₂ into reduced nitrogen compounds such as NH₃. New experiments were designed to test the relative efficiency of various potential catalytic materials and also to produce mixtures of inorganic solids and organics that could serve as analogs of primitive asteroidal material for later experiments.

Grains in protostellar nebulae are exposed to the ambient gas for hundreds or even tens of thousands of years at pressures ranging from 10⁻³ to 10⁻⁴ atm or less. We do not have such times available for laboratory experiments,

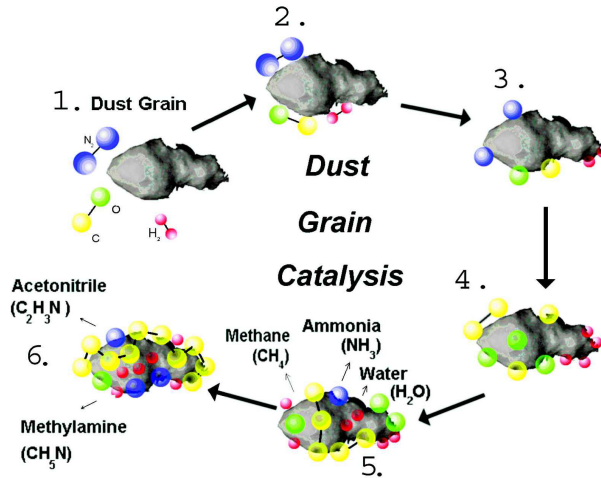


Fig. 5.6. A simplified and somewhat speculative representation of the possible reaction steps on or near the catalytic surface associated with individual and joint FTT and HBT syntheses in a protostellar environment. A possible sequence is as follows: (1) A warm fresh dust grain (e.g., iron silicate) and common nebular gases (H_2 , CO , N_2) exist, 0.1–1 AU from a protostar. (2) One or more of the gases are adsorbed onto the grain surfaces. (3) Molecules dissociate on the surface of the catalyst. (4) Increasingly longer carbon chains and other reactive atoms accumulate on the grain surface. (5) Organic products (CH_4 , etc.), H_2O , and NH_3 form on the grain surface and are released into the nebula. (6) As the grains become increasingly covered with organic products and NH_3 , a new suite of reactions are initiated, resulting in the synthesis of CN-bonded molecules [e.g., methylamine (CH_3NH_2) and acetonitrile (CH_3CN)]. Like the other (FTT and HBT) synthesis products, they too are released into the nebular environment (Hill and Nuth, 2003).

although we can reproduce the total number of collisions a grain might experience with components of the ambient gas by running experiments for shorter times at higher pressures. In the laboratory, experiments last from about 3 days at temperatures of 873 K to more than a month at 573 K. If an average experiment lasts a week (6×10^5 s), and if the only consideration for simulating the effects of the reaction is the total number of collisions of potential reactants with the catalytic surface, then one can simulate two centuries (6×10^9 s) of exposure to an ambient gas at 10^{-4} atm by running experiments at ~ 1 atm total pressure. This scaling assumes that the reactants strongly bind to the surface of the catalyst and that this is the rate-controlling step. CO and N_2 must be strongly bound in order to weaken their bonds and thus increase their rates of reaction with H_2 ; Kress & Tielens (2001) deduced that this is the rate-controlling step. If the rate-controlling step is the reaction of H_2 with the CO or N_2 bound on the

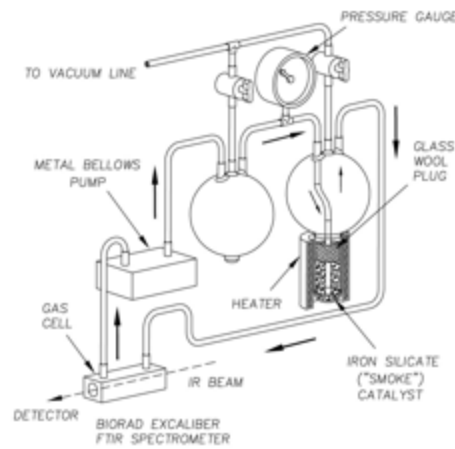


Fig. 5.7. Three-dimensional drawing of the experimental system used to assess the catalytic properties of the amorphous iron silicate smokes. The (smoke) catalyst is contained in the bottom of a quartz finger (attached to a 2-L Pyrex bulb) that can be heated to a controlled temperature. A Pyrex tube brings reactive gas to the bottom of the finger. The gas then passes through the catalyst into the upper reservoir of the bulb and flows through a copper tube at room temperature to a glass-walled observation cell (with ZnSe windows) in an FTIR spectrometer. From there, a closed-cycle metal bellows pump returns the sample via a second 2-L bulb and the Pyrex tube to the bottom of the catalyst finger to start the cycle over again (Hill and Nuth, 2003).

grain surface, then the important consideration is the number of collisions of H_2 with the CO or N_2 bound on the catalyst, rather than the number of collisions of CO or N_2 with the catalyst, and reaction time can once again be scaled to the number of collisions.

The experiments themselves were also very simple; see Fig. 5.7 (Hill & Nuth 2003). As the experiment proceeds they monitored progress by using periodic FTIR spectra to follow the loss of CO and the formation of methane, water, and carbon dioxide. They also monitored smaller spectral features due to ammonia and N-methyl methylene imine. Once the CO has been reduced to about 10 % of its starting concentration they took a final infrared spectrum, turned off the heater, cooled the system to room temperature, evacuated it to less than ~ 0.1 torr, then refilled the system with fresh gas and began a second run. Note, that they did not use a fresh batch of catalyst for this second run as they wanted to follow the changing properties of the catalyst as a function of exposure to the gas mixture and as a function of temperature. By making 15 runs with the same catalyst, they simulated

$\sim 3,000$ years of exposure of grains to nebular gas and built up a substantial coating of macro-molecular carbon, nitrogen, and hydrogen.

For a typical, textbook catalyst, the results of these experiments were counterintuitive (Nuth et al. 2008). With each additional run, the catalyst forms slightly larger clumps, thus reducing surface area. The active metal atoms at the surface become more oxidized due to reaction with water generated by the FTT reaction. Some reactive sites on the catalyst become coated by the macromolecular carbon generated in previous runs and some catalyst simply is lost to the system. Each of these factors should slow reaction rates in subsequent experimental runs, yet they observed an increased rate of reaction after the first few runs, followed by a steady rate of reaction thereafter. One model can explain all of these observations, including the large mass fraction of carbon and nitrogen deposited onto the grains after about 20 runs; namely, the macromolecular carbonaceous coating produced on the grains via these reactions is a better FTT and HBT catalyst than the inorganic sites it covers. Furthermore, these experiments seem to indicate that this same organic catalyst has formed on every inorganic surface tested, though at different rates. In other words, every solid surface in a protostellar nebula could grow this material as a natural consequence of the exposure of grain surfaces to CO, N₂ and H₂, three of the most abundant molecules in the universe. This hypothesis has several interesting consequences for the production of organic molecules via FTT and HBT reactions in protostellar nebulae, especially when combined with large-scale nebular circulation. The combination of a self-perpetuating catalyst that forms naturally on any grain surface, together with widespread outward transport of materials formed in the hot, dense inner regions of protostellar nebulae, makes these nebulae gigantic organic chemical factories that turn abundant CO, N₂ and H₂ into complex hydrocarbons and seed organic material throughout the nebula. If circumstances that favor the chemical evolution of simple organisms can occur in planetesimals formed from such materials, then primitive organisms might take advantage of this natural bounty.

5.6.2 Catalytic effects of dust on synthesis of bio-molecules

Silicates could have played an important role in driving the formation of complex molecular compounds relevant for prebiotic chemistry. Due to the low efficiency of formation of complex molecules in the gas phase, in fact, it is not feasible for an active gas-phase chemistry to take place at low temperatures with condensate molecules strictly in contact with dust (Gould & Salpeter 1963; Allen & Robinson 1977; Tielens & Hagen 1982). Labora-

tory experiments have shown that different chemical-physical mechanisms might be responsible for the richness of molecules observed in space. Surface catalysis at low temperatures by dust is considered necessary to justify the presence of, e.g., H₂, H₂O or CO₂, as demonstrated experimentally (Vidali et al. 2005; Perets et al. 2007) according to the Langmuir-Hinshelwood mechanism (Langmuir 1918). However, to describe the presence of more complex molecules, such as CH₃OH, or radicals and even organic refractory material, irradiation processes due to ions and UV photons are required (Moore & Hudson 1998; Greenberg et al. 1999; Strazzulla & Johnson 1991; Brucato et al. 2006b). Therefore, chemical compounds synthesized in the presence of dust grains may become even more complex in high-energy environments or if such materials are combined with fluids such as might exist in the interior of a carbon-rich asteroid.

It was estimated that between 10⁷ and 10⁹ kg yr⁻¹ of carbon contained in organic compounds was delivered to the Earth in the first billion years as interplanetary dust particles (IDPs) (Chyba & Sagan 1992). Carbonaceous chondrites, some of the most primitive objects of the Solar System, may contain up to 3% of organic matter and their possible role as sources of organic prebiotic material on Earth has been long emphasized. A minor part (10-30%) of the organic matter in the carbonaceous chondrites is made of a complex mixture of soluble molecules, some of which are similar to those found in biochemical systems. More than 70 different amino acids were identified in the Murchison meteorite with a total concentration of approximately 60 parts per million (Cronin et al. 1988; Martins et al. 2008). Nucleobases were also identified in the Murchison, Murray and Orgueil meteorites at a level of several hundred parts per billion, only guanine could be identified in a set of Antarctic meteorites (Botta et al. 2002).

The stable isotopes of C and N in this organic matter suggest an origin in the interstellar medium (Alexander et al. 1998; Busemann et al. 2006), but significant processing could have occurred in the solar nebula and in meteorite parent bodies. Although aqueous alteration in many parent bodies involved relatively oxidizing conditions and thus led to loss of organic material (e.g., conversion to CO₂ and carbonates, Naraoka et al. 2004), a few meteorites, particularly CM meteorites like Murchison, seemed to have been altered by reducing fluids (Browning & Bourcier 1998). Moreover, Shock & Schulte (1990) made thermodynamic arguments for amino acid synthesis by aqueous alteration of polycyclic aromatic hydrocarbons (PAHs), a common organic species in the interstellar medium and primitive meteorites, and via Strecker synthesis by reaction of ketones or aldehydes with HCN and NH₃ (Schulte & Shock 1992).

Synthesis of organic molecules occurring in space have been performed in laboratory following different strategies. Mainly simple nitrogen-bearing compounds such as hydrogen cyanide (HCN), isocyanic acid (HNCO), formamide (NH₂COH), ammonium cyanide (NH₄CN), or mixtures of H₂O, CO₂, CO, NH₃, CH₄, CH₂O, CH₃OH, etc. (Grim & Greenberg 1987; Demyk et al. 1998; Moore & Hudson 2003; Hudson et al. 2001; Palumbo et al. 2000, 2004; Brucato et al. 2006b,a) have been considered as potential astrobiological precursors. However, since carbonaceous chondrite meteorites have been shown to contain up to a few weight percent of water (Weidenschilling 1981) highly porous and permeable, water-rich parent asteroids would have been sites of hydrothermal circulation during their history. Water in the interior of asteroids would be liquified and mobilized by the heat from decaying ²⁶Al and ⁶⁰Fe, at least in the early Solar System. Additional internal heat would also be provided by serpentinization (Jewitt 2004) and possibly by impacts. With these physical conditions a rich chemistry might occur inside meteorite parent bodies, which is mainly driven by the catalytic effects of dust, temperature and by previous exposure of such material to UV photons and irradiation by energetic ions.

Prebiotic reactions have thus been studied in the laboratory in conditions simulating the environments found on the early Earth and in space. Silicate cosmic dust analogues were used as catalysts, in particular olivine (Mg,Fe)₂SiO₄. This is because olivine is continuously confirmed by observations to be ubiquitous in space. The chemistry studied was that of formamide (NH₂COH). This very simple molecule, containing only one carbon atom, was observed to be present in different space environments, as gas in the interstellar medium (Millar 2004) or in the long period comet Hale–Bopp (Bockelée-Morvan et al. 2000) and, tentatively, in the solid phase on grains around the young stellar object W33A (Schutte et al. 1999). Formamide is confirmed to be a promising route to understand the first chemical steps that brought simple C-bearing molecules towards largely complex mixtures of bio-macro-molecules. A large suite of pyrimidines (including cytosine and uracil) and purines have in fact been synthesized at 430 K using only formamide in the presence of cosmic dust analogue silicates with an efficiency an order of magnitude larger than for terrestrial olivine but, also with chemical specificity dependent on the fraction of metal (Mg and Fe) present inside the mineral structure (Saladino et al. 2005). Another important aspect is to stabilize the biomolecules against the degradation effects that strongly limit their lifetime. Cosmic dust analogue olivine has shown a high protective factor against degradation of polynucleotides, having a dual effect: to synthesize and protect biomolecules at the same time (Saladino et al. 2005).

The formation in space environments of solid formamide on grain surfaces was theoretically calculated starting with the reaction of CO with H. The resulting radical HCO reacts with atomic O, N and C and ultimately leads to formation of NH₂COH. Grain surface chemistry calculations predict abundances of the order of 1% for a wide range of space environmental conditions (Tielens & Hagen 1982) where low energy cosmic rays irradiate grains. In cold dense clouds, ions deposit about 30 eV/molecule in 10⁸ years, which is a factor of 10 less than in the diffuse medium (Moore 1999).

The first results obtained in the laboratory irradiating icy formamide pure and mixed with cosmic dust analogues (CDAs) at 20 K show that the presence of dust grains reduces the overall amount of synthesized species (Brucato et al. 2006b). This could be an effect related to the larger surface area of CDAs exposed to proton irradiation, which might favor a larger ejection of formamide into the gas phase. Olivine CDA acts chemically on the synthesis process of molecular species. In particular, NH₃ and CN⁻ molecules are absent when olivine CDA is present. In the latter case, this could be related to the charge exchange due to the presence of iron and magnesium metals in CDA and to the acid-base reaction of ammonia with HNCO. But CDA olivine also shows a specificity in driving the chemistry in the solid phase under ion irradiation. More important is the case of ammonium cyanate for its considerable theoretical importance in prebiotic chemistry. Thermal annealing of ammonium cyanate in aqueous solution forms urea (NH₂)₂ CO through dissociation into ammonia and isocyanic acid (Warner and Stitt 1933). Urea was also synthesized at 10 K by UV irradiation of isocyanic acid and tentatively detected in a protostellar object (Raunier et al. 2004). As observed by Brucato et al. (2006), ammonium cyanate synthesized by proton irradiation of pure formamide at 20 K is stable up to room temperature. Therefore ammonium cyanate and formamide could have an important linking role between astrophysical and terrestrial environmental conditions. Finally, CDA MgFeSiO₄ is a selective catalyst preventing formation of NH₃ and CN⁻ molecules and changing the relative abundances of NH₄⁺OCN⁻, CO₂, HNCO, and CO. Thus, CDAs significantly influence the chemistry of formation and evolution of ices in space under radiation processing at low temperatures.

5.7 Conclusion

Laboratory production of dust analogues is a highly specialized field that attempts to reproduce a subset of the basic properties of the solids that we expect to exist in a particular astrophysical environment. The synthesis of

dust in the outflows of evolved stars however, is a much more complex process that occurs under non-equilibrium, continuously-changing conditions and with the participation of many more chemical elements than can be accommodated by any practical experimental system. Even under the best of conditions it is difficult to control the rapid nucleation and growth of dust grains that occur in laboratory experiments where parameters such as temperature, pressure and concentration are used to constrain the final characteristics of dust analogues.

Dust also plays an active role in astrophysics, both as a proxy and recorder of conditions that it has experienced, and as a catalyst for chemical reactions in many low density astrophysical environments. Full chemical and structural characterization of the analogue grains serves the dual purpose of ensuring that the experimental conditions used are appropriate and of understanding how the processing conditions affect the properties of the dust. The nature of both natural and synthetic dust is directly related to its prior processing history and can sometimes serve as an indicator of the metamorphic history of the body in which it resided. Furthermore, astrophysical observations require the measurement of accurate optical properties of appropriate materials in the laboratory to ensure reasonable interpretation with respect to chemical composition, structure, temperature and the presence of several types of grains. We are aware that we have not covered all of the laboratory techniques that have been used to study the properties of solids, but we chose instead to focus on those efforts that have been most useful for the interpretation of astrophysical data. We have emphasized systematic studies that concentrate on the formation and evolution of the initial small scale grains that by aggregation and further processing control the properties of comets, asteroids and proto-planets.

Two of the first laboratory astrophysicists to recognize the potential to study chemical processes in space, rather than simply measure the spectral properties of potentially important gases and solids, were Mayo Greenberg and Bertram Donn who began their efforts to understand ices and grains in the late 1950s. They recognized that they should better understand the formation of dust in circumstellar outflows, the chemical reactions in ice coated grain mantles, or the catalytic role of solids in the generation of both simple molecules such as H_2 or the more complex organic materials that might promote the chemical evolution of life, by performing relatively simple experiments to delineate the roles of important variables. These experiments have since become more elaborate and sophisticated, but are still far from duplicating the conditions found in nature. Nevertheless, the results of these experiments have provided extraordinary insights into the way we view the

processes that shape our universe. Continuing increases in our ability to control the conditions in our experiments and to characterize their results should lead to further insight into the observations that flow from a remarkable and growing array of ground and space-based telescopes. Improved observational and laboratory data will lead to more detailed understanding of specific astrophysical phenomena such as the birth and death of stars, chemical processes in the ISM or even the origin of life.

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