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Origin and Evolution of Dust in Circumstellar and Interstellar Environments

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Abstract. Astronomical observations and analysis of stardust isolated from meteorites have revealed a highly diverse interstellar and circumstellar grain inventory, including both amorphous materials and highly crystalline compounds (oxides, silicates and carbonaceous). This dust is highly processed during its sojourn from its birthsite (stellar outflows and supernova explosions) to its incorporation into protoplanetary systems. Of particular importance is processing by cosmic rays in the interstellar medium and by strong shocks due to supernova explosions. The latter is predicted to lead to rapid destruction due to sputtering by impacting gas ions and shattering due to grain-grain collisions.

In recent years, much progress has been made in understanding the origin and evolution of interstellar dust. This is largely driven by new infrared spectroscopic tools becoming available for astronomical studies and ever more elegant laboratory techniques allowing a deeper and deeper probing of stardust isolated from meteorites. In this paper, we address a number of key questions relevant to studies of chondrites in meteorites: "What is the inventory of dust entering the Solar Nebula ?", "What processes played a role in its formation and evolution in the interstellar medium ?", and "What is the evidence for processing of interstellar dust in protoplanetary systems ?".

1. Introduction

The lifecycle of interstellar dust starts with the nucleation and growth of high temperature condensates such as silicates, graphite, and carbides at high densities and temperatures in the ejecta from stars. This ejected material is rapidly mixed with other gas and dust in the interstellar medium (ISM). In the ISM, dust cycles many times between the intercloud and cloud phases on a very fast timescale ($\simeq 3\times10^7$ yr). In the warm neutral and ionized intercloud media, dust is processed by strong shocks driven by supernova explosions. The hot gasses in the shock can sputter atoms from the grains. Also, high velocity collisions among grains can lead to vaporization, melting, phase transformation, and shattering of the projectile and target. In the denser media – diffuse and dense clouds –, gas phase species can accrete onto grains forming a mantle. Coagulation may also play a role in increasing the grain size inside diffuse and dense clouds. If the grain survives the onslaught of interstellar shocks, eventually, during one of these cycles, a grain may find itself in a dense cloud core when this core becomes gravitationally unstable against collapse. The grain may then wind up in the star or in the surrounding planet forming disk. The complete cycle from injection by a star until formation of a new star and any associated planets typically takes some 2×10^9 yr.

Over the last decade, our understanding of interstellar dust has increased with leaps and bounds. On the one hand, new space missions have provided us with access to the infrared universe. In particular, the Infrared Space Observatory, ISO, obtained complete 2.5-200 μm spectra of a multitude of sources. This has provided us with an unparalled view of the dusty universe (Tielens 2001; Waters 2000; Waters et al. 2000). Infrared spectroscopy is the best astronomical tool for studying the composition of dust in space. Based upon extensive laboratory studies, observed spectral features can be readily identified with definite minerals and carbonaceous compounds and the abundance of these species can be derived. As a result of extensive analysis of the wealth of ISO spectra, our understanding of the composition and evolution of interstellar dust has increased manifold. On the other hand, genuine stardust grains have been isolated from meteorites. Analysis of these stardust grains has revealed an isotopic composition which derives directly from the birthsites of these dust grains (Anders & Zinner 1993; Zinner 2003, 1998; Clayton & Nittler 2004). Detailed studies of these stardust grains has opened a new window on the dusty universe, providing new insights in the composition of stardust and the processes that play a role in their formation Bernatowicz et al. (1996). In addition, recent studies have started to explore the impact of interstellar processes on these grains (Bernatowicz et al. 2003).

The Chinese wish for their worst enemy, ‘may you live in interesting times’, seems particularly apt for astronomical dust. Interstellar dust is widely abhorred by astronomers and, indeed, dust in space has a turbulent and eventful life where many energetic processes contribute to its formation and subsequent modification until it eventually succumbs to the continued onslaught of shock destruction or star/planet formation. In this paper, we are concerned with this lifecycle of dust and we will focus on a number of questions, which are relevant for the field of meteoritics. Specifically: “What kind of dust entered the Solar Nebula?”, “What processes played a role in its formation and evolution in the interstellar medium?”, “How do the astronomical and meteoritical records compare?”, and “What is the evidence for processing in protoplanetary systems?”.

2. The Origin and Composition of Interstellar Dust

2.1. Dust Materials

Table 1 summarizes the various compound identified either through IR spectroscopy of circumstellar or interstellar dust or through studies of stardust recovered from meteorites. Each of the entries in this table is a story in itself, but space does not allow a detailed discussion. Instead the interested reader is referred to various reviews (Zinner 2003; Tielens 2001), which summarize these discussions and provide references to the original literature. Astronomical identifications which are particularly ambiguous are labelled with (?) in this table.

The most striking aspect of Table 1 is the diversity of dust compounds observed. Some 20 dust materials are present in the interstellar/circumstellar dust or stardust record. This diversity reflects to a large extent the heterogeneity of stellar sources contributing to the dust in the interstellar medium. Together these stellar sources represent a wide range in physical conditions (temperatures, pressures, elemental abundances) and, concommittant, dust compounds. Asymptotic Giant Branch (AGB) stars and type II supernovae are particularly rich in detected dust compounds.

For AGB stars, the astronomical and meteoritic stardust record are in good agreement in the types of dust present. It should be emphasized that most individual AGB objects only show a very limited number of dust compounds and that the diversity of dust reported in Table 1 refers to AGB stars as a class. In particular, the C-rich dust compounds are generally limited to AGB objects whose photosphere is carbon-rich (e.g., elemental $C/O > 1$), while the oxides and silicates occur generally in oxygen-rich objects (e.g., elemental $C/O < 1$). Some sources with mixed chemistry exist but this is thought to reflect a recent change over from O-rich to C-rich photosphere or storage of previously ejected material in a long-lived circumstellar disk. Finally, there is indirect astronomical evidence for a small amount of mass loss during the red giant branch phase, preceeding the Asymptotic Giant Branch phase. The composition and amount of dust formed in these outflows is unknown. Meteoritic studies suggest that many of the presolar Al_2O_3 grains are formed in red giant ejecta (Nittler et al. 1997).

In contrast to the observed richness of the AGB objects, the astronomical record of type II SNe is virtually non-existing. The best studied, recent supernova, SN 1987A in the Large Magellanic Cloud, showed a featureless mid-IR continuum spectrum, consistent with emission from optically thick clumps (Wooden et al. 1993) in the ejecta. The only other SN bright enough for a detailed study in the mid-IR, Cas A, showed mid-IR emission which seemed to originate from the fast moving, highly enriched knots and a spectrum consistent with amorphous silicates. Hopefully, the Spitzer Space Telescope with its greatly improved spectroscopic sensitivity will provide a good census of the dust production of SNe in the nearby universe. The meteoritic record suggests that dust production by supernovae is highly diverse but whether this reflects a sampling of a large variety of SNe with very different conditions or the large diversity of chemical zones in each SN remains to be seen. There is no direct astronomical or meteoritic stardust evidence for dust formation in the ejecta of SN type Ia (originating from low mass progenitors). However, such SNe may be a dominant source of iron in the interstellar medium. Because Fe is observed to be highly depleted in the ISM, it is likely that this iron is injected in the form of (nickel)iron grains.

Table 1. An inventory of circumstellar dust

material	AGB	post-AGB	PN	Nova	T Tauri	Herbig AeBe	RSG	Wolf Rayet	LBV	SN type II	Massive YSO
amorphous silicates	1, 2	1	1	1	1	1	1		1	1	1
crystalline forsterite	1, 2	1	1		1	1	1		1		
crystalline enstatite	1, 2	1	1		1	1	1		1		
aluminum oxide	1 (?), 2									2	
spinel	1 (?), 2									2	
TiO_2	2										
hibonite	2										
MgO	1										
Fe	1 (?)									1	
PAHs	1, 2	1	1	1		1	1	(1)	1		
Amorphous carbon	1	1	1	1				1			
Graphite	2			2						2	
Diamond		1				1				2	
SiC	1, 2		1	2						2	
other carbides	2	1 (?)								2	
Si_3N_4										2	
MgS	1	1	1						1		
carbonate			1 (?)		1 (?)	1 (?)					
ice	1	1	1		1	1	1				1

1 - Astronomical data; 2 - Meteoritic data: AGB: Low mass (< 8 $M_\odot$) stars on the Asymptotic Giant Branch. Post-AGB: Low mass (< 8 $M_\odot$) stars in transition from the AGB phase to the planetary nebula phase. PN: The white dwarf remaining after the phase of prodigious mass loss on the AGB ionizes the ejecta forming a glowing nebula called a planetary nebula. Nova: The cataclysmic nuclear explosion caused by the accretion of hydrogen onto the surface of a white dwarf star. T Tauri: A low mass (~ 1 $M_\odot$) protostar. Herbig AeBe: Intermediate-mass ($1.5 < M < 10$ $M_\odot$) pre main-sequence stars with spectral types A or B. RSG (Red supergiant): Late and cool ($T \sim 3000$ K) stage in the evolution of massive stars ($M > 8$ $M_\odot$). Wolf Rayet: Hot stars characterized by massive stellar winds; some condense carbon dust in their ejecta. LBV (Luminous blue variable): The most massive, brightest and bluest stars are variable and may experience periods of eruptive mass loss. SN type II: The explosion of a massive ($M > 8$ $M_\odot$) star at the end of its lifetime. Massive YSO: Luminous and massive protostar characterized by vast amounts of cold dust and gas.

Stardust studies have largely focussed on sources with a very discrepant isotopic elemental composition reflecting nucleosynthetic processes in the interiors of their stellar birthsites. Indeed, these isotopic signatures are the prime tracers of their presolar, stardust origin of these grains. Carbonaceous compounds have proven to be a secondary tracer of stardust among micron-sized grains recovered from meteorites. This reflects to a large extent the inherent difficulty of detection of oxide and silicate stardust against a endogenous background of oxygen-rich solar system material and at present only a handful of amorphous and crystalline silicate stardust grains have been identified in meteorites or interplanetary dust particles. Thus, stellar sources with copious amounts of circumstellar dust inherited from previous epochs in the stellar evolution (e.g., post-AGB or planetary nebulae) are readily recognized in astronomical observations but cannot be traced by meteoritic studies. Note that the astronomical spectra of post-AGB objects and PNe can be markedly different from their progenitors, the AGB stars. This may reflect an overall modification of AGB materials by the action of X-rays, EUV, FUV photons or the strong shocks driven into the environment during these later phases. This interaction may even lead to vaporization and/or condensation of new dust materials. Alternatively, these spectral differences may result from efficient excitation of species such as polycyclic aromatic hydrocarbon molecules by energetic photons available during these later phases. More importantly, young stellar objects, which could be very important contributors to the interstellar dust budget (see section 2.2.; Tielens (2003)), are difficult to recognize against Solar system condensates because of their mundane isotopic composition. For these types of grains, isotopic variations are expected at the percent level, due to either chemical/physical differentiation in the solar nebula or galactic chemical evolution over the preceding 1 billion years (cf., the ^{16}O record in chondrites and the Si-isotope distribution in SiC stardust).

Finally, many of the compounds identified through astronomical observations and meteoritic stardust studies are those expected based upon thermodynamic stability arguments in an atmosphere of the appropriate elemental composition (Grossman & Larimer 1974; cf., § 2.4.). Apparently, time scales suffice for the nucleation and condensation processes to approach equilibrium. The abundance of trace elements dissolved in carbide-stardust grains present a particularly striking example of this (Lodders & Fegley 1996, 1997; Bernatowicz et al. 2003). However, the presence of (very abundant) amorphous silicates, amorphous aluminum oxides, and amorphous carbon materials in stellar ejecta present a discordant view. These (main) condensation products seem to have formed at temperatures well below the condensation temperature where the kinetics of the condensation reactions inhibited the formation of the appropriate crystal structure. This contrast between the traces of crystalline grains and the majority of amorphous grains suggests that the former are the first condensates high up in the photosphere while the latter grow later on at lower pressures in the extended atmosphere. Since AGB stars have dust-driven winds, rapid expansion should accompany the episode of major dust condensation.

2.2. Sources of Interstellar Dust

A large number of stellar sources contribute to the dust in the interstellar medium (cf., Tables 1 and 2). Astronomical studies show that AGB stars are an important source of dust in the interstellar medium (Fig. 1). About half of the AGB-dust-mass is in the form of amorphous carbon dust injected by C-rich AGB stars, while the other half is in the form of silicates injected by O-rich AGB stars. In contrast, other known sources of

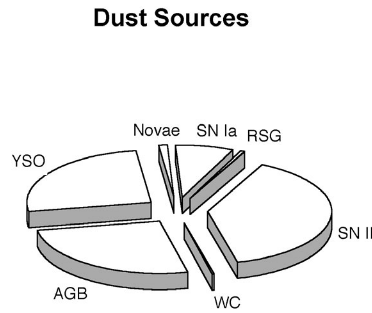

Figure 1. The contribution of different stellar sources to the interstellar dust budget. Note that all these values are very uncertain. Taken from Tielens (2001).

interstellar dust – Novae, WC Wolf-Rayet stars, red supergiants – contribute only traces of dust. The dust mass injected by supernovae is not well known. SN 1987A is known to have formed at least 10^{-4} $M_{\odot}$ of dust and perhaps as much as 0.1 $M_{\odot}$ of dust (Meikle et al. 1993; Wooden et al. 1993). A recent submillimeter study suggests that the more evolved SN, Cas A, was very efficient in forming dust, but this analysis depends much on the adopted dust properties. Moreover, the emission may be contaminated by swept up interstellar dust (Dunne et al. 2003; Dwek 2004; Krause et al. 2004). In Figure 1, we have assumed that all silicon, iron, and carbon ends up in dust in supernovae (Tielens 2001).

Young stellar objects may be another prominent source of dust in the interstellar medium (Dwek & Scalo 1980). A fraction of the material that enters the protoplanetary disk is ejected through a jet/wind once it has been transported to a region close to the protostar. Because much of the mass loss may be in the form of a neutral wind which is difficult to detect, estimated values for the fraction ejected vary substantially. Models for the X-wind – as an example of magnetocentrifugally driven flows – suggest that $^1/_3$ of the accreted material is ejected this way (Shu et al. 1994) (and $^2/_3$ is accreted into the central stellar object). Other models provide more conservative numbers of perhaps 0.1 for this fraction (Konigl & Pudritz 2000). In Figure 1, we have adopted the higher value which provides an upper limit on the contribution by YSOs. Observationally, it is unclear whether these winds are dusty; let alone whether such dust is newly condensed rather than entrained from the surrounding natal cloud. However, the physical conditions and timescales associated with the inner region of protoplanetary disks are very conducive to dust formation (§ 2.4.). Moreover, for the Solar Nebula, we know that a large fraction of the material in the inner 2 AU has been extensively processed (e.g., vaporized and recondensed) and likely this is a general aspect of protoplanetary disks. Indeed, mid-IR observations of T-Tauri stars and Herbig AeBe stars also show evidence for large scale reprocessing of dust in their surrounding disks (§ 4.3.). Figure 1 assumes that all the Si, Mg, and Fe in these winds is in teh form of silicates.

The interstellar medium is ‘ecologically’ speaking a disaster area where a large number of stellar sources pollute their environment with their garbage. Indeed, a large

Table 2. Interstellar gas and dust budgets

Source	$\dot{M}_H^a$ [$M_\odot$ kpc^{-2} Myr^{-1}]	$\dot{M}_c^b$ [$M_\odot$ kpc^{-2} Myr^{-1}]	$\dot{M}_{sil}^c$ [$M_\odot$ kpc^{-2} Myr^{-1}]
C–rich giants	750	3	–
O–rich giants	750	–	5
Novae	6	0.3	0.03
SN type Ia	–	0.3^d	2^d
OB stars	30	–	–
Red supergiants	20	–	0.2
Wolf Rayet	100	0.06^e	–
SN type II	100	2^d	10^d
YSO	$(1500)^f$		8

[a] Total gas mass injection rate.
[b] Carbon dust injection rate.
[c] Silicate, oxide, and metal dust injection rate.
[d] Fraction and composition of of dust formed in SN is presently unknown. These values correspond to upper limits.
[e] Dust injection only by carbon–rich WC 8–10 stars.
[f] Winds from young stellar objects merely take circumstellar gas and return it to the 'general' molecular cloud. This cycling occurs through the disk and dust entrained in these winds may have been modified or even completely vaporized and recondensed in the inner protoplanetary disk.
Taken from Tielens (2005). Except for SN type II^d, these values are uncertain by a factor ∼2.

number of stellar sources contribute substantially to the dust budget of the interstellar medium (Fig. 1). Because of the similarity and the inherent uncertainty of these values, it is unclear which source, if any, dominates the overall budget. It is important to realize that both the rate at which interstellar material is turned into stars (and planets) and the rate at which new material is injected into the ISM by old stars are small compared to the rate at which material is mixed in the interstellar medium. With a turbulent velocity of 10 km/s on a 200 pc scale in the warm intercloud medium of the ISM, an average batch of the ISM contains the 'ashes' of some 100 million AGB stars and a million supernovae. From that point of view, every stardust grain isolated from meteorites or IDPs is unique in its origin, composition, and history.

2.3. Observed Composition of Interstellar Dust

While the circumstellar dust record is rich and varied (Table 1), interstellar dust mainly consists of amorphous silicates and amorphous carbon. In addition, there is a small fraction (~ 0.05) of the elemental carbon locked up in Polycyclic Aromatic Hydrocarbon molecules – the extension of the interstellar grain size distribution into the molecular domain. There are strong upper limits on the abundance of SiC, oxide, and crystalline silicate grains – which are so apparent in the mid-IR spectra of AGB stars – in the interstellar medium. In particular, the abundance ratio of crystalline to amorhous silicates is less than 0.002 in the ISM while, from analysis of the mass budget of stellar dust sources, at least 0.05 is expected (Kemper et al. 2004). Hence, this discrepancy suggests that interstellar dust is substantially processed within the interstellar medium (cf., § 4.2.).

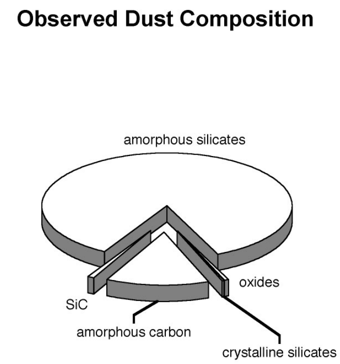

Figure 2. The observed composition of interstellar dust. Note that, at present, there are only upper limits on the presence of crystalline silicates ($< 0.2\%$; Kemper et al. (2004)), oxides ($< 0.2\%$; Kemper et al. (2004)), and SiC ($< 5\%$; Whittet (1990)) in the ISM.

2.4. Condensation and Growth of Dust

Theoretical and Experimental Condensation Studies Theoretical and experimental studies on the condensation and growth of dust are compared to astronomical observations in Figure 3. Theoretical studies of dust formation and the composition of circumstellar dust are mainly concerned with the thermodynamic condensation sequence. Taking into account a wide variety of gas phase and solid state compounds, such studies calculate the equilibrium composition of a gas of a given (Solar or non-Solar) elemental composition based upon measured and calculated thermodynamic properties of these materials (Salpeter 1977; Grossman & Larimer 1974). The results of such calculations are generally summarized using the condensation temperature – the temperature at which 50% of an element has condensed out – at a given pressure (Fig. 3). These studies show that, for an O-rich gas, oxides (Al_2O_3, corundum) are among the first condensates forming around 1200 K at low pressures and at $\sim$ 2000 K at high pressures. From abundance considerations, the main condensate, magnesium-rich olivine (Mg_2SiO_4, forsterite) forms at temperatures which are some 200 K lower.

A variety of laboratory studies on the condensation of dust have been performed, mainly focussing on the physical properties of the condensed grains (Nuth & Donn 1982; Rotundi et al. 2004; Hallenbeck et al. 1998; Fabian et al. 2000; Demyk et al. 2004; Nuth et al. 1982). The results for the critical SiO pressure at which nucleation takes place in an SiO-H_2 gas (Nuth & Donn 1982) are compared to the thermodynamic equilibrium calculations in Figure 3. These critical pressures are displayed as equivalent H_2 pressures adopting the Solar elemental Si abundance. This assumes implicitly that H_2 does not actively participate in the nucleation process, which is born out by these experiments. These experimental pressures for the onset of nucleation exceed the thermodynamic equilibrium calculations by many orders of magnitude. It is clear that non-thermodynamic considerations must play a key role in these experiments. Likely, at the short timescale for nucleation in these experiments ($\sim$ 10 s), the kinetics associated with the chemical pathways towards the critical nucleation clusters dominates. Based upon the extensive literature for soot chemistry in terrestrial environments, largely de-

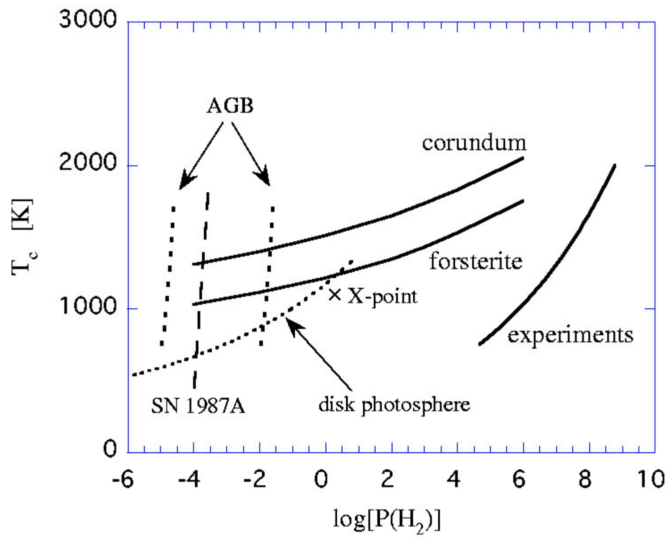

Figure 3. Theoretical, experimental and astronomical studies on the condensation of silicates and oxides in a gas with Solar elemental composition. Total hydrogen pressures are in dynes cm^{-2}. The solid curves labelled corundum and forsterite represent the results of thermodynamic equilibrium calculations for the condensation temperature at a given pressure (Salpeter 1977). The results of laboratory studies on the critical pressure at which nucleation (of Si_2O_3) was detected in a SiO gas at a given temperature is shown as the solid line labeled experiments (Nuth & Donn 1982). These critical SiO pressures have been converted into H_2 pressures using the Si elemental abundance. The two almost vertical short-dashed lines labelled AGB show the relation between pressure and temperature in the circumstellar winds of Asymptotic Giant Branch stars around the sonic point for two different mass loss rates ($10^{-7} - 10^{-4}$ $M_\odot$/yr). For these dust-driven winds, the bulk of the dust should condens close to the sonic point. The dashed line indicates the estimated gas pressure and temperature at day 615 in SN 1987A when dust formation was clearly proceeding (Wooden et al. 1993). The top part refers to the gas temperature in the C-O zone cooled by gaseous CO ($\sim$1800 K), while the bottom part is appropriate for the observed dust temperature (400 K). For comparison reason, calculated temperatures and pressures in the photosphere of a passively heated disk at a distance of 0.1-1 AU around a T-Tauri star are shown as a dotted line (Chiang & Goldreich 1999). For such an externally irradiated disk, temperatures in the interior are much less. Actively accreting disks will have much higher temperatures in their interiors (as well as in their photospheres). The X indicates the estimated conditions at the X-point in magnetocentrifugally driven flows from T-Tauri stars (Shu et al. 1994).

rived from the automotive and fuel industries, the chemical pathways towards carbon dust have been modeled in an astrophysical setting, using detailed reaction networks (Frenklach & Feigelson 1989; Cherchneff et al. 1992, 1996). These studies bear out the importance of kinetic considerations. In contrast, a comparable study of condensation in O-rich environments has not yet been done, because of the limited information on teh stability of small oxide clusters and the lack of relevant reaction rates (Köhler et al. 1997).

Astronomical Studies of Dust Condensation Astronomical observations show that silicate and oxide dust form readily in the ejecta of Asymptotic Giant Branch stars for mass loss rates in the range $10^{-7} - 10^{-4}$ $M_{\odot}$/yr. The physical conditions around the sonic point – where the bulk of the dust must condense – in these winds can be estimated from mass and momentum considerations (Fig. 3). At the lower mass loss rates ($\simeq 10^{-7}$ $M_{\odot}$/yr), the newly formed dust is dominated by oxides such as Al_2O_3 and MgFeO, but for mass loss rates exceeding some 10^{-6} $M_{\odot}$/yr amorphous silicates dominate the dust budget (Sloan et al. 1998; Cami 2001). The IR spectra of AGB stars with the highest mass loss rates ($\sim 10^{-4}$ $M_{\odot}$/yr) show evidence for forsterite and enstatite grains. It seems thus that, as the mass loss rate increases, the calculated thermodynamic condensation sequence is 'followed' to lower temperatures, possibly reflecting the increased importance of freeze-out in the rapidly expanding AGB shells for lower mass loss rates (Tielens et al. 1997; Cami 2001). The astronomical record on dust formation in supernova ejecta is very limited. Dust nucleation and growth has only been observed for SN 1987A where it occurred starting at day 600 and proceeding through day $\sim$800 (Wooden et al. 1993). The conditions in the chemically different zones of the ejecta were very different but likely this dust was formed in clumps in the Fe-rich and/or O-rich zones. The pressure in this zone has been calculated from a few simple considerations (Wooden et al. 1993). The temperature ranges from the observed dust temperature to the estimated gas temperature ($\simeq$ 1800 K). Overall, the physical conditions where dust condensation and growth is observed in astronomical settings is in good agreement with those expected from thermodynamic equilibrium calculations and occurs at pressures which are much lower than the experimental critical pressures (Fig. 3). Possibly, this reflects the much longer timescales for dust formation in these astronomical settings – ranging from weeks for supernovae to years for AGB stars – than in the experiments.

For comparison, the conditions in the photosphere of the inner (r in the range 0.1-1.0 AU), protoplanetary disks around T-Tauri stars are also shown in Figure 3. These are derived from theoretical models for passive disks irradiated by the central protostar (Chiang & Goldreich 1999). Internal temperatures will be lower for such passive disks but densities and pressures much higher. For actively accreting disks, viscosity can be an important heat source and the temperatures are much higher, both in the interior and in the photosphere. Except for the very inner region ($r < 0.1$ AU), passive disk are thus completely in the silicate/oxide stability regime and preexisting interstellar dust would survive. For actively accreting disks, on the other hand, the bulk of the dust in the inner protoplanetary system will have vaporized and recondensed, losing all stardust signatures. In view of the meteoritic record, the conditions of actively accreting disks are the more relevant ones for the Solar nebula during the phase of planet formation. For other protoplanetary systems, the situation is less clear although observations of crystalline silicates suggest that major reprocessing of the silicates has occured for Herbig AeBe stars (cf., § 4.).

The conditions in the X-point of magnetocentrifugally driven winds from T-Tauri stars are indicated by a X. The temperature has been calculated assuming that the region is optically thin (the small differences with the disk photosphere curve reflects slight differences in the assumptions). Thus, the pressure is considerably higher than in AGB winds. The timescales for expansion of the X-wind, on the other hand is of the order of days rather than $\sim$ year. However, given the pressure, it is nevertheless quite likely that dust nucleation and condensation proceeds to completion in these protostellar winds.

Stardust and Dust Condensation A rich, alternative source of information about grain formation in supernova ejecta has come from laboratory studies of presolar graphite. Croat et al. (2003) reported the results of coordinated ion microprobe and transmission electron microscopy (TEM) studies of supernova graphites from the KE3 separate of the Murchison CM2 meteorite. Isotopic analysis of individual graphites (1-12 μm) with the ion microprobe showed many to have large ^{18}O excesses combined with large silicon isotopic anomalies, indicative of a supernova origin. Detailed structural and compositional studies of such supernova graphites can be used to infer their condensation history, as well as some of the physical conditions in the mass outflow. TEM of ultramicrotome slices of these graphites revealed a high abundance of internal titanium carbides (TiCs), with a single graphite in some cases containing hundreds of TiCs. In addition to TiCs, composite TiC/Fe grains (TiCs with attached iron-nickel grains) and solitary iron-nickel grains were found. The average TiC grain sizes in supernova graphites are quite variable (from 30 to 230 nm). The TiC surfaces exhibit variable degrees of corrosion, and sometimes have partially amorphous rims (3 to 15 nm thick). Croat et al. (2003) speculated that the rims on the internal grains are most plausibly the result of atom bombardment caused by drift of grains with respect to the ambient gas, requiring relative outflow speeds $\sim$ 100 km/s. In general, the diversity in internal TiC chemical and physical properties suggests that TiCs condensed first and had substantially diverse histories prior to incorporation into the graphite, implying some degree of turbulent mixing in the SN outflows. In several graphites, TiCs showed a trend of larger V/Ti ratios with increasing distance from the graphite center, an indication of progressive equilibration with the surrounding gas before they were sequestered in the graphites. In general, no trend was seen in the TiC size vs. distance from the graphite center, implying that appreciable TiC growth had effectively stopped before the graphites formed, or else that graphite growth was rapid compared to TiC growth. The chemical variations among internal grains as well as the presence of partially amorphous rims and epitaxial Fe phases on some TiCs clearly indicate that the phase condensation sequence was TiC, followed by the iron phases (only found in some graphites) and finally graphite.

Reliable constraints on the conditions in AGB star envelopes come from the application of equilibrium thermodynamics to the chemical composition of presolar grains. For example, Lodders & Fegley (1997) noted that the pattern of trace element enrichment in 'mainstream' presolar SiC is exactly mirrored in the elemental depletion patterns observed astronomically in the atmospheres of N-type carbon stars. They showed that these depletion patterns are consistent with the trace element partitioning into condensing SiC predicted by equilibrium thermodynamics. As another example, TiC crystals (sometimes in solid solution with refractory elements like Zr) are often observed within presolar graphite spherules. They occur in $\sim {}^{1}/_{3}$ of well-graphitized spherules, and in many of these instances at the spherule centers (Bernatowicz et al. 1996). The clear implications are that TiC condensation preceded that of graphite and that TiC crystals sometimes served as heterogeneous nucleation centers for the growth of graphite. Application of equilibrium thermodynamics to these observations allows quantitative inferences to be drawn that can be checked against astronomical observation.

Figure 4 displays condensation temperatures for graphite, TiC and SiC as a function of the gas pressure and C/O ratio, under conditions of thermodynamic equilibrium.

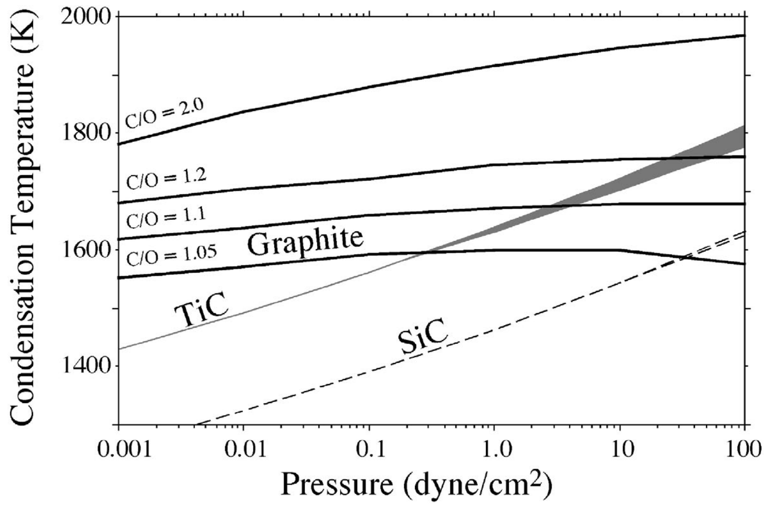

Figure 4. Equilibrium condensation temperatures for graphite, titanium carbide (TiC), and silicon carbide (SiC) as a function of total pressure and C/O ratio (from 1.05 to 2.0). The Ti/O and Si/O ratios are assumed to be solar. The TiC and SiC condensation temperatures, displayed as envelopes, are for C/O $>$ 1.05. Data are from Lodders & Fegley (1996).

Only ratios C/O $>$ 1 are shown, because at lower values all C is tied up in the very stable CO molecule in the gas phase; it is only when the C number density exceeds that of O that sufficient carbon is available to form graphite and carbides; see Lodders & Fegley (1996) and Sharp & Wasserburg (1995). Inspection of Figure 4 shows that the graphite condensation temperature is relatively insensitive to pressure, but strongly dependent on C/O, while the TiC condensation temperature depends on pressure but is insensitive to C/O. The fact that the condensation curves cross means that whether TiC will start forming before or after graphite depends on the ambient pressure. The higher the C/O ratio, the greater is the pressure required for TiC to condense before graphite.

For example, condensation of TiC before graphite will occur at $P \gtrsim 3$ dynes/cm^2 for C/O = 1.1, and $P \gtrsim 30$ dynes/cm^2 for C/O = 1.2. However, the C/O ratio cannot be increased much beyond this if TiC is to condense before graphite. As C/O approaches $\sim$ 1.5 the required pressure reaches photospheric values for AGB stars ($\sim$700–1400 dyne/cm^2), and at the photosphere the temperature is far too high for any grains to condense. Instead, the grains must condense at radii greater than the photospheric radius where both temperatures and pressures are much lower. So the presolar graphites with nuclei of TiC observed in KFC1 certainly indicate $1 \lesssim$ C/O $\lesssim 1.2$ in the circumstellar atmospheres where they formed, as originally argued by Sharp & Wasserburg (1995). This conclusion is robust, and moreover is consistent with astronomical observations of AGB stars (Lambert et al. 1986). Since the condensation curves for SiC parallel those for TiC, but at a temperature roughly 170 K lower, the equilibrium thermodynamics also predicts that SiC will only form before graphite a relatively high pressures, consistent with the fact that SiC is only very rarely observed to occur within presolar graphite. The discovery of small graphite grains enclosed within presolar SiC provides additional support for the condensation of graphite before SiC in stellar outflows (Stroud et al. 2002).

The plausibility of the C/O ratios inferred from thermodynamics means that confidence can be placed in correlated physical inferences about the circumstellar environment in which the graphite grains formed. As noted above, C/O ~ 1.1 requires a pressure $P \gtrsim 3$ dynes/cm^2 and a temperature of ~ 1600 K in the in the dust condensation zone for TiC to form before graphite. For the canonical dust-forming carbon star, IRC 10216, with a mass loss rate of $\sim 10^{-5}$ $M_{\odot}$/yr, these conditions refer to the gas at the top of the extended atmosphere – lifted by the periodical pulsational shocks – at a distance of $R \sim 1.5 R_{\star}$ (Cherchneff et al. 1992). The net outward velocities are only a small fraction of the terminal outflow velocities of $\sim 10 - 20$ km/s at this location, and the residence times in this location are of the order of years. Hence, despite the strong shocks traversing this region, thermodynamic equilibrium might well be attained as indicated by the TiC and SiC stardust grains. Alternatively, the presolar graphites containing TiC may have formed in density concentrations (clumps or jets) somewhat further out in the outflow (Bernatowicz et al. 1996), where the shocks have less effect but timescales are shorter. Indeed, IRC 10216 shows evidence for density enhancements in its circumstellar dust shell (Mauron & Huggins 2000; Chandrasekhar & Mondal 2001).

Daulton et al. (2002, 2003) determined the polytype distribution of presolar SiC from the Murchison CM2 carbonaceous meteorite using high-resolution TEM. These studies demonstrated that only the two simplest polytypes are present, the cubic 3C (β-SiC) polytype (79.4% of population by number) and the hexagonal 2H (α-SiC) polytype (2.7%). Intergrowths of these two polytypes are relatively abundant (17.1%). These measurements are consistent with mainstream presolar SiC thought to originate in the expanding atmospheres of AGB carbon stars. Equilibrium thermodynamics predicts relatively low SiC condensation temperatures in carbon stars (Fig. 4). Condensation temperatures of 2H and 3C SiC observed in the laboratory are generally the lowest of all SiC polytypes and fall within the predictions of the equilibrium calculations. These points account for the occurrence of only 2H and 3C polytypes of SiC in circumstellar outflows. The 2H and 3C SiC polytypes presumably condense at different radii (i.e., temperatures) in the expanding stellar atmospheres of AGB carbon stars.

Stroud et al. (2004) have analyzed the microstructure and isotopic composition of two presolar Al_2O_3 grains. Thermodynamic equilibrium calculations predict that aluminum oxide is among the first solids to condense out in stellar ejecta (Salpeter 1977; Grossman & Larimer 1974). However, because there are no direct molecular progenitors in the gas phase, homogenous nucleation of Al_2O_3 is expected to be inhibited (Donn & Nuth 1985; Donn 1976). Hence, it has been speculated that aluminum oxide nucleates heterogeneously on preexisting TiO_2 grains (Gail & Seddlmayer 1998) where the titanium oxide play the same role in the formation of aluminum oxides as the titanium carbide in the formation of (some) graphite stardust grains (see above). The lack of TiO_2 subgrains in these two Al_2O_3 stardust grains argues however, against such heterogeneous nucleation models (Stroud et al. 2004). Indeed, the variation in the Ti content of these grains suggests that titanium oxide did not play an important role in the growth of these grains. Nevertheless, it should be understood that titanium oxide may still have played an important chemical role in the *nucleation* of the first (unstable) clusters. Because the critical cluster size – below which clusters are unstable – is so minute and because any titanium involved in its formation may be afterwards lost chemically, the lack of Ti tracers is not conclusive. In particular, soot formation in acetylene-hydrogen plasmas is known to be triggered by seeding with silane (Cadwell et al. 1994; **?**).

3. Shock Processing of Dust in the ISM

3.1. Theoretical Studies

Interstellar shocks are an important destruction agent of interstellar dust (Draine & Salpeter 1979; Seab & Shull 1983; Jones et al. 1994, 1996). While the gas is stopped in the shock front, because of their inertia, dust grains will keep moving at $^3/_4$ of the shock speed relative to the gas. Since the grains are charged, they will gyrate around the magnetic field and acquire velocities with respect to each other. Moreover, given that the Larmor radius associated with this circular motion is typically very small, interstellar grains are position coupled to the gas. Upon compression, the magnetic field strength will increase and, because of conservation of magnetic moment, the grains will spin up (betatron acceleration). This acceleration is counteracted by collisions with the gas. This drag is more effective for small grains which are therefore less susceptible to betatron acceleration. In all, large grains will move at considerable speeds relative to the gas and to each other over much of the shock structure.

These relative motions leads to destruction due to sputtering and due to grain-grain collisions. At grain-gas velocities of 100 km/s, impinging H-atoms have some 50 eV of energy and He atoms some 200 eV. At these energies, this will, typically, result in sputtering yields of about 0.01 per impinging H-atom. Likewise, these velocities are well above the threshold for cratering, melting, and vaporization in collisions between two grains.

Over the years, a number of theoretical studies have appeared that detail the destructive effects of interstellar shocks (Draine & Salpeter 1979; Seab & Shull 1983; Jones et al. 1994, 1996). These studies calculate the shock structure, grain velocities, and sputtering rate and grain-grain collision rate as a function of position behind a shock of a given velocity. For a given grain size (distribution), this allows then the calculation of the fraction of a grain destroyed for shocks of different velocities. Convolving these results with models for the frequency of shocks of different velocities, results then in the lifetime against destruction of interstellar dust grains. The results of these studies show that sputtering is the dominant process returning solid material to the gas phase. This is a slow ‘chipping’ away of large grains where a 100 km/s shock will typically return some 10% of the grain mass to the gas phase. Small grains ($a \lesssim 100$ Å) are hardly affected by such relatively frequent, low velocity shocks (they are dragged to a halt before betatron acceleration kicks in) and are mainly (completely) destroyed by much less frequent, high velocity ($v_s \gtrsim 300$ km/s) shocks. Grain-grain collisions are important in redistributing the grain mass from large grains to small grains. Indeed, a single 100 km/s shock will lead to the complete disruption of essentially all large (300-3000 Å) grains considered (Jones et al. 1996). In contrast, vaporization by grain-grain collisions is of little consequence.

All calculations agree on the basic point that the overall lifetime of grains against the cumulative effect of strong shocks is some 500 million years, which is much less than the timescale (2.5 billion years) at which grains are replenished by stellar sources (Jones et al. 1994, 1996; Dwek & Scalo 1980).

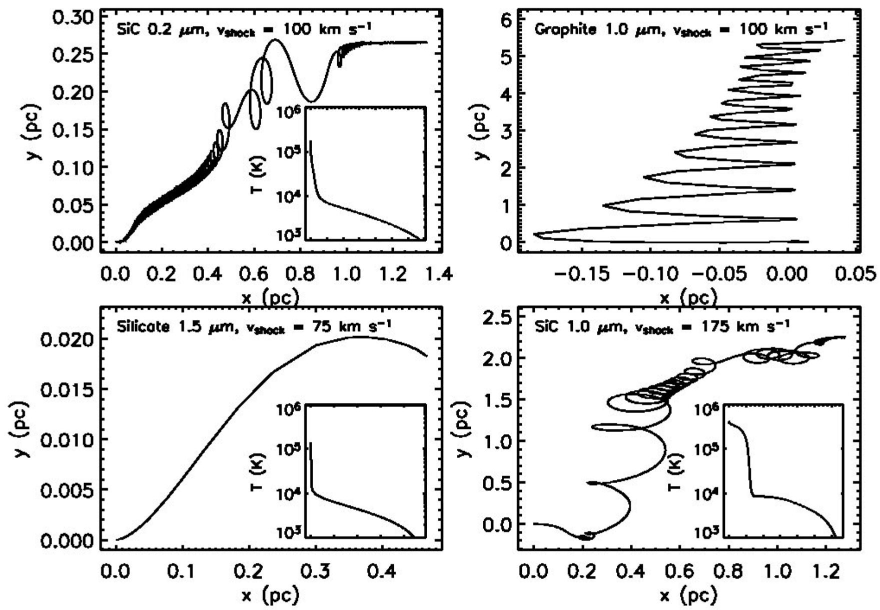

Figure 5. Calculated trajectories for individual dust grains in interstellar shocks (Slavin et al. 2004). These calculations are for plane-parallel shocks where the material enters from the left. Inserts show the calculated gas temperature as a function of the distance behind the shock front. The x-scale is the same as that in the trajectory panel. Top left: A typical interstellar grain ($a = 0.2\ \mu$m) is position coupled in a 100 km/s shock. Top right: a 1 μm-sized grain is rapidly Fermi accelerated across the shock front and reaches velocities exceeding 1000 km/s before complete destruction. The atoms injected into the gas phase will be further accelerated by the shock and are likely the origin of galactic cosmic rays. Note the difference in x- and y-scale. Bottom right: For slightly different conditions, a large grain will start to decouple from the gas. However, this grain is still largely destroyed. Bottom left: Grains larger than $\sim 1\ \mu$m readily decouple from the gas and essentially 'sail' through the shock without much destruction.

A key assumption in these calculations is that the grains are position coupled to the gas in the shock. This assumption breaks down when the grains become very large and their Larmor radius becomes comparable to the relevant shock-size scales (Slavin et al. 2004). At that point, the fate of the grain depends very much on the specifics (grain size, charge, composition, velocity). Globally, four different regimes can be discerned. Small ($\lesssim 0.3\ \mu$m) grains are position coupled and their behavior, including destruction, is well described by 'classical' grain shock calculations. For intermediate sized grains and intermediate shock velocities, the grain is reflected many times back and forth across the shock front, and every time it is accelerated to higher velocities. This Fermi acceleration process leads to very high velocities ($\sim$ 3000 km/s) before the grain is completely sputtered away. Parenthetically, this process may be the first step in the production of cosmic rays since the resulting fast moving ions can be further Fermi-accelerated to cosmic ray energies and this may be the origin of the non-solar composition of cosmic rays (Ellison et al. 2004). For somewhat higher velocities, large grains start to decouple but they are, nevertheless, still completely destroyed. At the highest velocities, the Larmor radius of the grains is so large that they traverse the shock without noticing its presence. As Figure 5 illustrates, grains larger than ~ 1 μm are fully decoupled from the gas and are not affected by interstellar shocks. The location of this transition – from fully destroyed to largely unharmed – is very sudden and its location (e.g., critical size) depends on the details (e.g., charge, size, material) but that large grains decouple follows directly from simple considerations. We further note that this also implies that young supernova remnants will selectively sweep up large interstellar grains in their interiors, while the smaller ones remain localized in the outer shells of swept-up interstellar material. Given that the Sun is presently traversing such a young SNR – the local bubble –, the Ulysses stream of interstellar grains (Grün et al. 1993) may well be sampling this collection process (Slavin et al. 2004).

3.2. The Astronomical Record

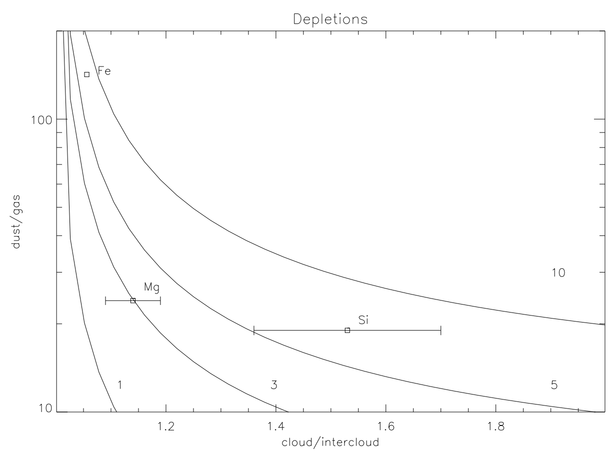

Figure 6. Observed depletions of silicon, magnesium, and iron in the ISM (Savage & Sembach 1996). The y-axis is the ratio of the abundance of an element in the dust phase to its abundance in the gas phase, both measured in diffuse clouds. The x-axis is the ratio of the depletion of these elements in the cloud medium to that in the intercloud medium. The solid lines are the results of a simple model balancing destruction in the intercloud medium with accretion in the cloud medium (Tielens 1998). The labels indicate the adopted values for the accretion rate relative to the cloud-to-intercloud mixing ratio. As these observations demonstrate, the rates for destruction in the intercloud phase, accretion in the cloud phase, and mixing between these phases have to be within a factor of a few of each other and are thus very rapid compared to the injection rate of dust by stars into the ISM.

Observations show that the gas phase abundance in the interstellar medium of major dust forming elements (e.g., Si, Fe, Mg) are much less than Solar or stellar abundances (Fig. 6; Savage & Sembach (1996)). This depletion is generally taken as evidence that a substantial fraction (~ 0.9) of these elements is locked up in dust grains (Field 1974). However, gas phase abundances are much higher in high velocity clouds (Routly & Spitzer 1952). Because these high velocities reflect the recent passage of a shock, this provides qualitative support for the importance of dust destruction by shock waves. A more quantitative comparison between models and observations is hampered by our lack of knowledge on the detailed velocity history of the observed gas (Cowie 1978).

Observations have also revealed a large and systematic difference in the depletion with location in the interstellar medium (Fig. 6; Savage & Sembach (1996)). Thus, gas phase depletions are systematically much less in the intercloud medium than in diffuse clouds. Now, dust is rapidly destroyed by shocks in the low density, intercloud medium, while accretion is limited to the denser environment of diffuse clouds. The large difference in the depletion between these two phases of the interstellar medium directly demonstrates then that the processes involved – shock destruction and accretion – operate on a timescale similar to the timescale at which material is mixed from the cloud to the intercloud medium and back (Tielens 1998). This mixing timescale is much less ($\simeq$ 30 million years) than the timescale at which new dust is injected into the ISM. Thus, specifically, some 10% of the iron, 15% of the magnesium, and some 30% of the silicon is returned to the gas phase upon each sojourn into the intercloud medium and then rapidly reaccreted once the material is cycled back to the cloud phase. For silicon and magnesium, these differences in depletion between cloud and intercloud phase are slightly larger than expected based upon the material properties (e.g., sputtering yields) of silicates, indicating that the re-accreted material is in the form of mantle with somewhat lower binding energy than silicates. Unfortunately, the abundance of carbon in the warm intercloud medium is inherently difficult to measure and no reliable estimates exist for the difference in depletion between the cloud and intercloud phases. Hence, whether mantles accreted in the diffuse ISM are carbonaceous in origin is presently unclear.

3.3. The Meteoritic Record

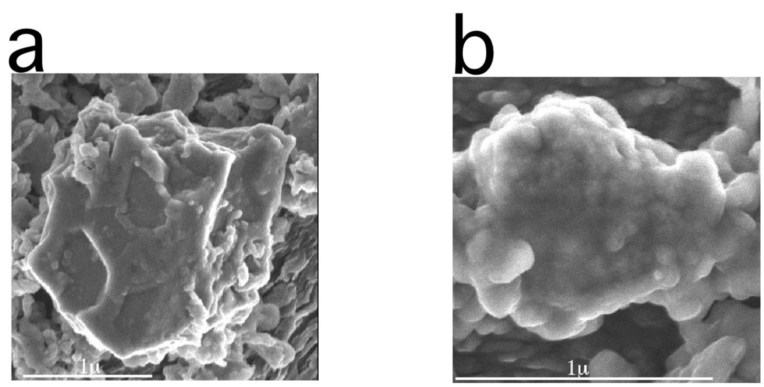

Figure 7. Field emission scanning electron microscope images of pristine presolar SiC grains from the Murchison meteorite (Bernatowicz et al. 2003): (a) exhibiting primary growth crystal faces and polygonal depressions; (b) coated with an apparently amorphous, possibly organic phase. Scale bars are 1 μm.

Because presolar grains were formed in various kinds of circumstellar winds and supernova ejecta, they must *necessarily* have traversed the ISM prior to their incorporation into the solar nebula. Surviving presolar grains thus serve as monitors of physical and chemical processes in the ISM. Bernatowicz et al. (2003) described a non-destructive technique used to isolate presolar SiC grains (in the size range 0.5–2.6 μm) from the Murchison meteorite and to identify them in their pristine state. Nine-tenths of the pristine SiCs were found to be bounded by one or more crystal faces. In addition, multiple polygonal depressions (generally < 100 nm deep) were observed in more than half of these crystal faces, and were shown likely to be primary growth features (Fig. 7). No other primary minerals were observed to be intergrown with or overgrown on the pristine SiCs, so the presence of overgrowths of other minerals cannot be invoked to account for the survival of presolar SiC in the solar nebula. An oxygen peak present in the X-ray spectra of most pristine grains implied the existence of silica coatings of as much as several tens of nm thickness, perhaps due to oxidation of the SiC in the solar nebula. However, the pristine SiC grains show little or no evidence of the surface sputtering or cratering that are predicted theoretically to occur in the ISM due to supernova shocks on the pristine grains.

One solution to this difference between theory and observation consists in assuming that only a subset of those grains (e.g., those that were unprocessed in the ISM) survived incorporation into the solar system, while those that were processed were either comminuted to sizes smaller than those studied by Bernatowicz et al. (2003), or else were entirely destroyed. It is difficult to evaluate this argument from the study of the pristine grains themselves, however there are other data that can be used to evaluate the plausibility of this 'all or nothing' hypothesis. Numerous studies have revealed a dependence of isotopic composition on grain size for Murchison SiC, for example in $^{14}N/^{15}N$ (Hoppe et al. 1996), $^{20}Ne/^{22}Ne$, $^{4}He/^{22}Ne$ (Lewis et al. 1990), $^{80}Kr/^{82}Kr$, $^{86}Kr/^{82}Kr$ (Lewis et al. 1990), $^{50}Ti/^{46}Ti$, $^{50}Ti/^{49}Ti$ (Amari et al. 1996), $^{88}Sr/^{86}Sr$ (Podosek et al. 2004), and $^{138}Ba/^{136}Ba$ (Prombo et al. 1993). These trends presumably reflect a dependence of isotopic composition and the densities of stellar envelopes (hence the sizes of grains condensed) on stellar characteristics such as metallicity and mass. If SiC grains in the ISM were extensively processed by shocks such that pervasive comminution of grains occurred, then it is difficult to understand how the observed isotopic covariance with grain size could have been preserved. The pristine SiC grains thus present us with a major discrepancy between observation and theory.

A possible way out of this discrepancy is to postulate that the SiC grains may have been protected during their residence in the ISM by surface coatings or mantles. Icy mantles present on the SiC grains during their residence in the ISM, whether chemically processed by UV radiation or not, would certainly have served to protect them against inertial sputtering, and possibly may have mitigated the effects of grain-grain collisions. Residues of such coatings may indeed be present on some pristine SiCs, because many (60%) are coated with an apparently amorphous, possibly organic phase (see Fig. 7). However, at present there are not sufficient data on the coatings to draw secure inferences as to their nature or origin. Alternatively, the SiC grains sampled by the solar nebula may represent relatively unprocessed grains that were produced by stars in a short time interval prior to the formation of the solar system. By 'short' in this case we mean that the mean time interval between the production of the grains and their incorporation into the solar nebula would have to be much less than the mean lifetime against grain destruction in the ISM. Unfortunately, there is at present no reliable independent means of determining the residence time of presolar grains in the ISM.

3.4. Summary

It has long been recognized that the short timescales for dust destruction – when compared to the injection timescale for new dust by stellar sources – are at odds with the observed high (90%) depletion of silicon, iron, and magnesium in the ISM (Dwek & Scalo 1980). The discussions in the preceding subsections suggest the following model for the processing of grains in the interstellar medium, which may alleviate this conundrum. Material is rapidly cycled between the intercloud and cloud phases of the interstellar medium. During each sojourn into the intercloud phase, a parcel of dust and gas typically experiences one 100 km/s shock. Because of sputtering, shock processing removes a thin layer (typically 50 Å) from a (2000 Å) grain. However, upon completing its cycle into the cloud medium, this material is reaccreted in the form of a mantle which protects the underlying material from sputtering in the next shock. Thus, because of this cycling, the actual (complete) destruction timescale for interstellar grains is much larger than the 'naively' calculated 500 million years (corresponding ot the cumulative 'chipping-away' timescale). However, while this model is attractive, some problems remain. In particular, because the interstellar grain size distribution is characterized by a preponderance of small grains (which carry most of the surface area), one would expect that most of the gas phase species accrete on the small grains and are therefore 'lost' for the protection of the large grains. Thus, within the framework of this model, gas phase species have to somehow selectively accrete onto large grains to form a protective mantle.

In addition to the problem of the lifetime of interstellar dust, there is also the problem of the existence of large single-grain stardust in meteorites. The theoretical studies show that grain-grain collisions are very effective in removing large grains from the interstellar grain size distribution (Jones et al. 1996). Essentially, any 100 km/s shock will catastrophically disrupt all grains larger than some 300 Å through grain-grain collisions. While coagulation in the cloud phase, may build up larger grain structures, this will not restore single grains. This problem is exacerbated by the absence of shock processing features in isolated SiC stardust grains (§ 3.3.). Several solutions to these problems are summarized in § 3.3. (Bernatowicz et al. 2003). Given the discussion above, the presence of a mantle is particularly interesting. Of course, in order to protect against the disruptive effects of grain-grain collisions, this coating has to be very thick, 1000's of Å rather than the 50 Å required to protect against sputtering. We also recall that theoretical studies show that large SiC grains sail 'unharmed' through interstellar shocks. The stardust record may thus be biased towards 'unprocessed' large grains. Conversely, this would imply that smaller grains should show more signs of shock processing.

4. Processing of Silicates

4.1. Crystalline and Amorphous Silicates

Crystalline silicates are an important component of the dust in circumstellar environments. Specifically, AGB stars which are one of the major 'dust factories' inject some 15% of their silicates in crystalline form (Sylvester et al. 1999; Kemper et al. 2004). Likewise, protoplanetary disks surrounding low and intermediate mass protostars show ample evidence for crystalline silicates in their mid-IR spectra (Malfait et al. 1998). It is therefore disconcerting that the interstellar medium shows no evidence for crystalline silicates; after all, in the lifecycle of the dust, the ISM separates the AGB dust formation sites from the end stages – newly formed stars and planets. Upper limits on the fraction of crystalline relative to amorphous silicates in the ISM are very strict (< 0.004) compared to the fraction injected (~ 0.05; Kemper et al. (2004)). Apparently crystalline silicates are rapidly converted into amorphous silicates in the ISM and back to crystalline silicates in protoplanetary disks.

4.2. Silicate Processing in the ISM

Different processes leading to amorphization of silicates in ISM have been proposed. These include melting due to the shock wave driven into a grain after grain-grain collisions. Typically, when the shock pressure exceeds 1 Mbar (e.g., collision velocities $>$ 1 km/s; Tielens et al. (1994)), shocked solid material enters the liquidus regime and the rapid quenching upon subsequent expansion will inhibit (re)crystallization (Tielens et al. 1987). The experimental evidence on crystallization/amorphization by shocks in solid material is ambiguous. Most of the silicate material is indeed quenched as a glass. However a minor fraction ($\sim$ 5 %) becomes crystalline. While this argues against melting in grain-grain collisions as a major process setting the amorphous/crystalline balance in the ISM, we note that laboratory studies have exclusively focussed on macroscopic samples and the ultrashort timescales associated with unloading of microscopic grains may strongly inhibit recrystallization.

Alternatively, as noted in § 3.2., there is a constant exchange between the solid phase and the gas phase in the ISM. It is conceivable then that, because of the low temperature, recondensation will preferentially lead to amorphous rather than crystalline silicates. Of course, serious discussion of this suggestion suffers from our general lack of insight in the chemical routes that would lead to oxide/silicate dust formation in the ISM. Here, we just note that likely this removal/accretion involves only a small fraction of the total dust volume.

Laboratory studies have shown that ion irradiation readily transforms crystalline into amorphous material (Demyk et al. 2004; Jäger et al. 2003). Experimental studies of astrophysically relevant materials have mainly focussed on irradiation by keV ions and these have revealed amorphization for fluences of 10^{18} cm^{-2}. Amorphization is limited to a depth commensurate with the penetration depth of such ions. For a 100 km/s shock, this corresponds to 10 Å for He, 25 Å for C, N, O, and 40 Å for Fe. Hence, ion bombardment in such low velocity shocks cannot process large grains. Ion irradiation by cosmic ray ions, which have much higher energies and hence penetration depth, may be much more effective (van Breugel et al. 2003).

4.3. Crystalline Silicates in Protoplanetary Disks

While interstellar silicates are amorphous, the abundance of crystalline silicates in proto-planetary disks is in some cases substantial. Mid-infrared spectra of vibrational resonances in the lattice of (crystalline) silicates are sensitive to the size, shape and chemical composition of the grains. In particular, mid-IR spectroscopy of crystalline silicates allows a determination of their *mineralogy*. A break-through in this area was achieved by ESA's Infrared Space Observatory (ISO). The ISO satellite provided spectra of protoplanetary disks in the 2-200 μm region with a spectral resolution $\lambda/\Delta\lambda$ between 300 and 2000. Access to this broad wavelength range is important for a proper determination of the mineralogy. In particular, the bands in the 30 to 70 μm spectral range are sensitive to the Fe/Mg ratio. Due to the limited sensitivity of the ISO spectrographs, only a handful of high-quality spectra were available until recently, of disks surrounding intermediate mass young stars, the Herbig Ae/Be stars. This situation is changing rapidly however due to the launch in 2003 of NASA's Spitzer Space Telescope (SST) which has a much improved sensitivity, although a somewhat lower spectral resolution and less wide wavelength coverage.

The ISO data of Herbig Ae/Be disks allowed the identification of crystalline silicates, in particular of olivines ($Mg_{2-2x}Fe_{2x}SiO_4$) and pyroxenes ($Mg_{1-x}Fe_xSiO_3$). The position of the emission bands is consistent with $x = 0$, i.e. forsterite and enstatite, the Mg-rich end members of the olivine and pyroxene families. A similar chemical composition of the crystalline silicates was found for the solar system comet Hale-Bopp (Crovisier et al. 1997), and for crystalline silicates that condense in the outflows of evolved red giants and red supergiants (Molster et al. 2002).

Crystalline silicates in disks surrounding solar type T Tau stars have been detected in the 10 μm spectral region using large ground-based telescopes (Honda et al. 2004; Przygodda et al. 2003). Much less is known about their longer wavelength bands, and therefore the mineralogy of the crystalline silicates in disks surrounding T Tau stars is not well constrained at present. The 10 μm data are consistent with a Mg-rich composition, as in the Herbig Ae/Be stars.

Ground-based spectroscopy in the 10 μm atmospheric window has provided data for some 50 Herbig Ae/Be and T Tau stars. Both classes of stars show a band which is dominated by amorphous silicates, with minor contributions from crystalline silicates (with some notable exceptions, however). The shape and strength of the 10 μm silicate band turn out to be correlated (van Boekel et al. 2003; Przygodda et al. 2004). This can be explained in terms of grain growth. Small, sub-micron sized dust particles that are in the Rayleigh limit have a strong contrast between emissivity in the continuum and in the Si-O resonance. These particles produce a strong emission band which peaks near 9.7 μm. Larger grains are no longer in the Rayleigh limit and their 10 μm spectra flatten and the contrast between continuum and resonance emissivity decreases due to radiation being absorbed and scattered in the grain. For typical amorphous silicate grains, this effect becomes important at 10 μm in the size range 1-2 μm. For even larger grains, the emission band is very weak and difficult to detect in astronomical spectra. Analysis of the 10 μm spectra of Herbig Ae/Be stars and T Tau stars shows that substantial removal of small grains (presumably due to aggregation) has occured in disks with ages between 1 and 10 Myrs. The data also show that this aggregation does not depend on the degree of crystallization in disks. This is easy to understand by considering that aggregation requires high density (and can happen throughout the disk), but crystallization requires high temperature.

In order to establish the spatial distribution of the crystalline silicates, high angular resolution mid-infrared observations are required. This has recently become possible by means of long baseline optical interferometry using large apertures, at the Very Large Telescope Interferometer (VLTI) of the European Southern Observatory. The Mid-Infrared Interferometric Instrument (MIDI) at the VLTI was able to spatially and spectrally resolve the innermost regions of the disks surrounding three nearby bright Herbig Ae/Be stars (Fig. 8; (van Boekel et al. 2004)). The crystalline silicate abundance was found to be more than about 50 per cent in the innermost 1-2 AU of these disks; in one star, the data are consistent with a fully crystallized inner disk region. The outer disk regions are (much) less crystalline, proving a radially decreasing abundance of crystalline silicates.

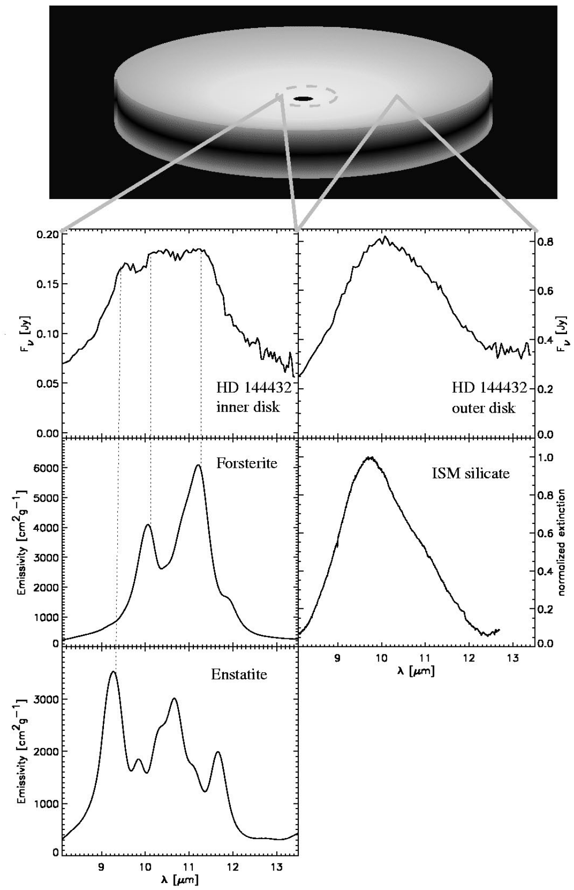

Figure 8. The spatial/spectral distribution of the 10 μm emission in protoplanetary disks around the Herbig Ae/Be star, HD 144432 (van Boekel et al. 2004). The interferometric study of this object reveals that the 10 μm band originating from the inner 2 AU of the disk shows the signature of crystalline silicates while the spectrum on large scales is dominated by amorphous silicates.

These results strongly suggest that the bulk of the crystalline silicates originates in the inner disk regions. The most obvious processes that can produce these crystals are thermal annealing of amorphous grains (at temperatures above the glass temperature, roughly 1000 K), and chemical equilibrium reactions at higher temperatures. This latter process is supported by the observation that HD 142527 has significantly more forsterite than enstatite in the inner (1-2 AU) disk regions, while in the outer (5-20 AU) disk regions the abundance of these minerals is about equal. Such abundance gradients are expected in disk models that include chemical equilibrium reactions and assume that material is *radially mixed* from the inner regions to larger distance from the star (e.g., (Gail 2004)). At temperatures above some 1400 K, mostly forsterite is formed. At lower temperatures, gas-phase-solid reactions convert this forsterite to enstatite. At even lower temperatures, but above the glass temperature, thermal annealing produces both olivines and pyroxenes, at abundance ratios that depend on the stochiometry of the amorphous interstellar dust grains that were accreted onto the young star.

Radial mixing provides a natural explanation for the presence of crystalline silicates in Herbig Ae/Be spectra with dust grain temperatures in the range 100-200 K, and in solar system comets such as Hale-Bopp, since these objects were formed at low temperatures, far from the regions in the solar nebula where substantial crystallization could have occurred. Gas-phase condensation at high temperatures in combination with radial mixing can also explain the Mg-rich nature of crystalline silicates.

Alternative explanations for the high fraction of crystalline silicates in protoplanetary disks involve local processes such as lightning and shocks (Harker & Desch 2002; Scott & Krot 2005). Such models – in which the silicates are only temporarily heated to the high temperatures required for crystallization (or vaporization and recondensation) – provide a natural explanation for the presence of cold crystalline silicates. The gradient in crystallinity observed by the MIDI instrument may then reflect a strong dependence of this processing on location in the disk. Alternatively, if this process were limited to the inner regions of protoplanetary disks (and the inner regions of the Solar nebula), efficient radial mixing would still be required. While such 'local' models would link silicate crystallization to the chondrule formation process, we emphasize that protoplanetary disks are expected to be highly turbulent and the temperatures in the inner disk are high enough for rapid vaporization, recondensation, and crystallization of silicates. Either model – vaporization/recondensation/annealing coupled with turbulent diffusion or lightning/shocks processing – will have to explain the key characteristics of the observations: The large variation in the crystalline fraction, the composition, the temperature, and the radial distribution. Much of this is still under active investigation as the right tools – IR spectroscopy over a wide wavelength range with Spitzer and mid-IR interferometry with MIDI/VLTI – are now coming on line.

4.4. GEMS

An important component of Interplanetary Dust Particles (IDP) is believed to derive from comets and hence may contain a largely pristine record of the material that entered the (outer) solar nebula and the processes experienced by this material. These IDPs consist of rather fragile conglomorates of silicates, metals and oxides, often bonded together by carbonaceous material. IDPs contain glassy spheroids with typical sizes of 0.2 μm; so-called GEMS – Glass with Embedded Metals and Sulphides. The metal and sulphide inclusions in the GEMS are typically ~ 10 Å . These GEMS are an important component within IDPs and may represent the most likely candidates for interstellar silicates (rather than solar system condensates; Bradley (1994)). The presence of paramagnetic inclusions and the good spectral match of 10 μm laboratory spectra of GEMS with interstellar spectra are often cited in support of this suggestion (Bradley 1994; Bradley et al. 1999; Martin 1995). IDPs and GEMS are extensively discussed by Keller & Messenger (this volume) and here we will focus on their implications for processing of interstellar grains.

The properties and morphology of GEMS are very characteristic for segregation induced by ion irradiation of silicate materials (Bradley 1994; Bradley & Dai 2004). Such processing requires high fluences of very energetic ions, which are not characteristic for the (bulk of the) solar nebula. Such an energetic ion environment can be found in very young supernova remnants during their adiabatic expansion stage (e.g., when radiative cooling of the shocked gas is unimportant) as well as in (some) planetary nebulae (from relatively massive progenitors) where jets extensively process the shells of material ejected during the preceding AGB phase (Westphal & Bradley 2004; Tielens 2003). Both of these environments are also prominent sources of silicate stardust and hence such dust would be expected to be heavily processed by energetic particles. High velocity jets from young stellar objects provide a third environment for such energetic processing of silicate material. These jets consist of disk material – either in a direct disk wind or accelerated through the X-point – and may contain small dust grains condensed out in the protoplanetary disk, in these ejecta themself, or entrained from the surrounding molecular cloud (cf., § 2.4.). In any case, dust formed in or entrained by these jets would be heavily processed. Recent analysis of the isotopic composition of GEMS show that some GEMS represent stardust with a nucleosynthetic origin in AGB stars, while others are rather mundane (Messenger et al. 2003). The former might be identified with silicates processed in PNe, while the latter more likely represent silicates formed around protostars, processed by YSO-jets, and deposited into the ISM.

5. Summary

We have reviewed the composition and origin and evolution of interstellar and circumstellar dust based upon astronomical observations and studies of stardust isolated from meteorites. There are a number of key issues to consider. First, are supernovae an important source of dust in the ISM ? There are a number of arguments in favor of a strong yes to this question. 1) The stardust record in meteorites contains a variety of SN condensates. 2) The physical conditions and timescales in the ejecta of SN 1987A were very similar to those in AGB winds which are known to be efficient dust producers. 3) SNe are an important source of heavy elements in the galaxy and in the ISM those are known to be locked up in dust. 4) Dust is abundant in the early universe where SNe are the only viable source of dust. Stardust attests to the wide variety of dust condensing in such environments. Given the conditions, the dust in SN may resemble dust formed by AGB stars with $\dot{M} \simeq 3 \times 10^{-7}$ $M_{\odot}$/yr, which is dominated by oxides (Cami 2001). Observationally, the situation is less clear. However, the Spitzer Space Telescope has the required sensitivity to sample all recent SN within 40 Mpc and, hence, these questions may be settled within the next three years.

Second, are young stellar objects an important source of (freshly condensed) dust in the ISM ? The answer to this question is less clear. Examining the mass budget, the winds from such object are potentially important. While their dust content is presently unknown, given the conditions (pressures, temperatures, timescale) in the inner regions of protoplanetary disks, dust formation could be very efficient. Dust formation is known to have been very efficient in the Solar nebula in those regions. The study of GEMS also provides support for a yes to this question. GEMS look highly processed and hence must have experienced a high radiation environment inconsistent with the outer solar nebula. Yet, some GEMS have a very mundane isotopic composition and cannot represent the alteration products of silicate stardust. Formation in protoplanetary disks and transport through protostellar jets/winds represent a promising origin for these GEMS. The stardust record has not yet been searched for silicates and oxides originating from such environments, but one might expect to see subtle variations (at the 0.1-1 % level) in the isotopes of Si and other species due to galactic chemical evolution. If the Stardust mission returns a large number of interstellar silicates with ‘normal’ isotopic composition, a large contribution by YSOs to the interstellar dust budget is almost unavoidable.

How important is kinetics in the formation of dust in the ejecta of stars ? Astronomically, the predominance of amorphous compounds (silicates, aluminum oxides, carbon) in stellar ejecta argues for dust condensation conditions well below equlibrium conditions for those compounds. Observations of AGB stars with low mass loss rates also suggest that kinetic effects (e.g., freeze out) are important. Analysis of SiC and TiC stardust grains, on the other hand, are in very good agreement with thermodynamic equilibrium calculations. In any case, the whole concept of thermodynamic condensation sequence has proven to be very powerful for stardust formation: essentially, all compounds predicted to be readily formed in stellar ejecta have indeed been identified in the astronomical and stardust record.

How much is dust processed by strong shock waves in the interstellar medium ? Theoretical studies of interstellar shocks predict strong processing. Studies of elemental depletions and their variations in the interstellar medium are also in favor of strong processing. Stardust studies on the other hand suggest very little processing. This discrepancy is not well understood but may point towards the importance of carbonaceous or oxide coatings in protecting dust grains against the effects of sputtering in shocks. The elemental depletion record also points towards rapid cycles of mantle accretion (in the cloud phase) and mantle erosion (in the intercloud phase). Astronomical observations have hitherto been fruitless in their searches for evidence for protective coatings. Stardust and IDP studies may be the most promising avenue for progress on this question. Supporting laboratory studies of the effects of shocks on interstellar grains will also be the key to settling this question.

What causes the variations in crystallinities between silicates in old star ejecta, the general ISM, and protoplanetary disks around protostars? Bombardment by cosmic ray ions provide a plausible crystalline-amorphous conversion process in the ISM. The high degree of crystallinity in protoplanetary disks points towards the importance of vaporization and recondensation under near-equilibrium conditions in the inner disks ($\lesssim$ 2 AU), followed by rapid transport outwards ($\gtrsim$ 10 AU). Here, laboratory experiments will be important as well to identify useful signatures of these processes.

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