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The mineralogy of cosmic dust: astromineralogy

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Abstract: Stardust is newly-formed in the ejected shells of gas that surround stars towards the end of their lives. Observations of the thermal emission from this dust, which is at relatively low temperatures ($T = 50$–200 K), in the circumstellar shells around these stars indicate that the dust consists of both amorphous and crystalline materials. The observed solid phases include: almost pure crystalline Mg-rich silicates (forsterite and clinoenstatite), amorphous silicates, diopside, spinel, oxides (corundum and $Fe_{0.9}Mg_{0.1}O$), and also carbon-rich solids such as: (hydrogenated) amorphous carbons, aromatic hydrocarbons and silicon carbide. Crystalline grains with isotopic signatures that indicate that they formed around evolved stars, and that therefore pre-date the formation of the solar system (*e.g.*, the pre-solar silicate, nanodiamond, silicon carbide, graphite, corundum, spinel, hibonite, titanium carbide and silicon nitride grains), have now been extracted from primitive meteorites. Pre-solar forsterite and amorphous silicate grains have also been extracted from interplanetary dust particles.

The dust formed around evolved stars is ejected into the surrounding interstellar medium by the relatively benign effects of stellar winds, where it is subject to stochastic and violent processing in fast supernova-generated shock waves. In this medium between the stars all the silicate dust appears to be completely amorphous and it is generally thought that dust processing, *via* ion irradiation/implantation in shocks and/or by cosmic rays, leads to the amorphisation of the crystalline silicate grains that were formed around the evolved stars. The formation of the dust, in circumstellar environments and subsequently ejected into the interstellar medium, is thus balanced by destructive processes that erode and eventually destroy it.

This paper introduces the subject of interstellar, circumstellar and pre-solar dust composition (Astromineralogy), discusses where the dust comes from, how it evolves and what its eventual fate might be.

Key-words: space, interstellar dust, circumstellar dust, stardust, astromineralogy.

Introduction

The space between the stars, the interstellar medium (ISM), has long been known to harbour copious quantities of gas and dust. The interstellar dust component of the ISM is responsible for the attenuation of the light from distant stars and galaxies. We now know that this dust is formed around stars at the end of their lives and we are thus able to observationally study newly-formed circumstellar dust (or stardust) in these environments. Fortunately, this dust has now passed from being an annoying obscuration into a whole field of study in its own, well-deserved right. Initially the proposed dust models were inevitably simple, *e.g.*, the dirty ice model, but have now advanced to the stage where we can now justifiably begin to call this field a branch of mineralogy (astromineralogy).

We have now amassed a wealth of information on interstellar and circumstellar dust from astronomical observations encompassing the far-ultraviolet to the mm wavelength regime. This is enormously augmented by the laboratory study of pre-solar grains; grains that pre-date the formation of the solar system and that were subsequently incorporated into meteorites and comets. Additionally, the so-called interplanetary dust particles (IDPs) are thought to be grain fragments from comets and asteroids that find their way into the inner solar system where they impact upon the Earth's stratosphere. There they can be non-destructively trapped into silica gel on panels suspended below the wings of high-flying NASA ER2 research aircraft at an altitude of 20–25 km (Sandford, 1987).

The study of the isotopic compositions of the pre-solar grains not only tells us about their origins but also enables us to, in turn, constrain and test our ideas of the nucleosynthetic processes that produce elements heavier than Helium within stellar interiors.

This review attempts to give an overview of the subject of astromineralogy; a science that is certainly in its infancy, is somewhat inexact and currently rather incomplete.

In order to help the reader navigate the inevitable astronomical terminology a Glossary and key to the acronyms follows.

Glossary and key to the acronyms

This section is designed to help the non-specialist negotiate the inevitable astronomical jargon.

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Amorphous silicates – identified *via* the infrared 9.7 μm Si–O stretching and 18 μm O–Si–O bending bands which are broad and featureless, indicating a lack of long-range structural order (see Fig. 2). This is the dominant state of silicate dust in the ISM.

Circumstellar (shells, nebulæ) – the regions surrounding stars which can extend out to hundreds of astronomical units from the star (1 AU = 1.496×10^{13} cm and is the Earth-Sun distance). PNe (see below) may be up to tens of thousands of AU across.

Cosmic rays – energetic (keV to GeV) electrons, protons, and ions originating from supernovæ.

Depletions/elemental depletions – the underabundance, in the gas phase, of the dust-forming elements (*i.e.*, of the atoms and ions of C, O, Mg, Si, Fe, etc.) with respect to an adopted standard for the elemental abundances in the ISM, *e.g.*, those for the Sun and meteorites (see Fig. 3).

Diffuse interstellar clouds – interstellar clouds in which the hydrogen is predominantly atomic (see ISM).

Evolved stars – the late stages in the life of low-mas stars ($M_\star < 8\ M_\odot$) when they have practically exhausted their hydrogen fuel, have left the main sequence of stellar evolution, shed their outer layers and expand to form red giants. Their ages are measured in billions of years (10^9 yr). This term encompasses stars of many types, including: those on the asymptotic and red giant branches of stellar evolution (AGB and RGB), stars luminous at radio wavelengths and showing OH radical and infrared dust emission (RL OH/IR), carbon-rich stars (C star) and, at later stages, planetary nebulæ (PNe, see below).

Extinction/reddening – a combination of the absorption and scattering of starlight by the intervening dust in the ISM (see Fig. 1). The term reddening comes from the fact that the transmitted light is redder than the source light.

(Hydrogenated) Amorphous Carbons – a very diverse, solid phase comprised solely of hydrogen and carbon, and consisting of aliphatic and aromatic carbon domains in variable proportions. Polycyclic aromatic hydrocarbons (PAHs) may be considered as the aromatic end-member of this class of solids.

Infrared Space Observatory, ISO – a European Space Agency (ESA) infrared satellite (1995–1998) with four onboard instruments: short and long wavelength spectrometers (SWS, 2.5–45 μm; LWS; 43–197 μm), a camera (ISOCAM, 2.5–17 μm) and a photometer (ISOPHOT, 2.5–240 μm).

Interplanetary dust particles, IDPs – particles of asteroidal and cometary origin orbiting in the interplanetary medium, samples are recovered in the Earth's stratosphere by aircraft (see Introduction).

Interstellar dust – dust in the ISM, a mix of stardust, re-processed stardust and dust formed *in situ* in the ISM.

Interstellar medium, ISM – literally the medium between the stars, defined by the ionised, atomic or molecular state of the most abundant element hydrogen. The diffuse, atomic ISM has a density of several tens of H atoms cm^{-3} and is almost transparent to stellar photons. The molecular ISM has H_2 densities $\sim 10^3$–10^6 cm^{-3} and is practically opaque to stellar photons.

Interstellar shock – a supersonically-propagating discontinuity in the density, temperature and velocity of the interstellar gas that can be caused by SN explosions or, more generally, arising from the jets and winds from stars. SN shock velocities may be as high as thousands of km s^{-1}.

Mass loss – the shedding of stellar mass into the circumstellar environment that occurs towards the end of a star's life (see Evolved stars) or around young, very massive stars such as Wolf-Rayet stars (see below).

Molecular clouds – interstellar clouds in which the hydrogen is predominantly molecular (see ISM).

Nanodiamonds – nanometre-sized diamond particles with hydrogen-terminated/passivated surfaces. The presolar nanodiamonds have sizes of the order of 3 nm.

Nova – a binary system containing a white dwarf in which there is episodic accretion of matter (principally hydrogen) from the companion star onto the surface of the white dwarf which then undergoes a cataclysmic nuclear explosion. Dust can form on rather short time-scales (of order months) in nova ejecta.

Planetary nebulæ, PNe – the final evolutionary stages of low-mass stars that have exhausted their hydrogen fuel (the PN phase lasts $\sim 10^4$ yr). The outer stellar layers are shed and the stellar remnant becomes a white dwarf (consisting of degenerate matter, with densities equivalent to an object with the mass of the Sun but the size of the Earth).

Pre-solar – matter, including stardust grains, that existed before the formation of the solar system and that is identified as such by its non-solar isotopic composition.

Solar mass, $M_\odot$ – the mass of the Sun, 1 $M_\odot = 1.989 \times 10^{33}$ g.

Stardust – silicate, oxide or carbonaceous dust formed in the circumstellar shells (see above) around evolved stars or supernovæ.

Stellar winds – the ejected matter generally arising from newly-forming stars and stars at the end of their life (see also Mass loss and Evolved stars). Stellar wind velocities can be anything from tens to thousands of km s^{-1}.

Supernovæ, SNe – the catastrophic explosion that ends the lives of stars more massive than 8 $M_\odot$ and that greatly affects the structure of the ISM (*via* shock waves) and the cycling of matter between its component phases. Stars that explode as SN live fast and die young (within millions of years). Dust formation can occur around SNe on timescales of the order of years.

Wolf-Rayet star, W-R – massive, hot stars ($M_\star > 20\ M_\odot$) that shed a significant fraction of their mass at rates of $\sim 10^{-5}\ M_\odot$ yr^{-1} in the form of stellar winds (see above) with velocities up to 2000 km s^{-1}. WC stars are carbon-rich Wolf-Rayet stars.

Dust in space

Table 1 shows a comparison of the known interstellar, circumstellar (stardust) and pre-solar dust compositions (see Jones 2001, 2005, and references therein). This table includes some relatively recent results for the pre-solar silicate stardust grains extracted from interplanetary dust particles, IDPs, (Messenger *et al.*, 2003) and a primitive

Table 1. A comparison of interstellar, circumstellar (stardust) and pre-solar (including some stardust) grain compositions. Here interstellar grains are those detected spectroscopically (*i.e.*, detected through characteristic absorption and/or emission bands) in the ISM, circumstellar grains are those detected spectroscopically in the circumstellar shells around stars and pre-solar grains are those meteoritic and interplanetary grains analysed directly in the laboratory and determined to pre-date the formation of the solar system. [*text*] indicates grains materials that have only been indirectly, rather than spectroscopically, identified in a given interstellar or circumstellar phase.

Interstellar	Circumstellar	Pre-solar
Hydrocarbons		
aromatic	aromatic	aromatic
aliphatic	aliphatic	—
—	—	graphite
—	[*nano*]diamond	nanodiamond
Silicates		
amorphous	amorphous	amorphous
—	Mg-rich crystalline (forsterite, Mg_2SiO_4; clinoenstatite, $MgSiO_3$; diopside, $CaMgSi_2O_6$)	Mg-rich crystalline (forsterite, Mg_2SiO_4; olivine; pyroxene)
Oxides		
[*MgO & FeO*]	crystalline oxides ($Fe_{0.9}Mg_{0.1}O$; spinel, $MgAl_2O_4$; corundum, Al_2O_3)	crystalline oxides (spinel, $MgAl_2O_4$; hibonite, $CaAl_{12}O_{19}$; corundum, Al_2O_3)
Carbides		
—	β-SiC	β-SiC
—	—	TiC & FeC (as graphite inclusions)
Nitrides		
—	—	Si_3N_4

meteorite (Mostefaoui & Hoppe, 2004). Note that there is in general a rather good correspondence between the different dust samplings presented in Table 1. Probably the most important exceptions to this are the lack of crystalline silicates and carbides in the ISM. The non-detection of these dust species may be due to their low abundance and the dilution of their observable characteristics by other more abundant dust species. However, the lack of crystalline silicates may also be due to their amorphisation by ion irradiation in the ISM; we will return this process later. We also note the non-detection of graphite in circumstellar regions and in the ISM.

Evidence for dust in space

The presence of dust in space is revealed by astronomical observations that also convey essential information about its very nature (chemical composition, size distribution, structure, shape, *etc*.). In the following we list some of the major evidence for the presence of, and nature of, dust in space:

Extinction or reddening: the light from a distant star, or galaxy, is diminished in intensity and 'reddened' due to absorption by dust and a preferential scattering of blue light. Extinction, primarily, conveys information on the dust sizes (5–500 nm) and its distribution which is approximately a power law, *e.g.* Mathis *et al.* (1977). Figure 1 shows the wavelength dependence of the interstellar extinction from the infrared (IR) to the ultraviolet.

Absorption spectroscopy: is analogous to the laboratory technique, except that the source is some distant star and the sample is an intervening cloud of interstellar gas and dust. This technique, in the IR, probes solid-state vibrational transitions and gives information on the nature of the interatomic bonding and on chemistry of the dust (see Fig. 2).

Polarisation: the starlight traversing the ISM becomes polarised by interaction with the dust (see Fig. 1). For example, the observed wavelength-dependence of the linear polarisation at optical wavelengths and, in the infrared, of the 9.7 μm Si–O silicate stretching band tells us that the silicate grains have sizes ~ 100–500 nm, have a magnetic moment, are non-spherical, are rotating and are aligned with the interstellar magnetic field.

Elemental depletions: using an assumed standard for the elemental abundances in the ISM, *e.g.*, those for the Sun and meteorites, we observe a clear underabundance, in the gas phase, of the dust-forming elements (*i.e.*, of the atoms and ions of C, O, Mg, Si, Fe, *etc*.). The missing atoms are assumed to be incorporated into dust and are therefore not directly observable (see Fig. 3).

Dust thermal emission: is the thermal emission (at IR-mm wavelengths) from dust that is heated by stellar photons, the larger grains are in thermal equilibrium with the stellar radiation field ($T \approx 15$–20 K) and the small grains, with heat capacities less than the mean stellar photon energy, undergo stochastic heating (to $T \sim 100$–1000 K) upon single photon absorption events. Figure 4 shows the typical

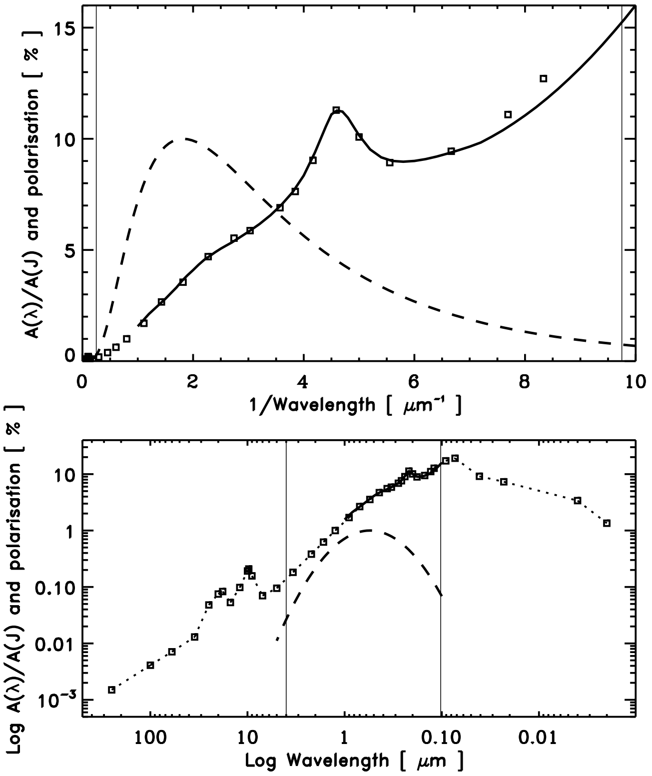

Fig. 1. Upper plot: the extinction curve (solid line) and the wavelength dependence of the interstellar polarisation (dashed line) in a linear extinction *vs.* linear inverse wavelength form. Lower plot: the same data as the upper plot but shown in a log-log form in order to show the behaviour over a wider wavelength range (the extinction is here shown as a dotted line for clarity). The thin vertical lines indicate the same wavelengths in each plot. Here the extinction, $A(\lambda)$, is normalised to a wavelength of 1.25 μm (the so-called J band).

dust thermal emission spectrum for the Galaxy from the near-IR to mm wavelengths.

Dust mineralogical nomenclature

Astromineralogy is by its very nature an inexact science because often no hands-on direct analysis is possible, except in the case of the pre-solar meteoritic and IDP grains. Thus, care is needed in applying the well-determined mineralogical nomenclature in the interpretation of astrophysical observations. Current observations of dust in space often do not allow us to identify the exact chemical composition of the detected minerals because the infrared spectroscopy is often of insufficient resolution. Studies of the interstellar depletions (*i.e.*, the quantity of a given element locked-up in dust) along various lines of sight, which can be used to indicate the chemical composition of the dust (*i.e.*, the stoichiometry), tell us nothing whatsoever about the mineralogical structure or phases of that dust. Jones (2000) therefore suggested the following guidelines for the astrophysical usage of the mineralogical nomenclature:

(1) Where a grain composition is determined by comparison with laboratory spectroscopic data on specific minerals, then the terms Mg-rich, Fe-rich *etc.* be applied to the generic mineral name when it is clear that the mineral is rich in a particular cation, *e.g.*, Mg-rich olivine, Fe-rich pyroxene, *etc.* Otherwise, just the generic mineral name should be used, *e.g.*, olivine or pyroxene. However, in certain cases, minerals such as forsterite can clearly be identified through their characteristic thermal emission spectrum at mid- to far-IR wavelengths (*i.e.*, 10–100 μm). In these cases the application of the specific mineral name would be justified.

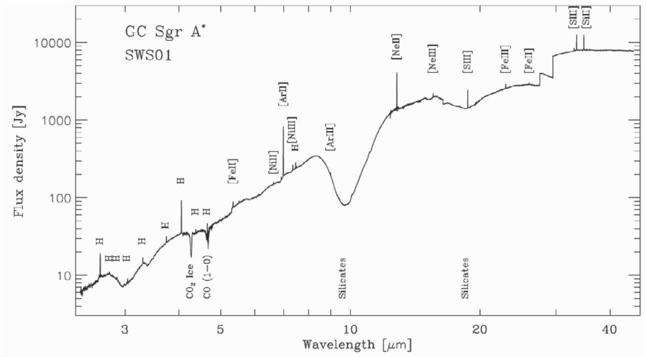

Fig. 2. The spectrum of the dust along the line of sight towards the Galactic Centre in units of Janskys. The major dust absorption features are the broad bands at ≈ 3 (H_2O ice OH stretching), 3.4 (hydrogenated amorphous carbon aliphatic CH stretching), 10 and 20 μm (both due to amorphous silicates) and also a narrower CO_2 solid-state ice absorption. The gas phase CO (1–0) line is also seen in absorption. Note that the discontinuities near 30 μm are artifacts. Also seen in the spectrum are emission lines of hydrogen (H) and ionic fine structure lines shown in square brackets, where [SIII] indicates a S^{++} line, [FeII] a Fe^{+} line etc. (Reproduced from Lutz *et al.*, 1996 with permission from A&A).

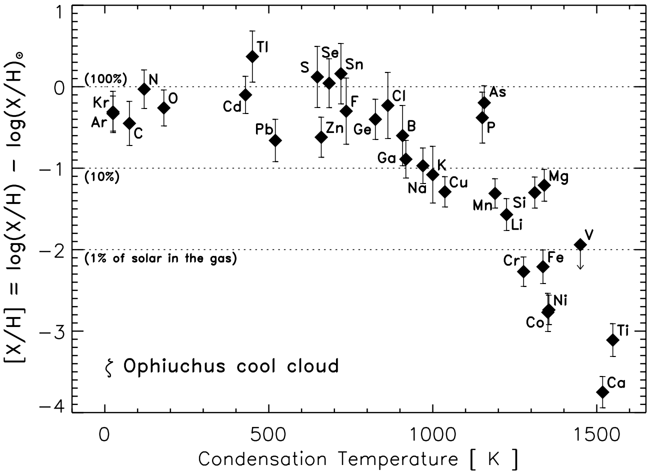

Fig. 3. The interstellar depletions as observed along the line of sight through the cool interstellar cloud towards the star ζ Ophiuchus, after Palme & Jones (2004). The depletions are plotted as a function of the elemental condensation temperature. (X/H) is the abundance of the element X with respect to hydrogen along the observed line of sight and $(X/H)_{\odot}$ is the solar abundance of the element here used as the reference.

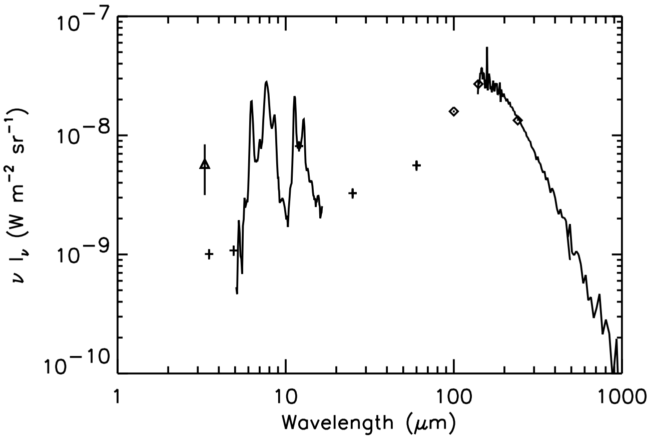

Fig. 4. The observed thermal emission spectrum of dust in the diffuse ISM taken from a selection of, mostly space-based, telescope observations. The units of the emission are given in intensity units multiplied by the frequency in order to give an idea of the relative energy contributions. Note that only broad-band photometric data (the data points), rather than spectra (the solid lines), are available over certain wavelength regions.

(2) Where the grain composition is determined from measurements of depletions alone (*i.e.*, where there is no complimentary spectroscopic information available) and only an inferred stoichiometry can be derived, which is dependent on the adopted reference abundance. Then the dust should simply be referred to as of a particular mineral "-type," and where relevant the cation enrichment indicated, *e.g.*, Mg-rich olivine-type silicate, olivine-type silicate, Fe-rich pyroxene-type silicate, *etc*.

In the second case, and on the basis of depletion studies alone, it is almost impossible to discern the difference between a silicate structure and a mix of oxides of the same stoichiometry. Indeed amorphous interstellar silicates might easily be considered in terms of a mixture of oxides. The use of a scheme such as the one suggested above hopefully avoids "over-specific" labels being attached to interstellar and circumstellar dust compositions and reflects the unavoidably inexact nature of cosmic mineralogical studies.

Dust formation

It has been long noted that elements with the highest condensation temperatures generally have the highest depletions in the ISM (see Fig. 3). The 'missing' elements are then assumed to be locked-up in dust where they are not directly observable. This would seem to be consistent with grain condensation in cool stellar atmospheres as originally suggested by Field (1974).

The dust life-cycle and stars

The life-cycle of dust in the ISM is intimately bound to the evolution of stars. For, in general, new dust (stardust) is formed around 'old' stars, *i.e.* in the circumstellar environments of evolved low-mass stars ($M_\star < 8\ M_\odot$, where $M_\star$ is the stellar mass and the solar mass $M_\odot = 1.989 \times 10^{33}$ g) nearing the ends of their lives or as they explode as supernovæ (SNe; in this case $M_\star \geq 8\ M_\odot$). Conversely, 'old' dust in the ISM is eventually incorporated into stars newly-forming in dense molecular clouds – clouds in which the density is of the order of a few thousand to a million hydrogen nuclei per cm^{-3}, where the predominant form of hydrogen is H_2 and much of the carbon and oxygen are in the form of CO molecules. The dust resides in the ISM for a considerable time and is processed during its time there. Old interstellar dust is therefore seen in the circumstellar nebulæ and discs illuminated by the newly-forming stars.

The presence of circumstellar dust around evolved stars is generally revealed by its opacity (absorption and scattering) and by its infrared thermal continuum emission. This dust is rather passively transported into the ISM, *via* stellar winds with velocities of the order of 10 km s^{-1}, where it is then subject to processing. This processing may be destructive, including erosion and fragmentation in SN-generated shock waves, or constructive *via* mantle accretion and coagulation in denser and more quiescent regions. Observations indicate that evolved stars with the highest mass-loss rates show the presence of dust, implying a clear link with dust formation in these environments (Jura, 2004; Waters, 2004).

Dust forms, predominantly, in the shells around evolved stars in the red giant branch (RGB) and asymptotic giant branch (AGB) stages of their evolution (*e.g.*, M giants, carbon stars and radio luminous OH/IR stars). However, some small fraction is also formed in the circumstellar shells around supergiants, novæ, planetary nebulæ (PNe) and WC stars, *e.g.*, Jones *et al.* (1997) and Dwek (1998). Dust is also known to form in the ejecta of SNe, although their exact contribution to the stardust budget, which could be large, is currently not well-determined. We shall now use the term *stardust* to indicate dust newly-formed in circumstellar environments.

Interstellar dust, the dust which resides in the ISM, is then likely to be a mixture of stardust, reprocessed stardust and a dust component formed *in situ* in the ISM. The latter is likely to be found on the surfaces of pre-existing grains rather than as a separate grain population due to the long time-scales that would be required for grain nucleation in the low densities of the ISM.

Sources of stardust

Table 2 shows the primary contributors to the stardust budget in our Galaxy (Dorschner & Henning, 1995; Dwek, 1998; Jones, 2001; Jones *et al.*, 1997). Note, in particular, the predominant dust contributions from the evolved stars, *i.e.*, the RGB/ AGB stars (M giants, RL OH/IR and C stars), and the large uncertainties for SNe. Currently we have no observational evidence that SNe are major dust producers because of the inherent difficulty in determining the SN-produced dust mass. In fact we do know that some supernovæ are dust producers for the supernova SN 1987a

Table 2. The contribution of stellar sources to the dust in the ISM (Dorschner & Henning, 1995; Dwek, 1998; Jones, 2001; Jones *et al.*, 1997). sil. indicates silicate/oxide dust species and C indicates carbonaceous dust species (including amorphous carbons, hydrogenated amorphous carbons, graphite and polycyclic aromatic hydrocarbons or PAHs). Note that where a range of values is given (novæ and supernovæ) this reflects the large observational uncertainties in determining the respective contributions.

Stellar source	Contribution ($\times 10^{-6}\ M_\odot$ kpc^{-2} yr^{-1})	Type(s) of dust
M giants	3	sil.
RL OH/IR	3	sil.
C stars	3	SiC, C
supergiants	0.2	sil.
novæ	0.003–0.2	sil., SiC, C
PN	0.03	C
WC stars	0.03	C
supernovæ	0.03–14	sil., C

was observed to produce at least $10^{-4}\ M_\odot$ of dust about 775 days after the explosion (Wooden *et al.*, 1993). If this is typical of SNe dust production then their total contribution to the Galactic dust budget would be low.

The dust from all circumstellar sources is injected into the ambient ISM by rather benign stellar winds and the total stardust formation rate is of order 8–30 × $10^{-6}\ M_\odot$ kpc^{-2} yr^{-1} averaged over the entire Galaxy (1 kpc is one kiloparsec or 3.086×10^{21} cm and the rate here is expressed per unit area of the Galaxy). These stardust sources are indeed reflected in the isotopic compositions of the analysed pre-solar grains which also show some grains of SN origin (Hoppe, 2004). The dust formation rate depends on the unknown efficiency of dust formation in SNe (Dwek, 1998; Jones *et al.*, 1997). However, even if SNe are not efficient at producing dust directly, they are the nucleosynthetic 'factories' that produce the elements that make up interstellar dust (*e.g.*, Fe, Si, Mg and O atoms that could later condense into silicate and oxide grains).

Dust around evolved stars

Our current knowledge of the nature of the stardust produced by RGB/AGB stars was enormously augmented by the 2–200 μm spectroscopic data furnished by the short wavelength spectrometer (SWS, 2.5–45 μm) and long wavelength spectrometer (LWS, 43–197 μm) instruments, and also by the infrared spectroscopic camera (ISOCAM), onboard the European Space Agency's Infrared Space Observatory (ISO). From these, and earlier, observations it is clear that the nature of the dust forming in these environments is a function of the chemical composition of the locally ejected material. In fact, it is the ratio of the abundances of carbon and oxygen (C/O) that is the critical parameter.

In particular, it was the spectroscopy performed by the ISO satellite that showed us that a significant fraction, perhaps as high as 15 %, of the stardust formed around oxygen-rich, evolved stars may be in the form of crystalline silicates such as Mg-rich olivines (forsterite, Mg_2SiO_4), pyroxenes (clinoenstatite, $MgSiO_3$) and diopside ($CaMgSi_2O_6$) (Waters, 2004). The relative fractions of these minerals vary with the type and evolutionary stage of the stars. We note, rather interestingly, that no iron-rich crystalline silicates have yet been identified in these regions. However, it is assumed that the amorphous silicates probably contain much of the iron but that for some reason, not yet fully understood, that they do not crystallise. The observed dust composition around some OH/IR stars is consistent with the condensation of dust from a gas of cosmic composition, *i.e.*, along the likely sequence diopside and forsterite condensing at high temperatures (~ 1000–1400 K) and then the conversion forsterite → clinoenstatite at lower temperatures (Demyk *et al.*, 2000). Note that the higher temperature Ca-containing melilite phase has not yet been observed in these circumstellar environments.

Observations of the dust in the shells around carbon-rich stars, by contrast, show dust species including SiC, amorphous hydrocarbons and polycyclic aromatic hydrocarbon-like species. Additionally, a broad emission band centred at ~ 30 μm has been attributed to MgS. The pre-solar meteoritic grains indicate that SiC and graphite grains also form here but they are not observed in the ISM probably because of their low abundance compared to other materials that dominate the dust absorption and emission.

A mixed O-rich and C-rich dust chemistry/mineralogy around stars is also possible and may be due to the nucleosynthesis switching from O-rich to C-rich, or vice-versa, or to binary systems in which the two stars have different compositions, *i.e.*, one O-rich and the other C-rich.

The details of dust formation

High rates of mass-loss from a star at the end of its life (10^{-5}–$10^{-7}\ M_\odot$ yr^{-1}) eject matter into a circumstellar shell. This stage of stellar evolution corresponds to high densities in the stellar photosphere which are thus conducive to stardust formation. Table 3 shows how the dust composition varies with the rate of mass loss from the star for O-rich evolved stars. Note that the stellar mass loss rate varies with both the age of the star and its mass. Also note that such high mass loss rates from a relatively low mass evolved star ($M_\star < 8\ M_\odot$) clearly cannot be sustained for long time-scales, with respect to the stellar age (of the order of 10^9 yr), because of the limited mass available. Thus, the mass loss phase from an evolved star is relatively short-lived (10^3–10^4 yr) and, hence, relatively few such objects are observed in the Galaxy.

The critical step in the grain formation process is the growth of the nuclei that seed grain growth in these dense stellar photospheres. It is these seed nuclei that then form the accretion/growth centres for the dust forming in the shells and winds around evolved stars (*e.g.*, the high temperature carbides seen as graphite inclusions, see Table 1).

Table 3. The dust composition as a function of the stellar mass loss rate given in units of solar masses ($1\ M_\odot = 1.989 \times 10^{33}$ g) of matter ejected per year ($M_\odot\ yr^{-1}$), after Waters (2004). PNe are planetary nebulæ. The last entry in the table indicates some rarer dust species that are also seen around a small number of RL OH/IR stars and PNe.

Stellar mass loss rate ($M_\odot\ yr^{-1}$)	Dust composition
$\approx 10^{-7}$	oxides ($Fe_{0.9}Mg_{0.1}O$; spinel, $MgAl_2O_4$; corundum, Al_2O_3) amorphous silicates (a minor component)
$\approx 10^{-6}$	amorphous silicates (observed in emission)
$\approx 10^{-5}$	amorphous silicates (seen in absorption) Fe-poor crystalline silicates (Mg-rich olivine and pyroxene, 5–15 % of the dust mass)
$> 10^{-5}$	H_2O ice also observed
RL OH/IR stars + PNe	diopside, $CaMgSi_2O_6$; calcite, $CaCO_3$; dolomite, $CaMg(CO_3)_2$ at < 1 % of the dust mass

Note that there is, in these environments, a window of opportunity for dust formation. Efficient dust formation requires high densities in a cooling gas. In a stellar wind expanding away from a central star the cooling of the gas is associated with a decrease in the gas density. The inner edge to the dust formation window is defined by the condensation temperature of the dust in the gas close to the star and the outer edge to the window is defined to be where the gas density is too low for significant grain growth to occur.

It was shown long ago that grain nucleation models based upon classical homogeneous nucleation theory are not valid (Nuth & Donn, 1983). Unfortunately the grain nucleation step is almost certainly the least understood stage in the dust formation process despite much progress that has been made in our understanding, *e.g.*, Frenklach & Feigelson (1989), Woitke *et al.* (1993) and Patzer *et al.* (1998). However, having said this, Gail and Sedlmayr and co-workers have undertaken a long-term investigation of dust formation in circumstellar shells using rather sophisticated models, *e.g.*, Dominik *et al.* (1989), Woitke *et al.* (1993), Gail & Sedlmayr (1999) and Schirrenmacher *et al.* (2003), and have had a great deal of success in explaining dust formation around evolved stars and in proto-planetary discs. Evidence from some pre-solar grains supports the generally-proposed dust condensation schemes. In particular, the discovery of refractory titanium and iron carbide inclusions at the centre of graphite pre-solar grains, indicates that the first dust species to form are very small seed grains composed of the most refractory/highest condensation temperature materials. The nature and details of the grain nucleation process will not be discussed further here. The interested reader can refer to the above articles and the references within for a more detailed understanding of this fundamental area.

Dust formation in the ISM

The observed depletions of the elements from the gas phase in the ISM (*e.g.*, see Fig. 3), used to derive the overall dust stoichiometry, can be explained by the low temperature process of grain growth *via* the accretion of atoms/ions from the gas phase (Savage & Sembach, 1996). These atoms having perhaps been previously-eroded from dust in energetic environments such as shocks. The observed elemental depletion patterns, as shown in Fig. 3, could then result from a selective accretion process in which the elements with high condensation temperatures accrete first. This basically reflects the fact that the highest condensation temperature materials are generally those with the highest interatomic binding energies.

It can be rather simply shown that the accretion time-scale for a cloud of hydrogen atom (*i.e.* proton) density n_H (cm^{-3}) is $\approx 10^9/n_H$ yr. For a cloud with a density of typically tens of H atom cm^{-3} the accretion time-scale will be of the order of 10^7–10^8 yr, *i.e.*, similar to the ISM cycling time-scale of $\sim 3 \times 10^7$ yr, which is primarily driven by the formation of massive stars in molecular clouds that eventually explode as SNe (McKee, 1989). Thus, the accretion of gas phase ions and atoms onto grains in the low-density ISM probably plays only a minor role in determining the observed elemental depletions patterns. In higher density regions the accretion will be faster but then the mantles will probably be formed far from equilibrium. We would therefore expect the grain mantles to be amorphous and chemically heterogeneous. However, Draine (1990) points out that selective accretion and desorption processes could provide the means to form chemically distinct carbonaceous and silicate/oxide dust species in the ISM. However, the

Table 4. The nature of the pre-solar grains extracted from meteorites. The respective stellar sources are: red giant or asymptotic giant branch stars (RGB/AGB stars), carbon-rich AGB stars (C-rich AGB stars), supernovæ, Wolf-Rayet stars (W-R stars). (ppm = parts per million, ppb = parts per billion.)

Composition	Typical sizes [μm]	Abundance	Stellar sources
nanodiamond	0.003	1400 ppm	SNe?
SiC (mainstream)	0.1–20	14 ppm	C-rich AGB stars
graphite	0.8–12	10 ppm	SNe, W-R stars
corrundum	0.3–5	0.1 ppm	RGB/AGB stars
SiC (X grains)	0.5–10	0.1 ppm	SNe
Si_3N_4	∼ 1	10 ppb	SNe
spinel	1–5	3 ppb	RGB/AGB stars
hibonite	1–5	1 ppb	RGB/AGB stars
amorphous silicate	0.15–0.6	5 grains	RGB/AGB stars
crystalline silicates (forsterite, olivine, pyroxene)	0.2–0.9	8 grains	RGB/AGB stars

exact pathways for this chemical segregation have yet to be uncovered.

Dartois *et al.* (2004) have shown that a hydrogen-rich, hydrogenated amorphous carbon solid (a-C:H) produced *via* the photolysis of methane at low temperatures gives a good fit to the diffuse ISM 3.4, 6.85 and 7.25 μm features which are due to the aliphatic C–H stretching and bending vibrations and the aromatic C–C stretch, respectively. Thus, it has been proposed (Dartois *et al.*, 2004; Jones *et al.*, 1990) that such a material forms by the accretion, and subsequent processing, of simple hydrocarbon 'molecular' species in the ISM. This interesting result may provide some indirect evidence for a selective hydrocarbon accretion process operating in the ISM.

In the low density ISM, where the extinction of starlight is relatively weak, the photodissociation of molecules by UV photons generally hinders the formation of complex molecules. However, and as the name implies, in heavily shielded, dense molecular clouds, rather complex molecules can form and can accrete onto the surfaces of the grains to form icy mantles. The ices generally consist of simple molecules such as H_2O, CO, CO_2, and CH_3OH, see for example Schutte (1999). Here the icy mantle is formed *via* the accretion of molecules, and their precursors, formed in the gas phase *via* rather well understood chemical pathways. Further chemistry may occur on the grain surfaces through reactions with accreted radicals/atoms/ions and UV photon-driven photolysis. Interstellar gas phase chemistry occurs over long time-scales in a very low density medium. The long time-scales and low densities allow 'unstable' radical species to exist in measurable abundances. The ISM can therefore serve, in some cases, as a ideal observational laboratory for determining the 'molecular' parameters of species that are difficult to measure in a terrestrial laboratory.

Icy mantle formation in the dense ISM is more than likely accompanied by relatively low-velocity grain-grain collisions leading to grain growth *via* coagulation. When star formation occurs in these regions the icy mantles may subsequently be processed into more complex chemical species by UV photons or evaporated into the gas phase.

The direct analysis of stardust

The pre-solar stardust grains extracted from the carbonaceous chondritic meteorites clearly survived residence in, and transport through, the ISM before their eventual incorporation into the solar system. We note that the, to date, extracted samples of stardust are very refractory materials (*e.g.*, diamond, SiC, graphite and Al_2O_3) and are not thought to be 'typical' interstellar grains. This is a bias that results from the harsh treatment with strong acids during the extraction process. However, crystalline silicate grains (forsterite, olivine and pyroxene) are now being extracted in quantity from IDPs, *e.g.*, Messenger *et al.* (2003), and from meteorites, *e.g.*, (Mostefaoui & Hoppe, 2004), using gentler extraction methods. These grains retain both their chemical and mineralogical integrity, and also an isotopic memory of their formation environment (their pre-solar signature). In addition to the crystalline silicates Messenger *et al.* (2003) and Mostefaoui & Hoppe (2004) also found amorphous, pre-solar silicates that may represent the stardust silicates that were chemically and mineralogically, but not isotopically, homogenised in the ISM through the effects of SN shocks.

How do we know that these grains are pre-solar? The simple answer to this question is that the isotopic compositions of many of these grains have been measured and that the measured values are often far from the solar system values. Thus, they must be of extra-solar origin. Additionally, the isotopic anomalies are found to be characteristic of the nucleosynthetic processes that occur within particular types of star at particular phases in their evolution. Hence we also know where they come from.

The variety of stardust grains and the relatively large numbers of different stellar birth sites that seem to be indicated (Hoppe, 2004) imply that stardust is transported over large galactic distance scales. Further, some fraction of this dust survives, or is never subjected to, processing in the ISM.

Dust evolution in space

Dust, far from being a passive component of the ISM, is an active participant in many astrophysical processes, *e.g.*, the catalytic formation of molecular hydrogen on grain surfaces, UV photon absorption leading to energetic photoelectron emission that subsequently heats the gas, etc. However, dust is itself also subject to violent processes that can substantially modify or even destroy it. The evolution of the physical characteristics of silicate grains in different environments is a good example of this.

The effects of interstellar shocks

Observations show clear correlations between the observed elemental depletions (the elements locked-up in dust) and the gas velocity and density along a given line of sight, implying that strong shock waves in the low density ISM destroy dust (Cowie, 1978; Routly & Spitzer, 1952).

Interstellar shocks, resulting from SN explosions, differentially accelerate and sweep up the gas and dust and the gas, because of its lower inertia, is swept up more rapidly than the dust. The shocks are magnetised and the grains are predominantly negatively charged, due to the fact that in the hot post-shock gas the electrons move faster, and collide more frequently with the grains, than the heavier ions. Upon the arrival of a shock the charged grains therefore gyrate around the magnetic field lines and undergo an acceleration. This acceleration is opposed by collisions with the shock-accelerated gas, which eventually result in a complete coupling between the shock-accelerated gas and dust, *i.e.* all the fluids move as one.

Dust destruction in SN-generated shocks has received much theoretical study, see McKee (1989) and Jones (2004) and references therein for a review of the subject. Theoretical studies (Jones *et al.*, 1994, 1996) seem to indicate interstellar grain lifetimes of the order of $4\text{–}6 \times 10^8$ yr. Here the lifetimes, defined as the time to destroy the entire dust mass in the ISM, are based on our current models for the degree of destruction of dust as a function of the shock velocity, the assumed structure of the ISM and the cycling times between the different phases of the ISM (McKee, 1989).

In contrast, the mass injection time-scale for stardust formed by evolved stars and supernovæ is longer and is of order 3×10^9 yr (Dwek, 1998; Jones & Tielens, 1994). Thus, there is a time-scale discrepancy which is clearly at odds with the observations of dust in practically all phases of the ISM. We are thus drawn to the conclusion that dust must also be formed, or rather re-formed, *in situ* in the ISM, as discussed above.

Interstellar silicate evolution

Observations of silicates in emission in evolved star dust shells (Waters, 2004) and in comets (Crovisier *et al.*, 1996; Hanner *et al.*, 1994) indicate the presence of Mg-rich crystalline silicates. These observations raise some interesting questions concerning the nature and evolution of silicate grains in the ISM. For instance, and in contrast to these results, observations of the interstellar silicate Si–O stretching and O–Si–O bending modes, which occur at 10-μm and 18-μm respectively, indicate that the silicate grains are completely amorphous (Mathis, 1990). Thus, some process amorphises crystalline silicates after their injection into the ISM. Additionally, some other process crystallizes amorphous interstellar silicates before their incorporation into cometary bodies and the dust shells around young stars. Generally comets are thought to be the pristine reservoirs of some of the nascent molecular cloud material from which the solar system formed. Thus, the mix of cold molecular cloud ices and crystalline silicates is something of a paradox.

It is perhaps easy to understand how high energy, atomic and ionic collisions in SN-generated shocks could amorphise a material. Indeed, Demyk *et al.* (2001) and Carrez *et al.* (2002a,b) undertook a lengthy series of silicate irradiation experiments that clearly indicate the efficiency of the implanatation/amorphisation process and, in some cases, a change in the stoichiometry of the target silicate. However, it is difficult to find a process in which amorphous grains could undergo crystallization without sustained heating to temperatures greater than 1000 K (Hallenbeck *et al.*, 1998). Thus, if the recrystallization of amorphous dust does occur it can only be in the vicinity the star where it would be hot enough to heat the dust to temperatures > 1000 K for extended periods. Hence, in order to explain the mixing of cold molecular cloud ices with crystallised silicates it is necessary to invoke some kind of radial mixing in the early solar nebula whereby silicate dust enters the inner regions of the pre-planetary disc, is partially crystallised and is then ejected into the cold outer regions where it can then accrete molecular ice mantles from the extended solar nebula and be incorporated into comets.

Summary

This paper is an attempt to introduce the exciting, and rapidly-developing, subject of interstellar and circumstellar dust (Astromineralogy) to the non-astronomical specialist. Our current understanding of the chemical and mineralogical composition of this dust is far from complete. However, thanks to major advances in detector technologies, we are now capable of detecting the effects of this dust from far-ultraviolet to mm wavelengths, *i.e.*, over four orders of magnitude in wavelength.

The effects of interstellar dust are evident in the night sky even with the naked eye. The dark lanes of obscuration that we see traversing the Milky Way are due to absorption by clouds of dust primarily located in the plane of the Galaxy. This obscuration, called extinction by astronomers, is due to the combined effects of absorption and scattering of starlight by small, nm- to μm-sized, dust particles. The variation of the extinction with wavelength, and the associated polarisation of the visible starlight by this dust provide critical information on the dust chemical/mineralogical composition, its size distribution and also on its magnetic properties. Additionally, we can now observe the IR to mm wavelength thermal emission coming from this dust which is primarily heated by stellar photons. Typical dust temperatures measured by these observations are of the order of 20 K for the larger, μm-sized grains. For the smallest, stochastically-heated, nm-sized particles the absorption of photons can lead to instantaneous, and very short-lived (a fraction of a second), peak temperatures of the order of hundreds of degrees K.

The formation of new dust, or 'stardust' is generally associated with the 'dying' phases in a star's evolution after it has left the main sequence, where is has safely spent most of its life. Observations show that the major dust-forming elements must be C, O, Si, Mg and Fe, with other elements (*e.g.*, Na, Al, Ca and Ni) making much smaller contributions. This simply reflects the relative abundances of the elements available, *i.e.*, the so-called 'solar' or 'cosmic' abundances that are determined by the nucleosynthetic reactions occurring in the interiors of stars. Spectroscopic observations reveal that the dust compositions are C-rich (complex solid hydrocarbons) and O-rich (silicates and oxides).

In detail, spectroscopic observations of circumstellar dust made with the ESA's Infrared Space Observatory, at 3–200 μm wavelengths, discovered thermal emission from crystalline silicates (at $T = 50$–200 K), in addition to the long-observed amorphous silicates, in the dust shells around evolved stars. Prior to the ISO mission all silicates in space were thought to be amorphous as a result of their rapid, non-equilibrium formation in low-density circumstellar shells. The observed crystalline minerals are: olivines, forsterite – $(Mg_x,Fe_{(1-x)})_2SiO_4$ ($x > 0.9$); pyroxenes, clinoenstatite – $Mg_xFe_{(1-x)}SiO_3$ ($x > 0.9$); diopside, $CaMgSi_2O_6$; spinel, $MgAl_2O_4$; and also the oxides, corundum – Al_2O_3, and an Fe/Mg oxide $Fe_{0.9}Mg_{0.1}$. The presence of these minerals is consistent with equilibrium condensation from a cooling gas of solar/cosmic chemical composition. Somewhat surprisingly, calcite, $CaCO_3$, and dolomite, $MgCa(CO_3)_2$, have also been detected at a low level. The route to their formation must seemingly be *via* a gas phase, rather than an aqueous phase, mechanism in the given circumstellar environments, although the exact details of their formation are not yet clear. Dust in C-rich circumstellar environments is known to include carbides and hydrogenated carbonaceous phases.

All of the minerals mentioned in the preceding paragraph were detected by indirect means, *i.e.*, no hands-on sampling was involved. However, the direct analysis of interstellar dust, and in particular stardust, in the laboratory has become possible over the last few decades with the recognition that there are pre-solar grains in primitive meteorites. Once recognised, these grains were extracted and extensively analysed. Isotopic analyses showed them to originate, primarily from evolved stars. However, some are also clearly associated with supernovæ. The analysed grains, perhaps not surprisingly, bear a close resemblance to the indirectly-detected circumstellar grains. These isotopically anomalous (*i.e.*, non-solar isotopic composition) crystalline grains, that pre-date the formation of the solar system, consist of nanodiamond, silicon carbide, graphite, corundum, spinel, hibonite ($CaAl_{12}O_{19}$), iron and titanium carbides, and silicon nitride. All of these pre-solar minerals were known about long before the ISO observations showed the presence of crystalline circumstellar grains. So, it should not perhaps really have been such a surprise that ISO detected crystalline circumstellar minerals. Rather more recently, pre-solar forsterite grains and some pre-solar amorphous silicate grains were detected in interplanetary dust particles, and the first pre-solar olivine, pyroxene and glassy silicate grains were extracted from a primitive meteorite. The anomalous isotopic compositions of these grains clearly indicate that these grains were formed around evolved, relatively low mass stars.

The dust formed around evolved stars is ejected into the interstellar medium by relatively benign stellar winds, there it is subject to stochastic, and often violent, processing in fast SN-generated shock waves. The differential acceleration of the gas and dust in these shocks results in high-velocity ion-grain impacts that can erode them and can also amorphise any crystalline materials. Thus, the formation of dust in circumstellar environments is opposed by destructive processes. Current models and observations seem to point to a rather shorter destruction than formation timescale for dust in the ISM. Thus, we currently need to invoke dust formation in the low density interstellar medium in order to account for the dust that we see there. This dust will likely be very different from stardust, being formed far from equilibrium it ought to be predominantly amorphous in nature.

In conclusion, we can say that the chemical and mineralogical composition of dust in the interstellar medium is very clearly spatially and temporally variant, and also in a state of constant flux. This inevitable complexity drives our interest and motivates us to try and fully understand its evolution from beginning to end.

The outlook, based on some recent results

Two NASA-led missions have recently brought us some new information on comets and cometary dust. It is currently too early to assess the full impact of these space missions but there is no doubt that their eventual influence on dust studies will be important.

The first of these missions was DEEP IMPACT which encountered comet 9P/Temel 1 and, at about 05h45 UTC on 4 July 2005, intentionally impacted a 370 kg projectile onto the comet resulting in an ejecta plume that was observed by fly-by spacecraft and by ground-based observatories. Observations of the plume within one second after the impact were subsequently explained in terms of a cloud of expanding, incandescent, liquid droplets cooling from ≈ 3500 K to 1000 K in less than half a second. The total mass of the droplets was about ten times that of the impactor. Spitzer Space Telescope observations of the comet dust coma before impact show a rather smooth, featureless spectrum indicative of large (radius > 100 μm), optically thick, silicate emission grains. After the impact the scattering produced by the coma increased enormously, indicating the presence of large amounts of sub-micron sized particles, dust much smaller than in the pre-impact coma. These observations can be explained by the break-up of the large, relatively fragile, pre-impact, cometary aggregates into the constituent sub-grains of about 0.1–1.0 μm in radius. Spectra (5–35 μm) taken 45 min after the impact show the presence of the strong silicate emission features of crystalline olivine and pyroxene, amorphous silicates, weak aromatic hydrocarbon emission bands, water ice, carbonates, amorphous carbons and, possibly, metal sulphides. The crystalline to amorphous silicate mass ratio was observed to be about 0.3, a ratio that was not significantly modified by any impact-melting devitrification or crystallisation. In total of the order of a few $\times 10^4$ tonnes of low-density (0.3 g cm^{-3})

comet material was released by DEEP IMPACT and much of this was dust of solar system and, possibly, interstellar origin. The initial mission results were published in 2005 (A'Hearn *et al.*, 2005) and in the 2006 Lunar and Planetary Science XXXVII Conference proceedings.

The second NASA mission, the seven year long STARDUST mission to comet Wild 2, parachuted back to Earth on 15 January 2006 a capsule containing samples of both cometary and interstellar dust. STARDUST passed within 240 km of the comet exposing one side of its aerogel-coated dust collector to the dust coming from comet Wild. During a longer exposure phase the other side of the panel was pointed in the direction of the interstellar dust flowing into the solar system. We are currently in the very early stages of the analysis of the dust brought back by STARDUST but initial results indicate that the comet dust is a mixture of both low and high temperature phases. The high temperature phases include olivine (forsterite) and minerals rich in calcium, aluminium and titanium. The cold phases are the interstellar ices associated with comets, but not brought back to Earth by STARDUST because of their high volatility and the lack of capsule refrigeration. Thus comets must contain matter formed close to the young Sun that was then later transported to the out reaches of the solar nebula and incorporated into icy aggregates. The interstellar dust samples are much rarer than the cometary grains because of the low flux of such particle entering the solar system. It is early days and this STARDUST sample has yet to be analysed in any detail.

No doubt the results of these two missions will add to our understanding of solar system and interstellar dust but will also probably add more questions that will challenge our current understanding.

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