Depletion patterns and dust evolution in the ISM

A.P. Jones
Institut d’Astrophysique Spatiale, Université Paris XI, Bât. 121, 91405 Orsay, France.

Abstract
We review the use of elemental depletions in determining the composition of interstellar dust and present a new interpretation of the elemental depletion patterns for the dust forming elements in a range of diffuse cloud types. We discuss this within the context of dust processing in the ISM and show that Si and Mg are selectively eroded from dust, with respect to Fe, as expected for a sputtering erosion process. However, we find that Si is preferentially and non-stoichiometrically eroded from dust with respect to Mg by some as yet unidentified process that may act in conjunction with grain sputtering. On this basis a new way of interpreting the depletions in terms of ‘continuous’ dust processing through erosion in the interstellar medium is presented. The observed depletion patterns can then be understood in terms of a gradually changing grain chemical composition as the erosion of the atoms proceeds non-stoichiometrically in the low-density interstellar medium. The stoichiometric erosion of multicomponent (e.g., core/mantle) single grains can qualitatively explain the observed depletions but is not consistent with the preferential erosion of Si from dust. We present suggestions for the usage of mineralogical terms within the context of interstellar and circumstellar dust mineralogy.
1. Introduction

Two connected quantities are pivotal in determining the mass and the composition of dust in the interstellar medium (ISM). Firstly, the absolute abundances of the elements with respect to hydrogen and, secondly, the fractions of these elements that are incorporated into dust. Many determinations of the dust composition based on measurements of the gas phase abundances of the elements that are normally found in dust have been made [e.g., Spitzer and Fitzpatrick 1993, 1995; Sofia, Cardelli and Savage 1994; Fitzpatrick 1995; Sembach and Savage 1996]. However, in order to calculate the ‘missing mass’, or the fraction of an element that is actually incorporated into dust, the absolute abundance of that element is required. A major problem with this is that the absolute abundances of the elements in all states (atomic, ionic, radical, molecular and solid state) along any line of sight cannot currently be measured at the same time because of the difficulty in observing the elements in the solid state directly. There is however likely to be some progress made on this problem very soon by the forthcoming Far-Ultraviolet Spectroscopic Explorer (FUSE) and Chandra X-ray Observatory (AXAF) missions which will be able to measure the abundance of an element in the gas and solid phases, respectively.

The abundance of the elements in the Sun, combined with the elemental composition of meteorites, provides an important ‘yardstick’ for interstellar (IS) dust studies because it is the best determined reference system that we have, and one that encompasses most of the elements in the periodic table [Anders and Grevesse 1989; Grevesse and Noels 1993]. In Figure 1 and Table 1 we show the solar abundances of Anders and Grevesse [1989] and Grevesse and Noels [1993] as a function of atomic number (Z), and use these as a qualitative measure of the chemical composition of the general ISM. The interesting ‘sawtooth’ pattern in Figure 1, peaked at even-numbered values of Z, or equivalently peaked at multiples of approximately four atomic mass units, arises from the ‘preferred’ nucleosynthetic formation of heavier elements from helium nuclei, $^{4}\text{He}^{++}$, during the nuclear ‘burning’ of hydrogen and helium within stars and supernovae. The apparently anomalously high abundance of Fe is due to its efficient formation in massive stars and supernovae.

Figure 1 allows some interesting general deductions to be drawn on the likely composition of interstellar dust. C, H, O and N are abundant and reactive elements and are the primary constituents of the detected polyatomic IS and circumstellar (CS) gas phase species [e.g., Ohishi 1997]. Additionally, C and O are also primary constituents in carbonaceous and silicate/oxide dust, respectively. N is not a major dust component, possibly because it exists as N$_2$ and the strong N=N bond inhibits reactivity [Gail and Sedlmayr 1986]. Ne and Ar are abundant but inert and do not participate in IS gas phase chemistry, but they can passively accrete onto cold dust in dense clouds. F, Cl and P are chemically reactive and principally found in the gas phase. Sulfur can form solid sulphides, but in the ISM it does not seem to be depleted into dust (see § 2). The remainder of the elements in Figure 1 form solid silicates and oxides, and are constituents in well-known mineral phases. On the basis of the abundances in Figure 1 we can divide the potential dust-forming elements into four groups:

- primary dust constituents (abundance $\geq 300$ ppm) C and O (filled diamonds in Figure 1).
- major dust constituents (abundance $\sim 30$ ppm) Mg, Si and Fe (filled circles in Figure 1).
- minor dust constituents (abundance $\sim 3$ ppm) Na, Al, Ca, and Ni (heavy circles in Figure 1).
- trace dust constituents (abundance $\sim 0.1 – 0.3$ ppm) K, Ti, Cr, Mn, and Co (light circles in Figure 1).

This simple classification is reflected in the IS silicate/oxide dust composition determined from IS depletions studies [e.g., Spitzer and Fitzpatrick 1993; Sofia, Cardelli and Savage 1994; Savage and Sembach 1996].

Solar abundances probably do not, however, apply to all phases of the ISM. A recent attempt at deriving an absolute IS reference abundance system was made by Snow and Witt [1996] (we refer to this reference abundance system as ‘SW96’). Their approach was to assume that the composition of the stellar atmospheres of newly-formed massive stars, e.g., B stars [Kilian 1992, 1994; Adelman, Robinson and Wahlgren 1993; Gies and Lambert 1992], completely sample the composition of the ISM from which they formed. The derived abundances from this study are about two thirds of the solar reference abundances of Anders and Grevesse [1989] and Grevesse and Noels [1993], and are summarized in Table 1. This result has major implications for IS dust models, most of which
have problems fulfilling these new abundance criteria [Snow and Witt 1995]. This is the so-called ‘carbon crisis’ which, in fact, is not restricted to carbon but also applies to Mg, Si and Fe as well. However, recent dust models by Mathis [1996] and Li and Greenberg [1997] have been successful in overcoming this crisis and meeting the new abundance criteria.

In the derivation of their reference abundance system Snow and Witt [1996] assumed that there was no elemental fractionation during star formation. This may not be an entirely valid assumption because of the role of magnetic fields during cloud collapse and star formation. Ciolek and Mouschovias [1996] determine that a relatively large fraction (≥ 90%) of the small IS dust grains may not reach the cores of pre-stellar clouds, and are therefore not incorporated into the forming star. The star will therefore be underabundant in the heavy dust-forming elements, and the ‘cosmic’ abundances determined from the stellar photosphere will be underestimated.

2. Depletions and Dust Composition

The depletion of the dust-forming elements in a given region of the ISM is determined by the dynamics of the accretion and erosion processes acting on the dust in that region. In denser regions of the ISM accretion is favoured by the increased collision rates between gas phase species and grains. Erosion is more likely in the lower density ISM due to the effects of shock waves. Thus, the depletion of the elements in the ISM will be driven by these two competing processes.

Field [1974] showed that the elements with the highest condensation temperatures generally have the highest depletion factors, and that this is consistent with grain condensation in cool stellar atmospheres. However, the observed effect is also consistent with the lower temperature process of grain growth via accretion in molecular clouds [e.g., Savage and Sembach 1996]. Thus, the elemental depletion patterns observed in diffuse clouds could arise from the selective accretion of elements with high condensation temperatures. The accretion timescale for a cloud of density, \( n_H \) \( (\text{cm}^{-3}) \), is \( \sim 10^9 / n_H \) yr. For a diffuse cloud with a density of typically a few tens of H atoms per cm\(^{-3}\) the accretion timescale is therefore of the order of \( 10^7 - 10^8 \) yr, i.e., similar to the neutral ISM cycling timescale of \( 3 \times 10^7 \) yr which is driven by massive star formation in molecular clouds [e.g., McKee 1989]. Thus, it is likely that accretion onto grains in the very diffuse ISM or intercloud medium could play only a minor role in determining elemental depletions. It is also clear that for accretion to be important some process must have previously transferred the elements into the gas phase from the dust.

The chemical composition of dust can also evolve in the ISM as grains lose atoms to the gas phase through the high energy processes that occur in the supernova-generated shock waves that permeate the low density ISM. They are particularly effective at processing dust in the warm intercloud phase [McKee 1989]. Behind a shock front charged grains are accelerated around the magnetic field lines as the postshock gas cools and compresses. This leads to high energy collisions between the gas atoms/ions and the grains resulting in the sputtering (erosion) of the grain surfaces, and also to collisions between grains which result in the vaporization and fragmentation of grains [Jones et al. 1994; Jones, Tielens and Hollenbach 1996]. Fragmentation leads to significant changes in the dust size distribution [Jones, Tielens and Hollenbach 1996] but it is sputtering that can change the dust composition. The effects of sputtering and vaporization on the gas phase abundances of C, Mg, Si and Fe as a function of shock velocity are shown in Figure 2 (data from Jones, Tielens and Hollenbach [1996]). In Figure 2 the stoichiometric sputtering of Mg, Si and Fe from the silicates was assumed. As the shock velocity increases an increasing fraction of the dust forming elements is transfered to the gas phase.

Evidence for the erosional processing of dust in the ISM comes from the measured abundances of the dust-forming elements in the gas phase as a function of the physical conditions along the line of sight [e.g., Routly and Spitzer 1952; Cowie 1978; Crinklaw, Federman and Joseph 1994]. These observations show increased gas phase abundances of the dust-forming elements with increased cloud velocity and with decreased density along the line of sight. In the latter case lower density gas implies more warm intercloud medium along the line of sight and therefore an increased probability of the dust and gas having been exposed to supernova shock waves.

In Figure 3 we show the gas phase abundances of the major, and some minor and trace, dust forming elements and sulfur for lines of sight through cool clouds in the disk and warm clouds in the halo of the Galaxy. The data in Figure 3 are taken from the extensive review of Savage and Sembach [1996] but include updated Mg depletions using the revised Mg\(^+\) oscillator strengths of Fitzpatrick [1997]. Interestingly, if
one compares the data in Figures 2 and 3, the warm cloud Fe depletions are consistent with dust that has been shocked to ~ 100 km/s, whereas the Mg and Si data are consistent with much higher shock velocities. This seems to be an indication that Mg and Si are more easily liberated from dust than the stoichiometric sputtering of silicates shown in Figure 2 indicates. The cool cloud depletions are, on the other hand, representative of highly-depleted unshocked dust. From the interpretation of the depletion data and the inherent patterns many authors have shown that the IS dust composition is consistent with a core and mantle grain structure [Spitzer and Fitzpatrick 1993, 1995; Sofia, Cardelli and Savage 1994; Fitzpatrick 1995; Sembach and Savage 1996; Savage and Sembach 1996]. These authors have shown that the depletion data is consistent with an Mg-rich silicate mantle surrounding and Fe-rich silicate/oxide grain core. In this work we have tried to avoid the use of the specific structural labels for dust components, i.e., core and mantle. We prefer the use of the generic terms ‘less refractory’ and ‘more refractory’ components because these do not imply any structural relationship between the different dust phases. Indeed core/mantle grain structures probably do exist in IS dust but such structures are not unequivocally indicated by the observed depletion data.

The data presented in Figure 3 are consistent with a more refractory oxide/silicate phase and a less refractory silicate phase. The cool cloud depletions give the maximal depletion silicate/oxide grain composition, and the warm cloud depletions represent the composition of a more refractory dust component that has survived erosion in the ISM. As noted above this is consistent with the presence of shocked dust in the halo clouds. The derived cool cloud and warm cloud dust compositions are sensitive to the assumed elemental abundances. However, the difference between the two sets of depletions in Figure 3, the material eroded into the gas phase, represents the composition of a less refractory silicate/oxide dust component. This composition is not sensitive to the assumed abundances because its composition is probed directly by the measured gas phase abundances, assuming that a major fraction of the elements was originally in dust [e.g., Spitzer and Fitzpatrick 1993; Sofia, Cardelli and Savage 1994; Fitzpatrick 1995; Savage and Sembach 1996]. Table 2 summarizes the elemental ratios for the silicate/oxide dust phase as a function of the assumed reference abundance system.

From the mineralogy of silicates and oxides the ratio $R = (\text{Mg} + \text{Fe})/\text{Si}$ can be used to determine the interstellar grain composition. A value of $R = 2$ is indicative of an olivine-type silicate stoichiometry, $[\text{Mg}_x\text{Fe}_{(1-x)}]_2\text{SiO}_4$ ($0 \leq x \leq 1$), whereas $R = 1$ implies pyroxene-type silicate stoichiometry, $[\text{Mg}_x\text{Fe}_{(1-x)}]\text{SiO}_3$ ($0 \leq x \leq 1$). Values of $R$ greater than 2 imply a mixed oxide and silicate material, and the oxide content increasing with $R$. We present the value of $R$ and the Mg/Fe ratio for the data of Savage and Sembach [1996], as a function of reference abundance, in Table 2 where we have used the Mg$^+$ oscillator strengths of Fitzpatrick [1997] to derive the Mg data. The overall dust composition (Table 2) is close to olivine-type stoichiometry for the solar reference abundance, and a mixed oxide/silicate material for the B star and SW96 reference abundances. The most refractory dust component (Table 2) appears to be an Fe-rich olivine-type silicate (solar reference), a mixed silicate/oxide (B star reference) or an Fe oxide (SW96 reference). The best determined dust phase, the least refractory material (Table 2), is consistent with Mg-rich olivine-type stoichiometry (solar, B star and SW96 reference abundances). We note that the dust compositions that we derive here, i.e., Mg-rich and Fe-rich olivine-type silicates and iron oxide, are essentially identical with those derived for the young, intermediate mass pre-main sequence Herbig Ae/Be star HD 100546 [Malfait et al. 1998]. It is necessary to give a word of caution here because although the depletion data may indicate a stoichiometry consistent with a particular type of silicate (olivine or pyroxene), this does not imply that the dust actually contains these specific mineral phases. However, as noted, the similarity between the chemical composition of the diffuse ISM dust, derived from depletions, and that of the dust around the young star HD 100546, derived spectroscopically, is a strong indication of the utility of depletion studies in determining the mineralogical as well as the chemical composition of dust in the ISM.
3. Depletions and Dust Processing

It is useful to compare the elemental depletion data for various lines of sight through diffuse clouds for a range of dust forming elements in order to search for systematics in the depletion patterns. To do this it is desirable to normalize the data to the abundance of a particular element [e.g., Si, Fitzpatrick 1995]. We prefer Fe for this purpose because it is abundant in dust and is less readily eroded from the dust than either Mg or Si, as we show later. In Figure 4 we show the fractions of the elements Mg, Si, S, Ti, Cr, Mn, Fe and Ni in dust normalized to that of Fe for the SW96 and solar reference abundances, and for the four major diffuse cloud types defined by Savage and Sembach [1996], namely; cool disk, warm disk, disk+halo and halo. In deriving Figure 4 the Savage and Sembach [1996] gas phase Mg abundances were multiplied by a factor of two to allow for the revised Mg$^+$ oscillator strength of Fitzpatrick [1997]. The cloud types represent a range of IS cloud conditions with elemental depletions decreasing from cool to halo clouds. It is clear from the depletion patterns seen in Figure 4 that the overall trends are only weakly dependent on the reference abundance system adopted. These same patterns are also seen for the B star reference abundances. However, in the B star and SW96 reference abundance cases there is clearly a problem with the Si and Mg abundances. For these elements the maximum observed gas phase Si and Mg abundances in the Savage and Sembach [1996] data, allowing for the revised Mg$^+$ oscillator strength of Fitzpatrick [1997], are greater than the relevant reference abundances. In the case of Mg we do however note that the minimum dust abundances in the Savage and Sembach [1996] data are lower limits, as shown in Figure 4. Thus, the B star and SW96 reference abundance cases there is clearly a problem with the Si and Mg abundances. In Figure 4 these effects are reflected in the negative fractions for Si and Mg in the halo cloud data. We note that the negative fractions simply reflect uncertainties in the adopted reference abundances. We are here only interested in the illustrated trends in Figure 4, and these are essentially independent of the reference abundance system adopted.

The trends in Figure 4 are for the most part linear, except for Si and perhaps Mg, indicating approximately constant fractional erosion of the elements with respect to Fe. The Si depletion data shows a clear ‘flattening’ with decreasing depletion into dust. A similar trend may also apply to the Mg data because of the lower limit values for the smallest depletions. These data thus seem to indicate a saturation effect in the erosion of Si (and Mg) from dust, i.e., Si (and Mg) atoms at low concentration in a a Fe-rich matrix are hard to remove. It is easier to understand this behaviour in the cases where the reference abundance is less than solar because it clearly corresponds to the removal of most of the Si (and Mg) from the dust — for solar abundances the saturation effect is more difficult to explain because in this case about half of the Si still remains in the dust. This may therefore be further evidence that the real IS abundances are less than solar but that they are somewhat larger than the indicated B star and SW96 values. A close look at the SW96 data in Figure 4 shows that there seems to be a preferential removal of Si atoms from dust with respect to Mg. For example, for the cool disk cloud averages 87% of Mg and 90% of Si are in dust. However, for the warm disk cloud averages 52% of Mg and 26% of Si are in dust. This trend is also true for the ranges of the observed values (the boxes in Figure 4). Figure 4 also shows the results of a stoichiometrically eroded core/mantle particle model. These show that such a model can match the depletion patterns well, except in the case of Si. We therefore conclude from these depletion patterns that Si is, initially at least, more easily eroded from dust than Mg, and much more easily eroded from dust than any of the other major, minor or trace elements in the dust. In a study of depletions and the lifecycle of IS dust Tielens [1998] reached a similar conclusion concerning the incorporation of Si into a rather volatile dust component. 

Grain erosion in the ISM is dominated by sputtering due to ion-gram impacts in supernova-generated shock waves [Jones et al. 1994; Jones, Tielens and Hollenbach 1996]. Thus, the changing elemental depletions in the ISM should reflect the mechanics of this process in which the lighter atoms are sputtered first (see for example the results of the 20 keV proton irradiation of olivine in Bradley [1994] which are consistent with this assumption). Thus, the elemental sputtering sequence for the most abundant isotopes should be

\[ ^{24}\text{Mg} > ^{28}\text{Si} > ^{48}\text{Ti} > ^{52}\text{Cr} > ^{55}\text{Mn} > ^{56}\text{Fe} > ^{59}\text{Ni}. \]

but from the cool and warm disk cloud depletion data in Figure 4 the elemental sputtering sequence seems to be

\[ ^{24}\text{Si} > ^{24}\text{Mg} > ^{48}\text{Ti} > ^{52}\text{Cr} > ^{55}\text{Mn} > ^{56}\text{Fe} > ^{59}\text{Ni}. \]

This is as expected for the mechanical sputtering process, except for the inversion of Si and Mg in the se-
quence. It therefore appears that the erosion of Si from dust can not be completely explained by sputtering but that some other process must also be operating. One difference between Si and the other metals that might account for this difference is that with silicate structures the Si atoms are always bound to oxygen atoms, whereas the metals are always present as interstitial cations with the structure. Thus, the effective cross-section of an Si atom in an implantation interaction may be larger. In other words the disruption of the silicate SiO$_4$ tetrahedra could facilitate the preferential removal of Si from the structure leaving the interstitial Mg, Fe, etc. behind. One would therefore expect to see this effect in the results of Bradley [1994] if this were the case, but clearly this is not so. We therefore need to invoke some other mechanism to explain the preferential loss of Si from dust.

4. The Silicon Erosion Problem

The preferential erosion of Si from IS dust discussed in the previous section is something of an enigma. Currently it appears difficult to resolve this problem without further laboratory studies on the erosion of silicates as a function of incident ion parameters. We suggest several possible effects may that warrant further investigation:

- The abundances of Si and Mg in the ISM may be higher than in the B star or SW96 reference systems. For example, 50% enhancements would bring the Si and Mg results more into line with those of Fe. This effect could not however explain the preferential erosion of Si in the disk clouds. Additionally, enhanced Si and Mg abundances do not seem very likely.

- The bulk of the interstellar Si and Mg, and some fraction of Fe, exist as less refractory silicate, e.g., [Mg$_9$,Fe$_{0.1}$]$_2$SiO$_4$, phase with most of the Fe in a more refractory silicate/oxide phase [e.g., Sofia, Cardelli and Savage 1994; Fitzpatrick 1995; Sembach and Savage 1996; Savage and Sembach 1996]. The stoichiometric erosion of such a two component mix can qualitatively explain the non-linear behaviour of Si and Mg (see Figure 4). However, the Si is clearly eroded more efficiently that the stoichiometric sputtering of an Mg-rich olivine can account for.

- There is some chemically selective erosional process at work in the diffuse ISM which results in the preferential disruption of the silicate SiO$_4$ tetrahedra and the subsequent loss of Si atoms from the grain.

- Not all the Si is bound into silicates/oxides in the ISM. Some fraction of the Si in an even less refractory material than Mg-rich olivine could explain its faster removal from dust than Mg [e.g., Tielens 1998].

5. Silicate Processing in the ISM

Recent observations of silicates in emission in asymptotic giant branch (AGB) star dust shells made with the Infrared Space Observatory (ISO) [Waelkens et al. 1996; Waters et al. 1996; Malfait et al. 1998] and in comets made with ISO, and with airborne and ground-based observatories [Crovisier et al. 1996; Hanner, Lynch and Russel 1994] indicate the presence of Mg-rich silicates that may be up to 50% crystalline. These observations raise some interesting questions concerning the nature of IS silicates. For instance, in contrast to the recent ISO results, observations of the silicate 10 µm Si—O stretching and 18 µm O—Si—O bending modes in the ISM indicate that IS silicates are amorphous [e.g., Mathis 1990]. Thus, some process in the ISM amorphitize crystalline silicates and/or some process crystallizes amorphous silicates before their incorporation into cometary bodies and the dust shells around young stars. It is perhaps easy to understand how atomic and ionic collisions in shocks and due to cosmic rays in the ISM could amorphitize a material. 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, Nuth and Daukantas 1998]. Thus, if the re-crystallization of amorphous IS dust does occur it can only be in the vicinity of stars hot enough to heat dust to high temperatures (> 1000 K) for long periods, e.g., in the compact H II regions around hot, massive stars. The results of such processing may already have been seen in the M17-SW [Jones et al. 1999] and Orion [Cesarsky et al. 1999] H II regions.

5.1. Amorphitization of Dust in the ISM

Clearly, some process in the ISM renders dust amorphous and alters its chemical composition. This is certainly the case for silicate grains, which have been shown to be partially crystalline in many CS shells [e.g., Waelkens et al. 1996; Waters et al. 1996], but completely amorphous silicate in the ISM [e.g.,
Mathis 1990]. However, whatever the process that renders crystalline CS silicates amorphous once injected into the ISM must also similarly affect the carbonaceous grain species. The effects of such processes on carbon grains have not yet been fully investigated.

It therefore seems likely that dust in the ISM will retain no ‘memory’ of its formation in a given stellar environment, but may instead be characterized by tracers of its processing in the intercloud medium or low density IS clouds, i.e., implantation processing. The heavily irradiationally processed morphologies seen in the glass with embedded metal and sulphide (GEMS) interplanetary dust particle component that have been proposed to be of IS origin [Bradley 1994] may directly sample this processing. However, the IS origin for the GEMS processing has yet to be proven. In contrast to the GEMS some presolar dust components extracted from primitive meteorites, e.g., SiC and graphite grains, show no such evidence of having been processed [Bernatowicz 1997]. These grains were formed around AGB stars, as their isotopic compositions extracted from primitive meteorites, e.g., SiC and graphite grains, show no such evidence of having been processed [Bernatowicz 1997]. These grains were formed around AGB stars, as their isotopic compositions extracted from primitive meteorites, e.g., SiC and graphite grains, show no such evidence of having been processed [Bernatowicz 1997].

5.2. Dust Processing: A New Scenario

The grain model of refractory Fe-rich oxide/silicate cores surrounded by silicate mantles [e.g., Spitzer and Fitzpatrick 1993, 1995; Sofia, Cardelli and Savage 1994; Fitzpatrick 1995; Sembach and Savage 1996; Savage and Sembach 1996] is based on an interpretation of the observed elemental depletions of, primarily, Mg, Si and Fe. This model is not without its problems, for instance, in Mg silicate smoke condensation experiments [Hallenbeck, Nuth and Daukantas 1998] the formed grains show pure silica cores surrounded by Mg silicate mantles, which seems to be inconsistent with the proposed IS core/mantle grain structure. Alternatively, if the silicate mantles are formed by the re-accretion of gas phase species onto oxide/silicate cores in the ISM it is hard to see how pure silicates, uncontaminated by carbon and ‘non-silicate’ elements, could form. It is also hard to see how the stoichiometric erosion of a single or multiple component grain can completely explain the observed depletions (e.g., § 3 and Figure 4). Given these apparent inconsistencies we suggest an alternative model to explain the observations.

We propose that dust is formed in stellar sources with an overall olivine-type stoichiometry consistent with ‘typical’ IS Mg, Si and Fe elemental abundances [e.g., Snow and Witt 1996]. We assume that the dust is a mix of amorphous and crystalline olivine, pyroxene and oxide grains as shown by the recent ISO observations [e.g., Malfait et al. 1998]. These grains are then ejected into the ISM where they are exposed to erosional processes in shock waves and in the low-density gas which preferentially remove Si with respect to Mg, and both Si and Mg with respect to Fe, principally through the effects of sputtering. However, the enhanced removal of Si with respect to Mg is probably not due to some purely mechanical sputtering process. The exact nature of the Si fractionation process is unknown, but it is likely to be a chemically-selective process or an indication that not all of the Si is in refractory silicate/oxide phases. An increasing degree of erosion and processing in the ISM (from cool disk to halo clouds) therefore leads to grains with an increasing value of $R = (\text{Mg} + \text{Fe})/\text{Si}$. This is due to the preferential erosion of the least resistant components first, e.g., the Mg-rich olivine-type silicates. In regions where the dust is heavily processed the remnant grains may be composed almost entirely of Fe oxides. They will contain only a minor fraction
of Si and Mg dispersed throughout the grains that is difficult to remove because it is so dilute. There is therefore a progressive enrichment in Fe with respect to Mg and Si as erosion proceeds. A gradual evolution in the grain composition such as this is consistent with the changes in the observed depletions on going from from high-depletion, cool clouds to low-depletion, halo clouds [Savage and Sembach 1996]. The observed ‘saturation’ effect seen at low Si depletions in the halo clouds seems to be consistent with an Si abundance of the order of 2/3 of the solar value (Figure 4), i.e., greater than the SW96 reference abundance value of about 1/2 solar.

In this model the observed IS depletion patterns are therefore assumed to arise from a progressive and continuous evolution of the overall chemical composition of the grains in the low density ISM, and not from the stoichiometric erosion of core/mantle dust particles. We therefore do not need to invoke a core/mantle grain structure, but we cannot rule out the possibility of non-stoichiometric erosion from core/mantle grains. We are currently developing this model for the progressive evolution of dust composition in conjunction with new data from dedicated laboratory experiments.

6. The Silicate Cycle in the ISM

The cycle of silicate grains in the ISM can be summarized as follows:

- New dust is formed around ‘old’ stars principally in their AGB phase and a significant fraction of this dust may be formed in a crystalline state. The overall dust composition is probably of olivine-type silicate, reflecting the ‘typical’ Mg, Si and Fe abundance ratios. Oxides of Mg and Fe may also be formed contemporaneously with the silicates in these CS environments.

- This dust is ejected into the ISM in the later stellar evolutionary stages through radiation pressure and stellar winds.

- In the ISM the dust is subject to erosive processing (sputtering) and implantation in supernova-generated shock waves and by cosmic rays. The effects of these processes are to reduce the total grain mass and to alter the overall grain composition (e.g., the preferential removal of Si with respect to Mg, and of both of these elements with respect to Fe). Additionally, the silicate grain size distribution will be modified by fragmentation in shock waves.

- ISM dust is incorporated into molecular clouds and then into new stars and CS shells through cloud collapse and star formation. During this phase the re-accretion of atoms eroded from the dust and other gas phase species occurs in conjunction with grain coagulation.

- Around young, hot, massive stars the dust is subjected to heating to high temperatures in compact H II regions and may undergo partial crystallization. Around the less massive stars near the end of their lifetime (in the AGB phase) new dust is formed. This dust is then eventually injected into the ISM, thus completing the cycle.

7. Interstellar Silicate Mineralogy

In view of the well-defined mineralogical terms now finding their way into the astrophysical literature, principally due observations of the dust shells around young and old O-rich stars made with ISO [e.g., Waelkens 1996; Waters 1996], it is perhaps useful to define specific guidelines for the usage of mineralogical terms in the astrophysics literature. For example, the olivine minerals, \( \text{Mg}_x \text{Fe}_{(1-x)} \text{Si}_2 \text{O}_4 \), have very specific chemical compositions in the geological context, e.g., forsterite \( (x = 0.9 - 1.0) \) and fayalite \( (x = 0.0 - 0.1) \). The same holds true for pyroxene and almost all other mineral phases. Unfortunately IS observations are often not detailed enough to identify specific minerals by their chemical composition. This is because the identifications are made through the use of infrared spectroscopy, which often does not permit the exact determination of the chemical composition, or via depletion studies which indicate chemical composition but not mineralogical structure. We therefore tentatively suggest that in the less than geologically exact science of IS and CS mineralogy (astromineralogy?) that caution be exercised in the naming of dust components and in the use of very specific mineralogical names.

As an example of the silicate nomenclature that could be useful in describing, specifically, the derived compositions of IS and CS dust we propose the following broadly-based scheme:

- Where the 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.

- Where the grain composition is determined from measurements of depletions (no spectroscopic information available) and only an inferred chemical composition can be derived which is dependent on the adopted reference abundance. The dust should then 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, based on depletion studies alone, it is almost impossible to discern the difference between a real silicate and a mix of oxides with the same stoichiometry, and indeed IS silicates might easily be considered in terms of a mixture of oxides.

The adoption of a scheme such as this will hopefully avoid 'over-specific' labels being attached to IS dust compositions. It is also hoped that it would reflect the unavoidably inexact nature of cosmic mineralogy in comparison with the precisely defined mineralogy on the Earth and in the Solar System.

8. Connection to the Local ISM Dust

Frisch et al. [1999] have used the standard depletion arguments to interpret the nature and composition of the dust in the local ISM in terms of the simple core/mantle grain model. They relate their findings to the direct observation of IS dust in the Solar System with the Galileo and Ulysses space missions. Table 4 shows their derived abundances for the grain cores and mantles based on the SW96 reference abundances. From the data presented in Table 4 the dust in the local ISM seems to be primarily composed of metal oxides, with more than 60% of the Si residing in the gas phase. In comparison with the above discussions this implies that the local dust has been heavily processed which is entirely consistent with the models for a shocked local ISM discussed by Frisch et al. [1999].

As Frisch et al. [1999] point out, there is a good correlation between the Mg$^+$ and Fe$^+$ in the local cloud which indicates that these elements are eroded from dust in a constant ratio. However, this constant erosion ratio does not apply to Si because of its high gas phase abundance. Thus, the same behaviour seen in the Savage and Sembach [1996] data as presented in Figure 4 is also manifest in the local ISM.

9. Conclusions

We have reviewed the use of elemental depletion patterns in determining the composition of interstellar dust in the diffuse ISM. A new interpretation of the elemental depletions of the dust forming elements in a range of diffuse cloud types is presented. We find that Si is preferentially eroded from dust, with respect to Mg and that both of these elements are preferentially eroded with respect to Fe, as generally expected for a sputtering process. However, the enhanced erosion of Si with respect to Mg is not yet understood and seems to require some as yet unidentified process that may act in conjunction with grain sputtering. It could also indicate that some fraction of the Si is in a more volatile non silicate/oxide phase. We suggest that further dedicated experimental work is necessary in order to understand the details of the ion-grain implantation and erosion interaction in the ISM.

On the basis of the analysis presented here a new way of interpreting the depletion patterns in terms of ‘continuous’ dust processing in the low density interstellar medium is suggested. In this scheme the processing is non-stoichiometric and leads to a gradual chemical evolution of the overall silicate/oxide composition from olivine-type silicate towards an Fe-rich mixed oxide phase. From the presented Si depletion ‘saturation’ effect we suggest that the Si abundance is of the order of 2/3 of the solar standard, and not 1/2 as implied by the SW96 Si reference abundance.

We discuss the likely origins of the processing of dust in the ISM and conclude that the effects of cosmic rays may be negligible. This is based on the fact that certain presolar grains extracted from meteorites (e.g., SiC and graphite) show no sign of processing in the ISM despite their long lifetimes. This then implies that supernova-generated shock waves may be the principal agent for dust processing in the ISM and that the presolar SiC and graphite grains escaped the effects of fast shocks in the ISM.

Suggestions for the usage of mineralogical terms within the context of interstellar and circumstellar mineralogy are presented.

Acknowledgments. The author wishes to thank the two anonymous referees of this paper for their very
References

Adelman, S. J., R. D. Robinson and G. M. Wahlgren, Elemental abundances of the B6 IV star Xi Octantis, *Astronomical Society of the Pacific, Publications*, 105, 327-331, 1993.

Anders, E., and N. Grevesse, Abundances of the elements: Meteoric and solar, *Geochim. Cosmochim. Acta*, 53, 197-214, 1989.

Bernatowicz, T. J., Presolar grain from meteorites, in From Stardust to Planetesimals, edited by Y. J. Pendleton and A. G. G. M. Tielens, pp 227-251, Astronomical Society of the Pacific, San Francisco, 1997.

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

Cesarsky, D., A. Jones, J. Lequeux and L. Verstraete, ISO observations of the Orion Nebula and of the Orion bar, *Astron. Astrophys.*, submitted, 1999.

Ciolek, G. E., and T. Ch. Mouschovias, Effect of ambipolar diffusion on dust-to-gas ratio in protostellar cores, *Astrophys. J.*, 468, 749-754, 1996.

Crovisier, J., T. Y. Brooke, M.S. Hanner, et al. The infrared spectrum of comet C/1995 O1 (Hale-Bopp) at 4.6 AU from the Sun, *Astron. Astrophys.*, 315, L385-L388, 1996.

Cowie, L. L., Refractory grain destruction in low-velocity shocks, *Astrophys. J.*, 225, 887-892, 1978.

Crinclaw, G., S. R. Federman and C. L. Joseph, The depletion of calcium in the interstellar medium, *Astrophys. J.*, 424, 748-753, 1994.

Field, G. B., Interstellar abundances: gas and dust, *Astrophys. J.*, 187, 453-459, 1974.

Fitzpatrick, E. L., *HST* observations of stars in the Galactic Halo: Results on Interstellar dust, in *The Physics of the Interstellar Medium and the Intergalactic Medium*, edited by A. Ferrara, C.F. McKee, C. Heiles and P.R. Shapiro, pp. 283-291, ASP Conference Series, Vol. 80, San Francisco, USA, 1995.

Fitzpatrick, E. L., The abundance of Mg in the interstellar medium, *Astrophys. J.*, 482, L199-L202, 1997.

Frisch, P. C., Dorschner, J.M., Geiss, J., et al., Dust in the local interstellar wind, *Astrophys. J.*, in press, 1999.

Gail, H.-P., and E. Sedlmayr, The primary condensation process for dust around late M-type stars, *Astron. Astrophys.*, 166, 225-236, 1986.

Gies, D. R., and D. L. Lambert, Carbon, nitrogen, and oxygen abundances in early B-type stars, *Astrophys. J.*, 387, 673-700, 1992.

Grevesse, N., and A. Noels, in *Origin and Evolution of the Elements*, edited by N. Prantzos, E. Vangioni-Flam and M. Cassé, pp. 15-25, Cambridge University Press, Cambridge, UK, 1993.

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

Hanner, M. S., D. K. Lynch and R. W. Russel, The 8–13 micron spectra of comets and the composition of silicate grains, *Astrophys. J.*, 425, 274-285, 1994.

Jones, A. P., A. G. G. M. Tielens, D. H. Hollenbach, Grain shattering in shocks: The interstellar grain size distribution, *Astrophys. J.*, 469, 740-764, 1996.

Jones, A. P., A. G. G. M. Tielens, D. J. Hollenbach, and C. F. McKee, Grain destruction in shocks in the interstellar medium, *Astrophys. J.*, 433, 797-810, 1994.

Jones, A. P., A. G. G. M. Tielens, D. J. Hollenbach, and C. F. McKee, The propagation and survival of interstellar grains, in *The Astrophysical Implications of the Laboratory Study of Presolar Materials*, edited by T. J. Bernatowicz and E. Zinner, pp 595-613, American Institute of Physics: Conference Proceedings 402, New York, 1997.

Jones, A.P., V. Frey, L. Verstraete, P. Cox and K. Demyk, The infrared emission from dust in the M17-SW H II region: partially crystalline silicates in the ISM?, in *The Universe as seen by ISO*, edited by P. Cox and M. Kessler, pp. ?-?, ESA Special Publications series (SP-427), Nordwijk, The Netherlands, 1999.

Kilian, J., Chemical abundances in early B-type stars. IV - He, CNO, and Si abundances, *Astron. Astrophys.*, 262, 171-187, 1992.

Kilian, J., Chemical abundances in early B-type stars. 5: Metal abundances and LTE/NLTE comparison, *Astron. Astrophys.*, 282, 867-873, 1994.

Lewis, R. S., S. Amari and E. Anders, Interstellar grains in meteorites: II. SiC and its noble gases, *Geochim. Cosmochim. Acta*, 58, 471-494, 1994.

Li, A. and J.M. Greenberg, A unified model of interstellar dust, *Astron. Astrophys.*, 323, 566-584, 1997.

Maltaits, K., C. Waelkens, L.B. F. M. Waters, B. Vandenbussche, E. Huygen and M. S. de Graauw, The spectrum of the young star HD 100546 observed with the Infrared Space Observatory, *Astron. Astrophys.*, 332, L25-L28, 1998.

Mathis, J. S., Interstellar dust and extinction, *Ann. Rev. Astron. Astrophys.*, 28, 37-70, 1990.

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

McKee, C. F., Dust destruction in the interstellar medium, in *Interstellar Dust*, edited by L. J. Allamandola and A. G. G. M. Tielens, pp 431-443, Kluwer Academic Publishers, Dordrecht, 1989.

Moore, M. H., The physics and chemistry of ices in the interstellar medium, in *Solid Interstellar Matter: The ISO Revolution* edited by L. d’Hendecourt, C. Joblin and A. Jones, pp. 199-217, Les Houches No 11, EDP Sciences, Les Ulis, 1999.
Ohishi, M., Observations of “Hot Cores”, in *Molecules in astrophysics: Probes and processes*, edited by E. F. van Dishoeck, pp. 61-74, Kluwer Academic Publishers, Dordrecht, 1997.

Routly, P. M., and L. Spitzer A comparison of the components in interstellar Na and Ca, *Astrophys. J.*, 115, 227-243, 1952.

Savage, B. D., and K. R. Sembach, Interstellar abundances from absorption-line observations with the Hubble Space Telescope, *Ann. Rev. Astron. Astrophys.*, 34, 279-329, 1996.

Sembach, K. R., and B. D. Savage, The gas and dust abundances of diffuse halo clouds in the Milky Way, *Astrophys. J.*, 457, 211-227, 1996.

Snow, T. P., and A. N. Witt, The interstellar carbon budget and the role of carbon in dust and large molecules, *Science*, 270, 1455-1460, 1995.

Snow, T. P., and A. N. Witt, Interstellar depletions updated: where all the atoms went, *Astrophys. J.*, 468, L65-L68, 1996. (SW96)

Sofia, U. J., J. A. Cardelli and B. D. Savage, The abundant elements in interstellar dust, *Astrophys. J.*, 430, 650-666, 1994.

Spitzer, L., and E. L. Fitzpatrick, Composition of interstellar clouds in the disk and halo. I HD 93521, *Astrophys. J.*, 409, 299-318, 1993.

Spitzer, L., and E. L. Fitzpatrick, Composition of interstellar clouds in the disk and halo. III HD 149881, *Astrophys. J.*, 445, 196-210, 1995.

Tielens, A. G. G. M., Interstellar depletions and the life cycle of interstellar dust, *Astrophys. J.*, 499, 267-272, 1998.

Waelkens, C., Waters, L. B. F. M., de Graauw, M. S., et al. SWS observations of young main-sequence stars with dusty circumstellar disks, *Astron. Astrophys.*, 315, L245-L248, 1996.

Waters, L.B.F.M., Molster, F. J., de Jong, T., et al. Mineralogy of oxygen-rich dust shells, *Astron. Astrophys.*, 315, L361-L364, 1996.

A.P. Jones, Institut d’Astrophysique Spatiale, Université Paris XI, Bât. 121, 91405 Orsay, France. (e-mail: ant@ias.fr)

February 1999; revised May 1999; accepted June 1999.
Figure 1. Solar abundances in parts per million (ppm $\equiv N/10^6H$) vs. atomic number [Anders & Grevesse 1989; with C, N and O data from Grevesse and Noels 1993], (solid line). The elements labelled above (below) the x-axis indicate those elements with a ‘preference’ for the gas (solid) phase. The ‘sawtooth’ pattern, with peaks at even Z values, arises from the nucleosynthetic formation of the elements from He nuclei, $^4He^{++}$. The dust-forming elements can be grouped into primary (C and O with abundances $\geq 300$ ppm, filled diamonds), major (Mg, Si and Fe with abundances $\sim 30$ ppm, filled circles), minor (Na, Al, Ca and Ni with abundances $\sim 3$ ppm, heavy circles), and trace (K, Ti, Cr, Mn and Co with abundances $\sim 0.1 – 0.3$ ppm, light circles) dust constituents.
Figure 2. Depletions of the dust-forming elements as a function of shock velocity, assuming the results of Jones, Tielens & Hollenbach [1996]. Carbon (solid), silicon (short-dashed), magnesium (dotted-dashed), and iron (triple dotted-dashed). The preshock fractions of the elements assumed to be in dust are O (0.16), C (0.58), Fe (0.95), Si (0.90), and Mg (0.95) [Draine and Lee 1984]. The results expressed in this form are independent of the assumed reference abundances. The sputtering of the silicate elements was assumed to be in their stoichiometric ratios.
Figure 3. Gas phase abundances for the major (Mg, Si and Fe), minor (Ni) and trace (Cr and Mn) dust-forming elements and S for diffuse lines of sight lines through cool clouds in the Galactic disk (filled circles) and warm clouds in the Galactic halo (open squares) for Solar reference abundances. The vertical bars indicate the ranges of the observed values; data taken from Savage and Sembach [1996]. For the Mg data we have adopted the current best estimate for the Mg$^+$ oscillator strength from Fitzpatrick [1997].
Figure 4. Fraction of an element in dust normalized to that of Fe for the major (Mg, Si and Fe), minor (Ni) and trace (Ti, Cr and Mn) dust-forming elements and sulfur. The Snow and Witt [1996] reference abundances (SW96) were used, with the adoption of 2/3 of the solar abundance for Mn. Data is presented for the four types of diffuse cloud defined by Savage and Sembach [1996], namely; cool disk, warm disk, disk+halo and halo. The boxes indicate the ranges of values over a number of lines of sight, and the lines connect the mean values for each cloud type. All data is taken from Savage and Sembach [1996], but the Mg abundances have been updated using the Mg⁺ oscillator strength of Fitzpatrick [1997]. The dotted boxes and short-dashed lines indicate the same data but assume solar reference abundances. The long-dashed lines show the results of a model core/mantle particle fit to the data assuming SW96 abundances with maximum dust phase abundances of 0% for S, 90% for Mg and Si, and 99% for Fe and all other elements. We have assumed that 80% of Mg and 70% of Si are in (Mg₀.₉,Fe₀.₁)₂SiO₄ mantles and that the core consists of Fe-rich olivine and oxides. The Mn, Cr, Ni and Ti fractions in each component are the same as for Fe. In the model the sputtering erosion of the elements was assumed to be in their stoichiometric ratios.
Table 1. Reference abundances for a selection of elements, including all the major dust-forming elements, presented as the number of atoms, N, per million H atoms (N/10^6 H ≡ ppm). Z is the atomic number and A is the atomic mass of the element.

| Element | Z | A | Solar a | B star b | SW96 c |
|---------|---|---|---------|----------|--------|
| C       | 6 | 12.0 | 355     | 204      | 214    |
| N       | 7 | 14.0 | 93      | 68       | 66     |
| O       | 8 | 16.0 | 741     | 380      | 457    |
| Mg      | 12| 24.3 | 38      | 23.4     | 25     |
| Si      | 14| 28.1 | 36      | 15.8     | 18.6   |
| S       | 16| 32.1 | 19      | 11.7     | 12.3   |
| Ca      | 20| 40.1 | 2.3     | 1.70     | 1.58   |
| Ti      | 22| 47.9 | 0.1     | 0.06     | 0.065  |
| Cr      | 24| 52.0 | 0.5     | 0.32     | 0.32   |
| Mn      | 25| 54.9 | 0.3     | —        | —      |
| Fe      | 26| 55.8 | 32      | 30.9     | 26.9   |
| Ni      | 28| 58.7 | 1.8     | 1.15     | 1.12   |

aAnders & Grevesse [1989]; except for C, N and O which are from Grevesse & Noels [1993].

bField B star abundances from Snow & Witt [1996] and references therein.

cSnow & Witt [1996].
Table 2. The elemental ratios for IS silicate/oxide grain components.  

| Component       | Solar reference $^b$ | B star reference $^c$ | SW96 reference $^d$ |
|-----------------|----------------------|-----------------------|----------------------|
|                 | (Mg+Fe)/Si | Mg/Fe | (Mg+Fe)/Si | Mg/Fe | (Mg+Fe)/Si | Mg/Fe |
| Overall         | 2.0       | 1.1    | 3.5       | 0.6    | 2.9       | 0.8   |
| Most refractory | 2.1       | 0.3    | 4.7       | 0      | $\infty$ | 0     |
| Least refractory| 1.8       | 4.1    | 1.8       | 4.1    | 1.8       | 4.1   |

$^a$Data from Savage and Sembach [1996] with Mg abundances updated using the Mg$^+$ oscillator strengths from Fitzpatrick [1997].

$^b$Anders & Grevesse [1989].

$^c$Field B star abundances from Snow & Witt [1996] and references therein.

$^d$Snow & Witt [1996].
Table 3. H\textsuperscript{+} implantation parameters for the gas behind a 100 km/s shock wave and for cosmic rays.

| Parameter               | Shock wave\textsuperscript{a} | Cosmic rays\textsuperscript{b} |
|-------------------------|---------------------------------|---------------------------------|
| Abundance (fraction)    | \(\sim 0.9\)                   | \(\sim 0.9\)                   |
| Energy                  | \(\sim 50\) eV                 | \(\sim 1\) MeV                 |
| Implantation range      | \(\sim 30\) Å                  | \(\sim 1\) \(\mu\)m            |
| Impacts/atom/10\textsuperscript{8} yr | \(\sim 10\)                   | \(\sim 0.1\)                   |
| Type of process         | stochastic                      | continuous                      |

\textsuperscript{a}Data from Jones, Tielens and Hollenbach [1996].

\textsuperscript{b}Data from Moore [1999].
Table 4. The dust composition in the local ISM (data taken from Frisch et al. [1999]).

| Element/Ratio | Total | Gas phase | Core+Mantle | Core | Mantle |
|---------------|-------|-----------|-------------|------|--------|
| Mg            | 25    | 7         | 18          | 12   | 6      |
| Si            | 19    | 12        | 7           | 3    | 4      |
| Fe            | 27    | 3         | 24          | 13   | 11     |
| (Mg+Fe)/Si    | 2.7   | 0.8       | 6.0         | 8.3  | 4.3    |
| Mg/Fe         | 0.9   | 0.8       | 0.9         | 0.5  | 2.3    |

*aAssuming the Snow and Witt [1996] reference abundances.*