INTERSTELLAR DEPLETION ONTO VERY SMALL DUST GRAINS

JOSEPH C. WEINGARTNER
Physics Department, Jadwin Hall, Princeton University, Princeton, NJ 08544; josephw@astro.princeton.edu

AND

B. T. DRAINE
Princeton University Observatory, Peyton Hall, Princeton, NJ 08544; draine@astro.princeton.edu

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ABSTRACT

We consider the depletion of elements from the interstellar gas onto a population of very small dust grains. Adopting a grain model in which \( \sim 4\% \) of the cosmic C abundance is in grains with radii \( \leq 10 \) Å, we find that the rate of accretion onto these grains is fast enough to account for the observed large depletions of elements like Ti, without invoking unreasonably high rates of mass transfer between interstellar phases or low grain destruction rates. If these grains are composed of arene rings, then only a limited number of metal atoms can be locked up in them. The depletion would be quenched when this limit is reached, unless there is a mechanism for transferring the metals to larger grains and refreshing the very small grain population—for example, by grain coagulation and shattering in the diffuse interstellar medium (ISM). If Fe depletes onto the very small grains, then for reasonable coagulation rates there is at least one metal atom per five C atoms in the very small grain population. Furthermore, \( \sim 60\% \) of the cosmic Fe is associated with the carbonaceous grain population. It is unclear whether this scenario is compatible with observations. However, if there is another population of very small grains, with a large capacity for holding Fe atoms, it might be the sink for the most heavily depleted elements.

Subject headings: dust, extinction — ISM: abundances

1. INTRODUCTION

Ultraviolet and optical absorption-line studies have shown that many elements in the interstellar gas have lower abundances, relative to hydrogen, than in the Sun or in nearby B stars. The depletion of species X is defined by

\[
\delta(X) = \frac{[n(X)/n_H]_{\text{gas phase}}}{[n(X)/n_H]_{\text{cosmic}}},
\]

where \( n(X) \) is the number density of species X and \( n_H \) is the number density of hydrogen. Savage & Sembach (1996) have recently reviewed depletion measurements for various interstellar environments.

The conventional explanation for interstellar depletions is that some of the atoms have been accreted by dust grains. However, efforts to quantify this hypothesis for the most heavily depleted elements in diffuse gas have encountered difficulties. For example, Draine (1990) found that implausibly high rates of mass transfer from molecular clouds to the diffuse medium were required, but noted that the inclusion of a population of very small grains might help. The existence of such a population is inferred from observations of 3–60 \( \mu \)m infrared emission, presumably generated by grains small enough to reach temperatures of 30–300 K or more upon the absorption of a single starlight photon (e.g., Draine & Anderson 1985). Very small grains are expected to be more effective accretors than bigger “classical” grains, for two reasons. First, they contribute more total surface area. Second, they tend to be negatively charged or neutral, whereas the classical grains tend to be positively charged. Since the depleted metals in the gas are generally singly ionized, the collision cross sections for small grains are enhanced and those for big grains are diminished.

In this study we repeat the analysis presented by Draine (1990), but including a population of very small grains. In particular, we will aim to account for the depletion of Ti, which has been observed in both a cool diffuse cloud and a warm diffuse cloud along the line of sight toward \( \zeta \) Oph. For the cool cloud toward \( \zeta \) Oph, \( \delta(\text{Ti}) = 1 \times 10^{-3} \); for the warm cloud, \( \delta(\text{Ti}) = 5 \times 10^{-2} \) (Savage & Sembach 1996). Although these particular clouds may not be typical, the severe Ti depletions appear to be. For sight lines along which the average H number density is 3 cm\(^{-3}\), \( \delta(\text{Ti}) = 2 \times 10^{-3} \) (Jenkins 1989), and Joseph & Jenkins (1991) found that \( \delta(\text{Ti}) < 4 \times 10^{-4} \) for the cool clouds toward \( \pi \) Sco. Although Ca is more severely depleted than Ti toward \( \zeta \) Oph, Crinklaw, Federman, & Joseph (1994) conclude that generally Ca is depleted to the same extent as Ti, as a function of average H number density along the sight line. Depletion studies involving Ca are complicated by the fact that some Ca is expected to be doubly ionized, but Ca\(^{++}\) has no resonance lines at wavelengths longward of 912 Å.

In § 2 we derive expressions for the rate at which ions are removed from the gas by accreting onto grains, and compute accretion timescales for three interstellar phases. In § 3 we consider a scenario for mass exchange between phases and derive the constraints which the observed Ti depletions impose on the timescales for dust destruction and mass transfer between phases. We conclude in § 4 by discussing the plausibility of the resulting scenario.

2. DEPLETION RATES

2.1. Rate Coefficients

Ions arrive at the surface of a spherical grain at a rate

\[
R_{\text{arr}} = \int_0^\infty dv \left[ \frac{2}{\pi} \right]^{1/2} \left( \frac{m}{kT} \right)^{3/2} v^2 \exp \left( -\frac{mv^2}{2kT} \right) n_{\text{max}}(v) vn,
\]

where \( k \) is Boltzmann’s constant, \( T \) is the gas temperature, \( m \) is the ion mass, \( n_{\text{max}} \) is the maximum impact parameter.
for which an ion strikes the grain, and \( n \) is the ion number density. When the grain is charged, the ion moves in a Coulomb potential for which (Spitzer 1941)

\[
b_{\text{max}}(v) = \begin{cases} 
0 & \text{for } \frac{mv^2}{2} < \frac{Z_g Z_i e^2}{a}, \\
\left(1 - \frac{2Z_g Z_i e^2}{m v^2} \right)^{1/2} & \text{for } \frac{mv^2}{2} > \frac{Z_g Z_i e^2}{a}, 
\end{cases}
\] (3)

where \( Z_g e \) is the grain charge, \( Z_i e \) is the ion charge, \( m \) is the ion mass, and \( a \) is the grain radius. For charged grains, we neglect the modifications to \( b_{\text{max}} \) that result from the “image charge” contribution to the interaction (Draine & Sutin 1987). Neutral grains are polarized by the ion’s electric field. Treating the grain as a perfect conductor, Draine & Sutin (1987) found that

\[
b_{\text{max}}(v) = a \left[ 1 + \left( \frac{4Z_g^2 e^4}{m v^2 a} \right)^{1/2} \right]^{1/2}.
\] (4)

The accretion timescale, \( \tau_a \), is defined and computed from

\[
\tau_a^{-1} = \frac{1}{n} \frac{d n}{d t} = A^{-1/2} \left( \frac{8 \pi k T}{m_p} \right)^{1/2} \int da a^2 \frac{dn_{\text{gr}}}{da} D(a), (5)
\]

where \( A \) is the mass number of the ion, \( s \) is the sticking coefficient of the ion on the grain, \( m_p \) is the proton mass, and \( n_{\text{gr}}(a) \) is the number density of grains with radii less than \( a \). The enhancement factor \( D(a) \) depends on \( Z_i \) and \( Z_g \). With \( Z_i \) fixed,

\[
D(a) = \sum_{Z_g} f(Z_g, a) B(Z_g, a),
\] (6)

where (Draine & Sutin 1987)

\[
B(Z_g, a) = \begin{cases} 
\exp \left( - \frac{Z_g Z_i e^2}{k T a} \right) & \text{for } Z_g Z_i > 0, \\
\left(1 - \frac{Z_g Z_i e^2}{k T a} \right)^{1/2} & \text{for } Z_g Z_i < 0, \\
1 + \left( \frac{\pi Z_i e^2}{2 k T a} \right)^{1/2} & \text{for } Z_g = 0.
\end{cases}
\] (7)

The grain charge distribution function, \( f(Z_g, a) \), is obtained using the method described by Weinigartner & Draine (1999). In Figure 1 we plot \( D(a) \), with \( Z_i = 1 \), for graphite and silicate grains in three interstellar environments: cold neutral medium (CNM), warm neutral medium (WNM), and warm ionized medium (WIM). The adopted hydrogen number density \( n_H \), gas temperature \( T \), and ratio of electron density to hydrogen density \( x_e \), for these three environments and for molecular clouds (MCs), are displayed in Table 1. Since photoelectric emission is important in the grain charging, a radiation field must be specified; we used the spectrum of Mathis, Mezger, & Panagia (1983). The absorption cross sections were calculated using a Mie theory code derived from BHMIE (Bohren & Huffman 1983), with dielectric functions as described by Draine & Lee (1984) and Laor & Draine (1993). In molecular clouds, the grains are predominantly neutral and \( Z_g = 0 \); thus \( D(a) \approx 1 \).

### 2.2. Grain Population

We consider two model grain size distributions, both of which are extensions of the MRN distribution (Mathis, Rumpl, & Nordsieck 1977),

\[
dn_{\text{gr}} = C a^{-3.5} n_H da, \quad a_{\text{min}} < a < a_{\text{max}}, (8)
\]

with coefficients given by Draine & Lee (1984): \( C = 10^{-25.13} \text{cm}^{-3.5} \) for graphite and \( C = 10^{-25.11} \text{cm}^{-3.5} \) for silicate. The MRN distribution runs from \( a_{\text{min}} = 50 \text{ Å} \) to \( a_{\text{max}} = 0.3 \text{ μm} \), but for the graphite component we extend the lower limit to 4 Å, about the minimum size expected to be stable against sublimation in the interstellar radiation field (Guhathakurta & Draine 1989). We do not similarly extend the silicate component, because the observed IR emission from diffuse clouds does not exhibit the 10 μm silicate feature (Mattila et al. 1996; Onaka et al. 1996). For our first distribution (distribution [i]), we retain the MRN power law throughout the extended size range. If graphite grains have a density of 2 g cm\(^{-3} \), then the grains with \( a \leq 10 \text{ Å} \) (\( \lesssim 240 \text{ C atoms} \)), contain \( \sim 2\% \) of the cosmic C abundance. This is conservative, as attempts to model the observed IR emission (e.g., Désert, Boulanger, & Puget 1990) have suggested values 2 or 3 times bigger. Therefore, for our second distribution (distribution [ii]), we adopt for the graphite component the form suggested by Draine & Anderson (1985), which differs from distribution (i) only for \( a < 30 \text{ Å} \), where

\[
dn_{\text{gr}} = C(30 \text{ Å})^{0.5} a^{-4.0} n_H da.
\] (9)
We consider mass exchange between the following three gaseous environments: warm, cold, and molecular. Hot ionized gas is neglected because of its small mass fraction. We also consider the removal of mass from the ISM during the star formation process, and the addition of mass to the ISM from evolved stars (stellar winds and supernovae) and from the infall of extragalactic material. For simplicity, we assume that the total mass and the metallicity of the ISM remain constant in time. To properly account for changes in metallicity with time, it would be necessary to consider the dependence of the dust abundance on metallicity and the distribution of newly formed metals over the interstellar phases. The fraction of mass removal due to star formation occurring in phase \( i \) is denoted \( p_i \), where \( i = c, w, \) or \( m \) for cold, warm, or molecular, respectively; we assume \( p_m = 1 \) and \( p_c = p_w = 0 \). We consider mass addition (both from evolved stars and infall) only into the warm and cold media, with the same relative contributions from the two sources in both media. Then the mass input can be treated as if it were derived from a single source, with Ti depletion \( \delta_{in} \); if there is no Ti in the accreted extragalactic material, then \( \delta_{in} \) has the same value as the depletion in the stellar outflow (relative to its enhanced metallicity). The timescale for injection of the entire mass of the ISM is denoted by \( \tau_{in} \), and the fraction of the input that goes into phase \( i \) is denoted by \( q_i \).

Ti is removed from the gas by accretion onto very small grains, with timescales \( \tau_{d,i} \). Since we wish to explain the most heavily depleted elements, we make the extreme assumption that atoms are only returned to the gas from grains when the grains are destroyed. We denote the timescale for the destruction of all the grains in phase \( i \) as \( \tau_{d,i} \), and the mass fraction in phase \( i \) as \( f_i \). In the warm and cold phases, grains are destroyed principally in supernova shock waves. The timescale for destroying all the grains in the ISM in these shocks is denoted \( \tau_i \); the fraction of this destruction occurring in the cold medium is denoted \( g_c \) \( [f_i \tau_{d,c} = g_c \tau_{d,c}^{-1}] \) and \( f_w \tau_{d,w} = (1 - g_c) \tau_{d,c}^{-1} \). We will suppose a small amount of additional grain destruction to take place in molecular clouds, with a timescale \( \tau_{d,m} \).

### 3.2. Steady State Equations

We suppose the following mass transfers occur: from warm to cold, cold to warm, cold to molecular, and molecular to warm, as indicated in Figure 4. We define the transfer timescales \( \tau_{ij} \) as the time to transfer the entire mass of phase \( i \) to phase \( j \). Assuming the depletions in each phase to remain constant yields

\[
\frac{1 - \delta_i}{\tau_{d,i}} + \sum_{k \neq j} \frac{f_j}{f_j \tau_{k,j}} (\delta_k - \delta_j) + \frac{q_j}{f_j \tau_{in}} (\delta_{in} - \delta_j) = \frac{\delta_j}{\tau_{a,j}},
\]

where \( \delta_i \) denotes the Ti depletion in phase \( i \) (McKee 1989; Draine 1990). Constant mass in each phase yields

\[
\sum_{i} \left( \frac{f_j}{\tau_{j,k}} - \frac{f_j}{\tau_{k,j}} \right) = \frac{1}{\tau_{in}} (q_j - p_j).
\]

We treat \( \delta_m \), \( \tau_{a,m} \), \( \tau_{a,w} \), \( \tau_{a,c} \), \( \tau_{d,m} \), and the mass fractions \( f_j \) as known quan-
depletion in molecular clouds $\delta_m$, and the four transfer timescales ($\tau_{wc}$, $\tau_{cm}$, $\tau_{cw}$, $\tau_{mw}$). If $\tau_d$ is also specified, the solution for the remaining variables is as follows:

$$\delta_m = \left\{ \begin{array}{ll} 1 & \text{for } \tau_d = 0 \\ \frac{f_m}{\tau_{d,m}} - \frac{f_w \delta_w - f_c \delta_c + \delta_in}{\tau_{a,w} - \tau_{a,c} + \tau_{in}} \left( \frac{f_m + f_m + 1}{\tau_{in}} \right)^{-1}, & \text{otherwise} \end{array} \right.$$  \hspace{1cm} (13)

$$\tau_{wc} = f_w (\delta_w - \delta_c) \left[ \frac{f_c \delta_c - g_i (1 - \delta_i)}{\tau_{a,c}} - \frac{g_i (\delta_{in} - \delta_c)}{\tau_{in}} \right]^{-1},$$ \hspace{1cm} (14)

$$\tau_{cm} = \frac{f_c}{g_i} (\delta_c - \delta_m) \left[ \frac{\delta_m - 1 - \delta_m}{\tau_{a,m} - \tau_{d,m}} \right]^{-1},$$ \hspace{1cm} (15)

$$\tau_{mw} = \left[ \frac{1}{\delta_c - \delta_m} \left( \frac{\delta_m - 1 - \delta_m}{\tau_{a,m} - \tau_{d,m}} \right) - \frac{1}{\tau_{in}} \right]^{-1},$$ \hspace{1cm} (16)

and

$$\tau_{cw} = f_w (\delta_w - \delta_c) \left[ \frac{f_c \delta_c - g_i (1 - \delta_i)}{\tau_{a,c}} - \frac{g_i (\delta_{in} - \delta_c)}{\tau_{in}} \right]^{-1},$$ \hspace{1cm} (17)

The destruction timescale $\tau_d$ is constrained by requiring the above quantities to be positive. For example, we assume $\delta_w \geq \delta_c$; then by demanding $\delta_{cw} \geq 0$, we find

$$\tau_d \geq g_i (1 - \delta_c) \left[ \frac{f_c \delta_c - g_i (\delta_{in} - \delta_c)}{\tau_{in}} \right]^{-1}. \hspace{1cm} (18)$$

Requiring $\delta_m \geq 0$ implies

$$\tau_d \leq [(1 - \delta_w) + g_i (\delta_w - \delta_c)] \times \left( \frac{f_w \delta_w - f_c \delta_c + \frac{f_m}{\tau_{d,m}} - \frac{1}{\tau_{in}}} {\tau_{a,w} - \tau_{a,c} + \tau_{d,m}} \right) \left[ \frac{\delta_m - 1 - \delta_m}{\tau_{a,m} - \tau_{d,m}} \right]^{-1}. \hspace{1cm} (19)$$

### 3.3. Illustrative Solutions

The mass of the ISM is estimated to be $\sim 5 \times 10^9 M_\odot$, and the star formation rate (or rate of infall plus stellar outflow) is $\sim 5 M_\odot$ yr$^{-1}$ (Timmes, Diehl, & Hartmann 1997 and references therein); hence we adopt $\tau_{in} \approx 10^9$ yr. In Table 2 we show the adopted values of $\tau_{a,i}$ (for each grain size distribution), $f_i$, and $\delta_i$; the accretion timescales were computed using equation (5), with $A = 48$ and $s = 1$. For

| Case | Distribution | $\delta_{in}$ | $\tau_d$ | $\tau_{wc}$ | $\tau_{cm}$ | $\tau_{cw}$ | $\tau_{mw}$ | $\delta_m$ |
|------|--------------|---------------|----------|-------------|-------------|-------------|-------------|----------|
| A    | (i)          | 0.1           | 1.4 $\times$ 10$^9$ | 1.5 $\times$ 10$^7$ | 4.5 $\times$ 10$^7$ | 4.7 $\times$ 10$^7$ | 8.7 $\times$ 10$^7$ | 5.9 $\times$ 10$^{-4}$ |
| B    | (ii)         | 0.1           | 6.3 $\times$ 10$^9$ | 7.3 $\times$ 10$^6$ | 2.4 $\times$ 10$^7$ | 2.0 $\times$ 10$^7$ | 4.3 $\times$ 10$^7$ | 6.1 $\times$ 10$^{-4}$ |
| C    | (ii)         | 1.0           | 1.6 $\times$ 10$^9$ | 7.6 $\times$ 10$^6$ | 2.4 $\times$ 10$^7$ | 2.1 $\times$ 10$^7$ | 4.4 $\times$ 10$^7$ | 6.1 $\times$ 10$^{-4}$ |

Note—For $\delta_w = 5 \times 10^{-2}$, $\delta_c = 1 \times 10^{-3}$, sticking coefficient $s = 1$, mass number $A = 48$ (Ti), $q_i = 0.1$, $g_i = 0.05$, $\tau_{in} = 1 \times 10^9$ yr, and $\tau_{a,i} = 1 \times 10^{10}$ yr. All timescales are in years.
the warm and cold media we take \( Z_i = +1 \), while for molecular clouds we take \( Z_i = 0 \), as well as raising \( a_{\text{min}} \) to 150 Å. The adopted values for the mass fractions \( f_i \) are rather uncertain, and not necessarily constant in time.

In Table 3 we present three illustrative solutions. Case A uses distribution (i), with \( \delta_{\text{in}} = 0.1 \), and cases B and C assume distribution (ii), with \( \delta_{\text{in}} = 0.1 \) (case B) and 1 (case C). For each case the adopted value of \( \tau_d \) lies at the center of the allowed range of values, which generally has a width \( \lesssim 10^7 \) yr.

The results are quite insensitive to \( q \) (the fraction of infall entering the cool phase), which we set to \( q = 0.1 \), and to \( g \) (the fraction of grain destruction taking place in the CNM), which we set to \( g_s = 0.05 \). Only \( \delta_m \) is sensitive to \( \tau_{a,m} \), which we set to \( 1 \times 10^{10} \) yr, and to \( \tau_{a,m} \) (although \( \tau_{cm} \) and \( \tau_{mvw} \) begin to increase significantly when \( \tau_{a,m} \) gets so large that \( \delta_m > \delta_i \), but this regime is unrealistic). For distribution (ii), \( \tau_d = 1.4 \times 10^9 \) yr when \( \delta_{\text{in}} = 0 \) and increases with increasing \( \delta_{\text{in}} \); above \( \delta_{\text{in}} = 0.72 \), there is no solution (although if \( \delta_{\text{in}} \) is increased to \( 1.4 \times 10^{10} \) yr, there are solutions up through \( \delta_{\text{in}} = 1.0 \)). For distribution (ii), \( \tau_d \) increases from \( 6.3 \times 10^8 \) yr for \( \delta_{\text{in}} = 0 \) to \( 1.6 \times 10^9 \) yr for \( \delta_{\text{in}} = 1 \).

4. DISCUSSION

4.1. Overall Timescales and Depletions

Jones and collaborators have made a series of models for grain destruction in shocks (Jones et al. 1994; Jones, Tielens, & Hollenbach 1996). They find that the smallest grains are the most resilient, since most destruction results from nonthermal sputtering off betatron-accelerated grains, and the larger grains are more effectively accelerated by the betatron mechanism. Less frequent, faster shocks efficiently destroy smaller grains through thermal sputtering. Furthermore, they find that shattering in collisions between larger grains produces large numbers of very small grains. Presumably these very small grains later coagulate to form bigger grains, maintaining the overall grain distribution. Since atoms which have accreted onto very small grains are incorporated into larger grains via coagulation, it would seem most appropriate for our purpose to adopt the timescale for destruction of the entire distribution. Jones et al. (1996) estimate the lifetime of carbonaceous grain material throughout all the phases of the interstellar medium, \( \tau_d = 6 \times 10^8 \) yr, which about equals the value adopted in § 3 for case B, but is about a factor of 2 smaller than the values adopted for our other examples. The derived transfer timescales are in the expected range (McKee 1989). Thus, our case B example shows that accretion onto very small carbonaceous grains can occur fast enough to result in the depletions of even the most heavily depleted elements, if they stick perfectly.

4.2. Sticking Coefficients

The “sticking” coefficient \( s = p_1 p_2 \), where \( p_1 \) is the probability that the impinging ion (e.g., Ti\(^+\)) will be trapped on the grain surface long enough (\( \gtrsim 10^{-12} \) s) to get rid of its kinetic energy and “thermalize,” and \( p_2 \) is the probability that the atom will then remain on the grain for \( \gtrsim 10^8 \) yr, until the grain is overrun by a supernova blast wave. This requires that the atom not be removed by either photodesorption (by a UV photon) or chemical reaction (with impinging H or O, in particular). For cold (\( T \lesssim 20 \) K) grains in cold gas (\( T \lesssim 100 \) K), it seems likely that \( p_1 \) is of order unity for species other than the inert gases.

The probability \( p_2 \) is most likely highly variable from one species to another. We would require \( p_2 \) to be of order unity for Ti and other species that are strongly depleted, and \( p_2 \ll 1 \) for species like N and S, which are not depleted. Photodesorption can keep a grain surface “clean” of species that are susceptible to photodesorption (Draine & Salpeter 1979), since the lifetime against photodesorption by ambient starlight could be as short as \( \sim 3000 \) yr for an atom or molecule. Efficient photodesorption has been observed for UV-irradiated \( \text{H}_2\text{O} \) ice (Westley et al. 1995, 1996), but the photodesorption cross sections for various metals at the various bonding sites on very small carbonaceous grains are not known. The small (carbonaceous) grains might consist of layers of fairly extended arene sheets.

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4.3. Saturation of Very Small Grains with Metals

Another consideration bearing on the sticking of metals regards the finite number of bonding sites in the very small carbonaceous grain population. Klotz et al. (1995) noted that in the most common PAH complexes, each metal is bonded by six \( p_2 \) electrons on the same ring, implying that rings adjacent to a metal-bonded ring are not available to bond other metal atoms. They concluded that there can be at most one metal per two rings, or 12 C atoms. However, there are many different possible bonding modes (Maslowsky 1993), so we shall be more flexible in our criterion for what constitutes a “full” grain. Suppose fast accretion can be maintained as long as there are at most \( \beta \) metal atoms per C in the very small carbonaceous grains. (Klotz et al. would only consider \( \beta \leq 1/12 \).) Then the very small grains become saturated when their metal content reaches \( \beta \), and must be replaced by a fresh population of very small carbonaceous grains that are largely metal-free and therefore capable of accreting metals. We will refer to this as “refreshment” of the small-grain population, and will let \( \tau_{\text{re}} \) denote the timescale for this refreshment of the small carbonaceous grains. This refreshment would presumably occur via coagulation of very small grains onto classical grains, balanced by the shattering of classical grains to create “fresh” very small grains. If the coagulation takes place in molecular clouds and the shattering in the warm medium, then the refreshment rate \( \tau_{\text{re}} < \tau_{cm} \), the rate for exchange of mass from CNM to molecular clouds. In this scenario, rapid refreshment would require rapid mass exchange between the molecular clouds and other phases. Alternatively, both shattering and coagulation might occur in the CNM. In this case, we demand that \( \tau_{\text{re}} \geq \tau_{\text{coag}} \), where the timescale for grains to exit the very small grain population by coagulation is roughly approximated by

\[
\tau_{\text{coag}} \approx \left( \frac{\tau_v}{a^2 \frac{dn_a}{da}} \right)^{-1} \approx 1 \times 10^7 \text{yr} \left( \frac{\text{km s}^{-1}}{v} \right) \left( \frac{30 \text{ cm}^{-3}}{n_\text{H}} \right)^{-1}.
\]
The evaluation is for grain distribution (ii). Interstellar turbulence and radiation pressure could conceivably lead to relative speeds between grains of \(v \approx 1 \text{ km s}^{-1}\), although estimated drift speeds resulting from anisotropic radiation tend to be about a factor of 50 smaller (Weingartner & Draine 1999).

If there are \(\gamma\) metal atoms per C atom in the entire carbonaceous grain population, then freshly shattered very small grains will presumably have \(\sim \gamma\) metals per C as well. Thus, grains of size \(a\) remain unsaturated if

\[
\tau_{re}(a) \leq \tau_{\text{max}}^\text{a}(a) = (\beta - \gamma) N_C(a) R_a(a),
\]

where \(N_C(a)\) is the number of C atoms in a grain, and \(R_a(a)\) is the rate at which metals stick to the grain. We express \(\tau_{\text{max}}^\text{a}(a)\) in terms of its value for \(a = 10 \text{ Å}\):

\[
\frac{1}{\tau_{\text{max}}^\text{a}(a)} = \frac{D(a)}{D(10 \text{ Å})} \left(\frac{10 \text{ Å}}{a}\right) \sum_M \frac{1}{\tau_{\text{max}}^{10 \text{ Å}}(a)M},
\]

where the sum is over all metals \(M\) which accrete onto the very small grains. For the CNM,

\[
\tau_{\text{max}}^{10 \text{ Å}}(a) = 11.6 \text{ yr} \left(\beta - \gamma\right) \left(\delta_c x_{\cos} \left(\frac{48}{A}\right) \frac{1}{s} \right)^{-1},
\]

where \(x_{\cos}\) is an element’s cosmic abundance, relative to H. To approximate \(\gamma(M)\), the contribution to \(\gamma\) from metal \(M\), we assume that \(M\) is not at all incorporated into the carbonaceous grains during their formation processes. Balancing the addition of \(M\) (by accretion in the CNM, with timescale \(\tau_{a,c}\)) against the removal of \(M\) (during grain destruction, with timescale \(\tau_{d,\text{gr}}\), and star formation, with timescale \(\tau_{in}\)), we find

\[
\gamma(M) = \left(\frac{f_c \delta_c x_{\cos}}{\tau_{a,c}}\right)_M \frac{m_c}{m_{\text{gra}}} \left(\frac{1}{\tau_{in}} + \frac{1}{\tau_d}\right)^{-1},
\]

where \(m_{\text{gra}}\) is the mass of the entire carbonaceous grain population, per H atom.

In Table 4 we display \(\tau_{\text{max}}^{10 \text{ Å}}(a)/(\beta - \gamma)\), and \(\gamma(M)\) for several elements, adopting \(m_{\text{gra}} = 5.3 \times 10^{-27} \text{ g (H atom)}^{-1}\). The values of \(\tau_{a,c}\) to be used in equation (24) are determined from equations (18) and (19) by demanding that \(\tau_d \approx 6 \times 10^8 \text{ yr}\), and are denoted \(\tau_{a,c}^{\text{a}}\) in Table 4; the values of \((48/A)^{1/2}/s\) for use in equation (23) follow from these required values of \(\tau_{a,c}\), assuming distribution (ii). Some metals might accrete onto only the silicates, resulting in the growth of these grains, and not contribute to the need to refresh the very small carbonaceous grains. With \((48/A)^{1/2}/s = 1\), and adopting the graphite form of distribution (ii) for the silicates, except with lower cutoff at 15 Å (10 Å), \(\tau_{a,c} = 2 \times 10^8 \text{ yr} \times 10^8 \text{ yr}\). Thus Mg and Si could possibly only accrete onto the silicates. Iron is a marginal case; however, it would be strange if Fe did not stick well to the very small grains when Ti and Ni do. Excluding Mg and Si, but including Fe, we find \(\gamma = 8.3 \times 10^{-2}\) and \(\tau_{\text{max}}^{10 \text{ Å}}(\beta - \gamma) = 2.9 \times 10^8 \text{ yr}\). Setting \(\tau_{a,c}(a) \approx 1 \times 10^7 \text{ yr}\), we find the minimum possible value for \(\beta\) for which grains with size \(a\) can be effectively refreshed. This ranges from \(\approx 0.35\) for \(a = 4 \text{ Å}\) to \(\approx 0.12\) for \(a = 10 \text{ Å}\).

Thus, if Fe depletion is due to accretion onto very small carbonaceous grains, then Fe is a major component in the composition of these grains, and \(\approx 60\%\) of the cosmic Fe resides in the entire carbonaceous grain population. Although there appears to be no reason to exclude this possibility, it is certainly unexpected. The alternative, that Fe depletes by accreting onto silicate grains, is unattractive: (1) it is not clear that the accretion rate onto the silicates is fast enough, and (2) one would expect Fe to stick to arene grains if Ti does.

### 4.4. Another Grain Population?

Perhaps there is a population of noncarbonaceous very small grains, onto which the most heavily depleted elements accrete. Tielens (1998) has recently inferred that the timescale for the return of Si from grains to gas is about an order of magnitude less than that for Fe, since Si is much less depleted in the warm phase. In computing our Table 4, we took the same \(\tau_d\) for each species, resulting in different transfer timescales, as exemplified by \(\tau_{\text{mv}}\), the time for transferring gas from molecular clouds to the warm phase. Of course, \(\tau_{\text{mv}}\) should be the same for each species. If we take \(\tau_{a,c} = 3 \times 10^6 \text{ yr}\) for Si, appropriate for accretion onto an MRN silicate distribution extended down to 15 Å, then we find \(\tau_{d} = 1.4 \times 10^6 \text{ yr}\) and \(\tau_{\text{mv}} = 7 \times 10^7 \text{ yr}\). The same \(\tau_{\text{mv}}\) is obtained for Ti and Fe if their accretion timescales are increased by slightly less than a factor of 2, and \(\tau_d = 1.0 \times 10^6 \text{ yr}\). Thus, we can imagine a silicate grain population deficient in Fe and with a destruction timescale somewhat less than the 4 \times 10^6 \text{ yr} derived by Jones et al. (1996), along

| M      | \(\log x_{\cos}\) | \(\delta_c\) | \(\delta_t\) | \(\tau_{a,c}^{\text{a}}\) | \(\tau_{\text{max}}^{10 \text{ Å}}(\beta - \gamma)\) | \(\gamma(M)\) | \(\tau_{\text{mv}}\) |
|--------|-----------------|-------------|-------------|----------------|----------------|----------------|-------------|
| Mg..... | -4.42           | 0.13        | 2.8 \times 10^{-2} | 6.0 \times 10^6 | 3.1 \times 10^8 | 7.6 \times 10^{-2} | 9.0 \times 10^7 |
| Si..... | -4.45           | 0.30        | 4.9 \times 10^{-2} | 1.3 \times 10^7 | 4.1 \times 10^8 | 5.6 \times 10^{-2} | 3.3 \times 10^8 |
| Fe..... | -4.49           | 5.6 \times 10^{-2} | 5.4 \times 10^{-3} | 1.0 \times 10^6 | 3.2 \times 10^8 | 7.4 \times 10^{-2} | 4.4 \times 10^7 |
| Ca..... | -5.66           | ...         | 1.9 \times 10^{-4} | 5.5 \times 10^4 | 7.3 \times 10^5 | 3.3 \times 10^{-3} | ...         |
| Ni..... | -5.75           | 3.1 \times 10^{-2} | 1.8 \times 10^{-3} | 3.4 \times 10^5 | 5.9 \times 10^8 | 4.1 \times 10^{-3} | 2.9 \times 10^7 |
| Cr..... | -6.32           | 8.5 \times 10^{-2} | 5.2 \times 10^{-3} | 1.0 \times 10^6 | 2.2 \times 10^10 | 1.1 \times 10^{-3} | 6.6 \times 10^5 |
| Ti..... | -7.07           | 5.0 \times 10^{-2} | 1.0 \times 10^{-3} | 2.0 \times 10^6 | 1.3 \times 10^{-11} | 1.8 \times 10^{-4} | 3.7 \times 10^7 |

**Note:** The second, third, and fourth columns are taken from Savage & Sembach 1996, Table 5. All timescales are in years. The depletions \(\delta_c\) and \(\delta_t\) are for the line of sight to ζ Oph. \(\tau_{a,c}^{\text{a}}\) is the accretion timescale required to yield the observed depletions for a destruction timescale \(\tau_d = 6 \times 10^8 \text{ yr}\). The depletion \(\delta_t\) for Ca in the warm cloud is unknown. We assumed that \((1 - \delta_c)/(1 - \delta_t)\) is the same for Ca as for Ti in computing \(\tau_{a,c}^{\text{a}}\). \(\tau_{\text{max}}^{10 \text{ Å}}\) is the maximum allowed refreshment timescale for \(a = 10 \text{ Å}\) carbonaceous grains, where \(\beta\) is the maximum allowed number of metal atoms per carbon atom, and \(\gamma\) is the number of metal atoms per carbon in “fresh” carbonaceous grains.
with a more resilient, Fe-rich grain population that includes very small grains. Metallic Fe grains are ruled out because they would produce excessive magnetic dipole emission at 90 GHz (Draine & Lazarian 1999). Sembach & Savage (1996) have suggested oxides as a grain component, on the basis of gas-phase abundance measurements in diffuse halo clouds. They found more Fe plus Mg per Si in dust than expected for pure olivines or pure pyroxenes.

A 20 μm feature has recently been detected in emission in warm circumstellar dust shells, and attributed to FeO grains (Waters 1998). Since single-photon heating of the very small interstellar grains results in emission at λ ≥ 5 μm, candidate materials will be constrained by the observed emission spectrum of diffuse clouds. Koike et al. (1981) and Henning et al. (1995) have experimentally determined IR optical constants for well-known iron oxides, and reported Q_{abs}/a for spheres in the Rayleigh limit (Q_{abs} is the absorption efficiency factor). We reproduce their band positions in Table 5. It is important to note that the band positions depend on the particle shape. Henning et al. (1995) also calculated absorption for two continuous distributions of ellipsoids and found that the FeO band position shifts from 19.9 to 21.0 μm or 23.4 μm. Serna, Ocaña, & Iglesias (1987) and Wang, Muramatsu, & Sugimoto (1998) discussed the effect of particle shape on the hematite spectrum. We suspect that the 9 μm feature in the Koike et al. hematite spectrum is due to an impurity in their sample; this feature is absent in the Nyquist & Kagel (1971) spectrum and present, but attributed to an impurity, in the Sadler spectrum (Ferraro 1982). Thus, the Mattila et al. (1996) and Onaka et al. (1996) studies do not rule out very small grains with iron oxide composition, since the longest wavelength they observed is 11.7 μm. Spectrophotometry of the emission from diffuse clouds in the 15–30 μm range would resolve the issue, but are beyond current capabilities. Thus, at this time we cannot exclude the possibility that a significant fraction of interstellar Fe resides in ultrasmall Fe oxide particles.

### 4.5. Conclusion

Observations of infrared emission in the 3–60 μm range indicate that there is a population of very small dust grains, extending down to sizes of a few angstroms. The presence of several spectral features associated with polycyclic aromatic hydrocarbons and the absence of the 10 μm silicate feature imply that there are carbonaceous grains with a < 10 Å, but no such silicate grains. The rate at which gas collisions collide with these ultrasmall grains greatly exceeds that for collisions with bigger “classical” (a ≥ 0.01 μm) grains. If the elements that are most heavily depleted in the ISM stick efficiently upon collision, then accretion onto very small grains occurs quickly enough to account for their depletions. This fast accretion is completely independent of the model adopted for the classical grains, which is currently controversial (Mathis 1996). Efficient sticking requires resistance against photodesorption in the interstellar radiation field and against chemical attack. Furthermore, if the depletion of the more abundant element, Fe, is due to accretion onto very small carbonaceous grains, then Fe would be a major component in the composition of these grains, at a level which might be chemically impossible. Perhaps Fe does not stick well to the very small carbonaceous grains, instead depleting onto a silicate population extending down only to ≈ 10–15 Å. Alternatively, there might be another population of very small iron-rich grains. There are well-known oxides which cannot be ruled out to date but which have spectral features in the 15–30 μm range.

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### TABLE 5

| Mineral            | IR Band Position (μm) | Reference          |
|--------------------|----------------------|--------------------|
| Hematite (α-Fe₂O₃) | 9, 18, 21, 30         | Koike et al. 1981  |
| Magnetite (Fe₃O₄)  | 17, 25                | Koike et al. 1981  |
| Wüstite (FeO)      | 19.9                  | Henning et al. 1995 |

**Note:** We suspect that the 9 μm feature in the hematite spectrum is due to an impurity.