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# The destruction and growth of dust grains in interstellar space – III. Surface recombination, heavy element depletion and mantle growth

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**Summary**. It is shown that metallic elements in interstellar clouds will be trapped on the surfaces of graphite and iron grains, leading to their differential gas-phase depletion, whereas non-metal elements will be ejected as saturated hydrides from such grains (and as monohydrides from other grains), with no consequent depletion. A consideration of surface reaction pathways leads to the prediction that Na, K and Zn should undergo less depletion than other metals, in accordance with observations. The factors governing the return of depleted metallic species to the gas phase are discussed. In diffuse clouds the growth of mantles is prevented by photodesorption and by the ejection of non-metal atoms during surface recombination, but in dense clouds which have sufficient ultraviolet shielding, and where the non-metals are in saturated molecules, mantle growth will take place. Upon exposure to the unshielded interstellar ultraviolet radiation field such mantles will rapidly be destroyed. Thus mantles should be found only in dense, shielded regions of interstellar space.

## 1 Molecular recombination on grain surfaces

In this section molecular recombination on grain surfaces will be discussed, with the emphasis being on recombination on chemisorbing surfaces (e.g. graphite or iron), since (a) such grains probably contribute the major fraction of the total interstellar grain surface *area*, and (b) the sticking probability of impinging atoms will be higher for chemisorbing surfaces than for physically adsorbing surfaces. However, where appropriate, reference will be made during the section to the corresponding behaviour on physically adsorbing grains (e.g. silicates).

Barlow & Silk (1976) have considered in detail the theoretical and experimental evidence for the chemisorption of hydrogen atoms on graphite, and have concluded that H atoms (but not $H_2$ molecules) will be chemisorbed on the surfaces of graphite grains in interstellar space, with $H_2$ recombination proceeding without any hindrance. Here, the formation on grain surfaces of molecules other than $H_2$ is considered, starting with the cases of C, N, O and F atoms on a graphite surface, for which there exist quantum mechanical calculations of adsorption energies by Bennett, McCarroll & Messmer (1971b).★ Table 1 presents the adsorption energies, $E_{ads}(M)$, and the surface migration activation energies, $\Delta E_m(M)$, for M = H, C, N, O and F. The value of $E_{ads}(H)$ is taken from Bennett, McCarroll & Messmer (1971a) who calculated it directly using the EHT method, without need for renormalization. The value of $\Delta E_m(H) = 0.10$ eV is the activation energy for $H_2$ recombination on graphite experimentally determined by King & Wise (1963), in good agreement with the prediction of $\Delta E_m(H) = 0.09$ eV from Bennett *et al.* (1971a).

**Table 1.** Adsorption energies for atoms on graphite and heats of formation of hydride molecules.

| Atom M | $E_{ads}(M)$ (eV) | $\Delta E_m(M)$ (eV) | $D(MH)$ (eV) | $D(MH_2)$ (eV) | $D(MH_3)$ (eV) | $D(MH_4)$ (eV) |
|---|---|---|---|---|---|---|
| H | 1.1 | 0.10 | 4.48 | | | |
| C | 9.4 | 2.9 | 3.47 | 9.02 | 12.62 | 17.04 |
| N | 5.7 | 0.90 | 3.2 | 7.5 | 12.0 | |
| O | 3.8 | 0.70 | 4.40 | 9.51 | | |
| F | 2.0 | 0.35 | 5.84 | | | |

Datsiev & Belyakov (1968) have measured a heat of adsorption of 3.4 eV for $O_2$ molecules on graphite, which, upon adding the dissociation energy of $O_2$ and dividing by two, yields an adsorption energy per O atom of $E_{ads}(O) = 4.2$ eV, in reasonable agreement with the prediction of $E_{ads}(O) = 3.8$ eV from Bennett *et al.* (1971b). The fact that $E_{ads}(C)$ on graphite is larger than the sublimation energy of graphite can be attributed to the fact that the carbon atom is predicted to be chemisorbed only 0.75 Å above the graphite basal plane, compared to a normal lattice spacing in the basal plane of graphite of 1.42 Å and an interlayer spacing of 3.37 Å (Willis, Feuerbacher & Fitton 1971).

Inspection of the values of $\Delta E_m(M)$ presented in Table 1 shows that atomic hydrogen has by far the lowest activation energy for migration on the surface. Thermal migration by atoms other than H can be neglected for normal graphite grains temperatures ($\leqslant 33$ K; Leung 1975). In addition, quantum mechanical barrier penetration by atoms other than H can be neglected because of their large mass (*cf.* Watson & Salpeter 1972) and because of their much larger activation energy barriers. Thus all atoms except H will be immobilized upon sticking to a surface site on a graphite grain.

It was shown by Barlow & Silk (1976), using the model of Goodman (1972), that recombining H atoms should leave the surface of a graphite grain with excess kinetic energy, due to the $H_2$ recombination energy being converted into kinetic energy away from the surface, thus overcoming the adsorption potentials felt by the two component H atoms. Consider now the general case of an atom M recombining with an H atom on any grain surface. Note that there will be no activation energy to be overcome for molecular recombination of atoms adsorbed on graphite since (a) not all the adsorbed atom valence bonds are utilized

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★ Bennett *et al.* normalized their adsorption energy results in the usual way for CNDO calculations, i.e. by dividing their results by a factor corresponding to the ratio of the calculated cohesive energy of graphite (they found 26.3 eV per atom) to the experimental cohesive energy of graphite. However, in their initial paper they assumed an experimental cohesive energy (sublimation energy) of 5 eV per atom, whereas the true experimental cohesive energy of graphite is 7.35 eV per atom (Gaydon 1968), as later pointed out by McCarroll & Messmer (1971). With this correction McCarroll & Messmer (1971) obtained the same ratio of calculated to experimental energy for the case of graphite as they found for the case of boron nitride using the same CNDO method. The results given by Bennett *et al.* (1971b) and by McCarroll & McKee (1971) have thus been renormalized here, using a cohesive energy of 7.35 eV per atom for graphite.

in the chemisorption bond to graphite, e.g. only 3.3 for C, 2.4 for N, 1.5 for O and 0.85 for F according to Bennett *et al.* (1971b), (b) the bonds to the surface are not normal valence bonds (i.e. where the one electron is shared between two atoms), due to the fact that the lattice atoms are not free atoms. Instead, Bennett *et al.* (1971b) found that two lattice atoms, partially donating three electrons each, contributed to a single bond with one adsorbed H atom. Two adsorbed atoms on a surface can, however, form true valence bonds between each other, so that bonds between recombining atoms take precedence over bonds to the surface. The model of Goodman (1972) is now generalized to the case of a surface diffusing H atom recombining with an adsorbed atom M. Before recombination the total energy of the system is given by

$$\epsilon = V(\mathrm{H}) + V(\mathrm{M}) + E(\mathrm{H}) - E_{\mathrm{ads}}(\mathrm{H}) - E_{\mathrm{ads}}(\mathrm{M}) \tag{1}$$

where atoms H and M are vibrating with energies $V(\mathrm{H})$ and $V(\mathrm{M})$ with respect to the surface and $E(\mathrm{H})$ is the translational energy of the H atom along the surface. After recombination the total energy of the system is given by

$$\epsilon = I(\mathrm{MH}) + E_{\mathrm{t}}(\mathrm{MH}) + E_{\mathrm{n}}(\mathrm{MH}) - D(\mathrm{MH}) \tag{2}$$

where $I(\mathrm{MH})$ is the internal (vibrational and rotational) energy of the newly formed molecule, $E_{\mathrm{t}}(\mathrm{MH})$ and $E_{\mathrm{n}}(\mathrm{MH})$ are the translational energies of the molecule, tangential and normal to the surface respectively, and $D(\mathrm{MH})$ is the recombination (dissociation) energy of the molecule.

Conservation of tangential momentum (see Goodman 1972) gives

$$E_{\mathrm{t}}(\mathrm{MH}) = (m_{\mathrm{H}}/m_{\mathrm{H}} + m_{\mathrm{M}})\, E(\mathrm{H}),$$

where $m_{\mathrm{H}}$ and $m_{\mathrm{M}}$ are the masses of the H atom and other adsorbed atom respectively. With $V(\mathrm{H}) = V(\mathrm{M}) = 2kT_{\mathrm{g}}$ and $E(\mathrm{H}) = kT_{\mathrm{g}}$, where $T_{\mathrm{g}}$ is the grain surface temperature, we obtain by equating (1) and (2)

$$E_{\mathrm{R}}(\mathrm{MH}) \equiv I(\mathrm{MH}) + E_{\mathrm{n}}(\mathrm{MH}) = D(\mathrm{MH}) - E_{\mathrm{ads}}(\mathrm{H}) - E_{\mathrm{ads}}(\mathrm{M}) + \left(4 + \frac{m_{\mathrm{H}}}{m_{\mathrm{H}} + m_{\mathrm{M}}}\right) kT_{\mathrm{g}} \tag{3}$$

where $E_{\mathrm{R}}(\mathrm{MH})$ is the total energy of the newly formed molecule available for sharing between internal and kinetic energy. For grain temperatures $\lesssim 100\,\mathrm{K}$ the last term on the right-hand side of equation (3) can be neglected.

A molecule normally recombines into a highly excited vibrational–rotational level of the ground electronic state, and Williams (1968) has shown that hydride molecules on graphite grain surfaces can make the necessary stabilizing transition through rotational de-excitation by electrons tunnelling through from the surface, although vibrational de-excitation transitions are much less efficient, even if account is taken of the closer distance to the surface for the chemisorption case ($\sim 1$ Å), compared to the distance of $\sim 3$ Å used by Williams (1968) for the physical adsorption case. De-excitation of newly formed molecules by phonons is shown to be unimportant by Williams (1968). Barlow & Silk (1976) have proposed a model by which a newly formed $H_2$ molecule, vibrating internally at a frequency of $\sim 10^{15}$/s, converts its internal energy into translational energy away from the surface by means of a collision with a surface atom. The maximum vibrational frequency of a lattice atom ($3.8 \times 10^{12}$/s for graphite; Dolling & Brockhouse 1962) is much lower than that of the molecule and so the surface atom behaves as a rigid body, allowing the molecule to convert its vibrational energy into translational energy in the rebound. These considerations should hold for most recombining molecules, whose initial vibrational frequencies are $\geqslant 10^{14}$/s (although very heavy atoms may not satisfy this condition) and which, for the cases of H, C, N, O and F for example, are chemisorbed at distances of $\sim 1$ Å from the graphite basal plane

(Bennett *et al.* 1971b), making interaction with a lattice atom highly likely. Experimental evidence on $H_2$ recombination on metal surfaces in support of this model was cited by Barlow & Silk (1976). The condition for desorption of a molecule upon recombination is thus that the molecular recombination energy exceed the sum of the chemisorption binding energies of its component atoms, i.e. $D(\mathrm{MH}) > E_{\mathrm{ads}}(\mathrm{H}) + E_{\mathrm{ads}}(\mathrm{M})$. Table 1 tabulates $D(\mathrm{MH})$ for M = C, N, O and F. It can be seen that of the atoms in the table, only F will be desorbed as a monohydride. However, the remaining cases have further valence bonds with which to recombine with more H atoms. The initial monohydride formation will have removed a bond from the surface, thus reducing the binding energy of the atom in the hydride to the surface. Further recombination with H atoms will remove more surface bonds and if the total heat of formation $D(\mathrm{MH_n})$, of molecule $\mathrm{MH_n}$ exceeds $E_{\mathrm{ads}}(\mathrm{M}) + nE_{\mathrm{ads}}(\mathrm{H})$, then desorption can occur. Table 1 lists $D(\mathrm{MH_n})$ for the appropriate cases (the dissociation energies and heats of formation of the various molecules are taken from Gaydon (1968)). The table shows that C can be desorbed as $CH_4$, N and $NH_3$, O as $H_2O$ and F as HF. Thus desorption always occurs in the form of a saturated hydride.

No quantum mechanical calculations of adsorption energies exist for atoms adsorbed on graphite other than those considered above. However, Levine & Gyftopoulos (1964) and Gyftopoulos & Steiner (1967) have produced an empirical theory for the adsorption energies of various metal atoms on metal surfaces. The model calculates the strength of the ionic (charge exchange) bond and covalent (electron sharing) bond between a surface and an adatom, based on concepts of orbital electronegativity. The theory allows the calculation of adsorption energies to be made using known sublimation energies, work functions, etc. The theory is applicable to tetravalent atoms as well as to true metal atoms, and should be valid for the semi-metal material graphite.

According to the theory, the adsorption potential between a metallic atom and a surface consists of covalent and ionic components, $E_{\mathrm{ads}}$(covalent) and $E_{\mathrm{ads}}$(ionic). The theory allows for a variation of surface coverage by the adatom species (which mainly affects the ionic contribution). From Levine & Gyftopoulos (1964), the covalent bonding contribution to the adsorption energy is given by

$$E_{\mathrm{ads}}(\mathrm{covalent}) = (H_s H_a)^{1/2} S_{sa} Q_{sa} \tag{4}$$

where $H_s$ and $H_a$ (in eV) are the heats of sublimation of the substrate material and bulk adsorbate, respectively. $S_{sa}$ is the angular efficiency of the orbitals, given by

$$S_{sa} = 2/(S_s/S_a + S_a/S_s) \tag{5}$$

where $S_s$ and $S_a$ are the angular strengths of the valence orbitals of the substrate and adsorbate atoms, respectively (defined by Levine & Gyftopoulos 1964). $Q_{sa}$ is the charge efficiency, given by

$$Q_{sa} = (1 - F^2/e^2)^{1/2} \tag{6}$$

where $e$ is the charge of an electron and $F$, the charge transfer factor, is defined below. $Q_{sa}$ allows for the reduction in overlap energy when charge is transferred and is equal to unity when the bond strength is purely covalent ($F = 0$) and equal to zero when the bond is purely ionic ($F = e$).

From Gyftopoulos & Steiner (1967) the ionic bonding contribution to the adsorption energy is given by

$$E_{\mathrm{ads}}(\mathrm{ionic}) = V_a(\phi_s - \phi_a)(1 - M)\frac{F}{e} - V_a D_1 \frac{F^2}{2e^2}. \tag{7}$$

Here $V_a$ is the valence of the adsorbed atom and $\phi_s$ and $\phi_a$ (in eV) are the work functions of the substrate material and of the bulk state of the adsorbate, respectively. $M$ is a Morse function, to which the overlap charge is proportional, such that $M = 0$ at zero surface coverage ($\theta = 0$) and $M = 1$ at monolayer surface coverage ($\theta = 1$). Gyftopoulos & Steiner (1967) give the following expression for $D_1$,

$$D_1 = 1.3(\phi_s + \phi_a) - \frac{28.8\,\mathrm{eV}}{(r_s + r_a)} \tag{8}$$

where $r_s$ and $r_a$ (in Å) are the atomic radii of the substrate and adsorbed atoms, respectively.

As shown by Gyftopoulos & Steiner (1967), the value of $F/e$ in equations (6) and (7) can be obtained from the solution of the equation

$$\frac{F}{e} = \frac{(\phi_s - \phi_a)(1 - M)}{(H_s H_a)^{1/2} S_{sa}(1 - F^2/e^2) + D_1}. \tag{9}$$

Thus, when the surface coverage $\theta$ is equal to zero, the total adsorption energy is given by

$$E_{ads}(\theta = 0) = (H_s H_a)^{1/2} S_{sa} Q_{sa} + V_a(\phi_s - \phi_a)\frac{F}{e} - V_a D_1 \frac{F^2}{2e^2}. \tag{10}$$

When the surface coverage $\theta$ is equal to unity the total adsorption energy is that due to covalent bonding alone since $M = 1$ and $F/e = 0$. Therefore

$$E_{ads}(\theta = 1) = (H_s H_a)^{1/2} S_{sa}. \tag{11}$$

We adopt the following parameters for the graphite substrate: a work function $\phi_s = 4.7$ eV, from Willis *et al.* (1971), a sublimation energy $H_s = 7.35$ eV, from Gaydon (1968), an orbital strength $S_s = 1.87$, from Levine & Gyftopoulos (1964), and an atomic radius $r_s = 0.70$ Å, from Weast (1968). Table 2 presents the calculated values of $E_{ads}(\theta = 0)$ and $E_{ads}(\theta = 1)$, for all of the elements for which $\phi_a$, $H_a$, $S_a$, $V_a$ and $r_a$ were available, these quantities also being tabulated in Table 2.

The only experimental metal–graphite adsorption energy that could be found for comparison with the results of Table 2 is that of caesium on graphite, measured by Milstead, Riedinger & Zumwalt (1966). For low surface coverages they obtained $E_{ads}(\mathrm{Cs}) = 3.9$ eV, compared to the value of 3.6 eV predicted in Table 2, and for high surface coverages they found $E_{ads}(\mathrm{Cs}) = 1.7$ eV, compared to the predicted value of 2.0 eV. The agreement can be considered satisfactory.

In the last column of Table 2 the dissociation energies $D(\mathrm{MH})$ of the monohydrides of various elements M are tabulated. Comparison of $D(\mathrm{MH})$ with $E_{ads}(\mathrm{M}) + E_{ads}(\mathrm{H})$ (where $E_{ads}(\mathrm{H}) = 1.1$ eV) should reveal whether an atom M will be trapped or desorbed upon recombination. The value of $E_{ads}(\theta = 1)$ is more appropriate for this comparison than $E_{ads}(\theta = 0)$, since surface coverages approaching $\theta = 1$ are expected due to the depletion of the interstellar heavy elements. Inspection of Table 2 reveals that none of the atoms M will be desorbed as a monohydride from the surface of a graphite grain.

The tetravalent elements Si, Ge, Sn and Pb form stable tetrahydrides with heats of formation of 13.2, 12.0, 10.5 and 8.5 eV respectively (Gaydon 1968; Mackay 1966), compared to total adsorption binding energies, $E_{ads}(\mathrm{M}) + 4E_{ads}(\mathrm{H})$, of 10.2, 9.7, 9.2 and 8.2 eV. Thus Si, Ge and probably Sn should desorb as tetrahydrides but Pb may be trapped (this is also likely because of its high mass). This behaviour is a reflection of the fact that the later tetravalent elements behave more like metals. Boron, whose chemical properties are akin to those of a non-metal, forms stable di- and trihydrides. The total heat of formation of $BH_3$ is

**Table 2.** Parameters for the determination of adsorption binding energies, $E_{\text{ads}}$, on graphite surfaces.

| Adsorbed atom M | $\phi_a$ (eV)★ | $H_a$ (eV)★ | $S_a$† | $V_a$ | $r_a$ (Å)★ | $E_{\text{ads}}$ ($\theta = 0$) (eV) | $E_{\text{ads}}$ ($\theta = 1$) (eV) | $D$(MH)‡ |
|---|---|---|---|---|---|---|---|---|
| Li | 2.49 | 1.66 | 1.0 | 1 | 1.45 | 4.51 | 2.91 | 2.43 |
| Be | 3.92 | 3.38 | 1.29 | 2 | 1.05 | 5.43 | 5.02 | 2.3 |
| B | 4.5 | 5.74 | 1.58 | 3 | 0.85 | 7.26 | 6.40 | 3.4 |
| Na | 2.28 | 1.1 | 1.0 | 1 | 1.80 | 4.20 | 2.36 | 2.05 |
| Mg | 3.68 | 1.51 | 1.29 | 2 | 1.50 | 3.50 | 3.11 | 2.0 |
| Al | 4.08 | 3.37 | 1.58 | 3 | 1.25 | 5.40 | 4.90 | 2.9 |
| Si | 4.52 | 4.69 | 1.87 | 4 | 1.10 | 6.40 | 5.84 | 3.06 |
| K | 2.24 | 0.91 | 1.0 | 1 | 2.20 | 3.55 | 2.15 | 1.9 |
| Ca | 2.71 | 1.84 | 1.29 | 2 | 1.80 | 4.31 | 3.44 | ~1.7 |
| Ti | 3.95 | 4.87 | 2.62 | 2 | 1.40 | 5.75 | 5.66 | |
| V | 4.12 | 5.32 | 2.62 | 2 | 1.35 | 5.96 | 5.91 | |
| Cr | 4.60 | 4.11 | 2.31 | 2 | 1.40 | 5.38 | 5.38 | 2.8 |
| Mn | 3.83 | 2.08 | 2.62 | 2 | 1.40 | 4.55 | 4.35 | 2.4 |
| Fe | 4.40 | 4.30 | 2.62 | 2 | 1.40 | 5.34 | 5.32 | 2.43 |
| Co | 4.40 | 4.39 | 2.62 | 2 | 1.35 | 5.39 | 5.37 | |
| Ni | 5.03 | 4.44 | 2.62 | 2 | 1.35 | 5.41 | 5.40 | 2.6 |
| Cu | | 3.5 | 1.29 | 2 | 1.35 | | 4.7 | 2.8 |
| Zn | 4.24 | 1.34 | 1.29 | 2 | 1.35 | | 2.9 | 0.85 |
| Ge | 4.5 | 3.89 | 1.87 | 4 | 1.25 | 5.54 | 5.34 | 3.2 |
| Rb | 2.09 | 0.83 | 1.0 | 1 | 2.35 | 3.52 | 2.05 | 1.7 |
| Sr | 2.74 | 1.68 | 1.29 | 2 | 2.00 | 3.98 | 3.28 | 1.65 |
| Sn | 4.38 | 3.11 | 1.87 | 4 | 1.45 | 4.90 | 4.78 | 2.7 |
| Cs | 1.81 | 0.80 | 1.0 | 1 | 2.60 | 3.63 | 2.02 | 1.8 |
| Ba | 2.74 | 1.68 | 1.29 | 2 | 2.15 | 4.22 | 3.43 | 1.8 |
| Pb | 3.97 | 2.01 | 1.87 | 4 | 1.80 | 4.14 | 3.84 | 1.8 |

★ From CRC Handbook of Chemistry and Physics (Weast 1968).
† From Levine & Gyftopoulos (1964).
‡ From Gaydon (1968).

11.53 eV (Gaydon 1968), compared to $E_{\text{ads}}(\theta = 1) + 3E_{\text{ads}}(\text{H}) = 9.7$ eV. Thus boron should be desorbed as $BH_3$.

For the other di- and trivalent elements no stable dihydrides are known, and if they do exist their recombination energies must be considerably less than those of the monohydrides. Further H atom addition to the monohydrides of these elements will instead lead to the reaction

$$\text{MH} + \text{H} \rightarrow \text{M} + \text{H}_2. \tag{12}$$

Such reactions are exothermic by the difference in the dissociation energies of $H_2$ and MH. Since a bond must be broken during such a reaction, there will be an activation energy $E_{\text{act}}$. However, according to Glasstone, Laidler & Eyring (1941), the activation energy of a three-centre reaction

$$\text{X} + \text{YZ} \rightarrow \text{XY} + \text{Z} \tag{13}$$

is generally small in the exothermic direction, particularly if X is a hydrogen atom. They estimate that the activation energy should be approximately 5.5 per cent of the bond energy being broken, so in this case $E_{\text{act}} = 0.055\,D(\text{MH})$. Inspection of the values of $D$(MH) in Table 2 reveals that $E_{\text{act}}$ will always be less than 0.15 eV, which can easily be overcome through quantum tunnelling by a H atom on a grain surface. The energy $E_{\text{react}}$ liberated by the reaction is given by

$$E_{\text{react}} = D(\text{H}_2) - D(\text{MH}) \tag{14}$$

where $D(\text{H}_2) = 4.5\,\text{eV}$. This energy will be available for sharing between the resultant metal atom and $H_2$ molecule. It is expected that in most cases the majority of $E_{\text{react}}$ will be taken up by the lighter $H_2$ molecule, but in a certain fraction of cases the metal atom will find itself with the majority of the liberated energy. If $E_{\text{ads}}(\theta = 1)$ for a metal atom M is less than $E_{\text{react}}$, then it is possible for the metal atom to be ejected from the surface. Inspection of Table 2 shows that the alkali atoms Na, K, Rb and Cs, and also Zn, can be ejected in this manner. All other metal atoms will be trapped. In the cases where the majority of $E_{\text{react}}$ goes to the $H_2$ molecule it will usually be larger than $2E_{\text{ads}}(\text{H})$ (= 2.2 eV) and thus sufficient to desorb the $H_2$ molecule. In the cases where $E_{\text{react}}$ is shared more equally between the atom M and the $H_2$ molecule, neither will be ejected by the reaction. The effect of reactions such as (12) on the depletion patterns of Na, K and Zn will be discussed in the next section.

If Fe grains exist, the the analogous adsorption binding energies to these calculated for graphite in Table 2 can be calculated by the methods outlined above. In general, the values of $E_{\text{ads}}(\theta = 1)$ for metal atoms on Fe grains are found to be about a factor of 1.3 less than for graphite grains. Since the adsorption energy of H on Fe is larger, at 1.4 eV (Hayward & Trapnell 1964), the conclusions on which atoms are trapped and which are desorbed are the same.

An earlier version of this work (Barlow 1974) considered only physically adsorbing grains, using data on the physical adsorption binding energies of various elements calculated by Aannestad (1972). For silicate surfaces Aannestad found that $E_{\text{ads}}(\text{Ca}) = 7.7\,\text{eV}$, $E_{\text{ads}}(\text{Ti}) = 5.5\,\text{eV}$ and $E_{\text{ads}}(\text{Fe}) = 2.7\,\text{eV}$. Comparing these with the appropriate values of $D(\text{MH})$ in Table 2 (since $E_{\text{ads}}(\text{H}) \sim 0.06\,\text{eV}$ on silicates and can be neglected) it can be seen that Ca and Ti atoms will definitely be trapped on silicates and Fe might be trapped. For all of the other elements tabulated by Aannestad (1972), the hydride recombination energy exceeds their adsorption energy on a silicate surface and so they should be desorbed as monohydrides. The large physical adsorption binding energies of Ca and Ti are due to their extremely large atomic polarizabilities.

Allen & Robinson (1975) have proposed a model for molecular formation on small grains whereby the molecular recombination energy is rapidly transferred to the grain material, leading to a rise in grain temperature and subsequent thermal desorption of the molecule. However, their assumption that the recombination energy can be efficiently transferred to the grain can be questioned, since typical vibrational frequencies of newly formed molecules are $10^{14}$–$10^{15}$/s, compared to maximum phonon frequencies of a few $\times 10^{12}$/s for typical grain materials. Since the vibrational energy of a newly formed molecule must be removed in quantal amounts, de-excitation by phonons would thus appear to be an unlikely mechanism for energy removal.

## 2 Heavy element depletion in interstellar space

Field (1974) has suggested that elemental depletions in the interstellar medium are determined by grain condensation processes in circumstellar regions, such that the relative depletion of each element correlates with its condensation temperature. According to Field's model, relative depletions along different lines of sight ought to be fairly constant, but in fact depletions are known to vary widely. Barlow & Silk (1977) have proposed a model which incorporates a constant underlying depletion of certain heavy elements (e.g. Fe and Si) due to grain membership as suggested by Field, and they account for the variation of depletion factors along different lines of sight in terms of the adsorption and trapping of metal elements on to grain surfaces, the cycling of such absorbed atoms back to the gas phase being accomplished by sputtering in intermediate velocity shocks (~ 30 km/s). Barlow & Silk (1977) also showed that higher velocity shocks could destroy refractory grains and thus account for the undepleted abundances of Fe and Si seen by Jenkins, Silk & Wallerstein (1976) and Shull, York & Hobbs (1977) in high-velocity cloud components.

The results of the previous section predict that in the diffuse interstellar medium non-metallic elements should not be depleted by trapping on grain surfaces (in sufficiently dense, shielded clouds, depletion of these elements will occur however, see Section 3). The results of Jenkins *et al.* (1976) and Shull *et al.* (1977) indicate that sulphur and phosphorus have cosmic gaseous abundances in most lines of sight. The results for other non-metals are ambiguous for some lines of sight, since as pointed out by Steigman, Strittmatter & Williams (1975) and Gomez-Gonzalez & Lequeux (1975), circumstellar H II regions can make significant contributions to some absorption components, thus complicating their interpretation. The results of Section 1 predict that boron should not be depleted in diffuse clouds. As pointed out by Audouze & Lequeux (1976), the upper limit for the abundance of boron, derived by Morton, Smith & Stecher (1974) for the $\zeta$ Oph line of sight, is consistent with an undepleted cosmic abundance equal to that found for $\alpha$ Lyrae by Boesgaard *et al.* (1974). For the case of silicon, in five low-velocity cloud components analysed by Shull *et al.* (1977) the value of $\delta_{\mathrm{Si}}^{-1}$ was $12.5 \pm 1.5$,[★] compared to values of $\delta_{\mathrm{Fe}}^{-1}$ ranging from 13 to 60. The non-varying depletion of silicon was interpreted by Barlow & Silk (1977) as reflecting its underlying depletion due to grain membership (presumably silicates). No surface trapping of Si on grain surfaces is expected according to the model presented in the previous section, whereas Fe *is* expected to undergo differential depletion due to this mechanism, superimposed on its underlying depletion due to grain membership. Thus the constancy of $\delta_{\mathrm{Si}}^{-1}$ and the variation of $\delta_{\mathrm{Fe}}^{-1}$ can be accounted for.

Carbon presents an interesting case, since although there should be no differential depletion of this element due to adsorption, there should be a relatively constant underlying depletion due to membership of graphite grains. The work of Mathis, Rumpl & Nordsieck (1977) indicates that in order to fit the strength of the interstellar 2200 Å extinction feature, a carbon abundance relative to hydrogen, $n_{\mathrm{C}}/n_{\mathrm{H}} = 1.7 \times 10^{-4}$, is required to be locked up in graphite grains. Adoption of the revised solar abundance of carbon derived by Mount & Linsky (1975), $(n_{\mathrm{C}}/n_{\mathrm{H}})_{\odot} = 2.3 \times 10^{-4}$, implies that a relative abundance $n_{\mathrm{C}}/n_{\mathrm{H}} = 6 \times 10^{-5}$ will remain in the gas phase in the interstellar medium. This corresponds to an apparent depletion by a factor of 6 of the formerly adopted solar carbon abundance, $n_{\mathrm{C}}/n_{\mathrm{H}} = 3.7 \times 10^{-4}$. Chaisson (1975) and Knapp, Kuiper & Brown (1976) have found that carbon is depleted by a factor of 6 relative to sulphur (which is undepleted) in the $\rho$ Oph C II region. In addition, the work of Encrenaz, Falgarone & Lucas (1975), Tucker *et al.* (1976) and Dickman (1976) indicates that, with the adoption of an interstellar $\mathrm{C}^{12}/\mathrm{C}^{13}$ ratio equal to 40, the CO to H nucleus ratio, $N_{\mathrm{CO}}/N_{\mathrm{H}}$, is $4\text{–}8 \times 10^{-5}$ in clouds with $A_V \approx 2\text{–}6$, consistent with most gas-phase carbon atoms in such clouds being locked up in CO molecules. These results imply that if carbon and sulphur are the major source of electrons in *diffuse* interstellar clouds, then $n_{\mathrm{e}} = 10^{-4} n$ where $n$ is the H nucleus number density. Inspection of Tables 1(A) and (B) of Barlow & Silk (1976) reveals that with an apparent depletion by a factor of 6 of the formerly adopted cosmic abundance of carbon, the observed temperatures of diffuse clouds can easily be accounted for by known heating mechanisms.

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[★] $\delta_{\mathrm{M}}^{-1}$ is defined as the factor by which the gas-phase abundance of an element M is depleted with respect to its cosmic abundance. The 'cosmic' abundances referred to are those of Withbroe (1971).

Turning now to the metallic elements, the results of the previous section predict that Na, K and Zn will exhibit a depletion behaviour different from that of the other metals, in that the reaction given by equation (12) will prevent these three elements from being depleted on to grain surfaces in diffuse clouds. As discussed, statistically only a small fraction of reactions of the type (12) are likely to transfer sufficient energy to desorb Na, K or Zn atoms, so in order for no depletion to occur, sufficient H atoms must interact with the absorbed atoms between successive captures of these atoms by a grain. For instance, assuming a gas-phase abundance of Na relative to hydrogen of $10^{-6}$, 140 H atoms will land directly on an absorbed Na atom (area of surface site $\sim 10^{-15}\,\mathrm{cm}^2$) for every Na atom landing on a grain of radius $1.5 \times 10^{-6}$ cm. Thus successive reactions of the type $\mathrm{Na} + \mathrm{H} \rightarrow \mathrm{NaH}$; $\mathrm{NaH} + \mathrm{H} \rightarrow \mathrm{Na} + \mathrm{H}_2$ can take place 70 times. When account is also taken of the interaction with diffusing H atoms we see that there should be sufficient reactions to desorb the Na atom. Note that as the density of a cloud increases most H atoms are converted to $\mathrm{H}_2$ molecules. These $\mathrm{H}_2$ molecules will not react with adsorbed metals since the dissociation energy of $\mathrm{H}_2$ is larger than the recombination energy of metal hydride molecules. Thus at high cloud densities with low H atom abundances Na, K and Zn will begin to be depleted.

We will now review some of the observational data on the depletions of Na, K and Zn. Jura (1975) has found that towards stars with $E(B-V) \leqslant 0.10$, Na is only lightly depleted, if at all. For diffuse clouds $[E(B-V) \lesssim 0.3]$ Lequeux (1975) has found that $\delta_{\mathrm{Na}}^{-1}$ and $\delta_{\mathrm{K}}^{-1}$ are similar and between 3 and 10, in agreement with Crutcher (1975b) who has found that, within a factor of 2, $\delta_{\mathrm{Na}}^{-1} \sim 6$ in such clouds. Hobbs (1974) has also found that Na and K show similar depletions in diffuse clouds and he estimated depletion factors of 2–4. Towards $\xi$ Per $\delta_{\mathrm{Na}}^{-1}$ and $\delta_{\mathrm{K}}^{-1}$ are $<3$ and towards $\zeta$ Per $\delta_{\mathrm{Na}}^{-1}$ and $\delta_{\mathrm{K}}^{-1}$ are $\sim 3$ (Lequeux 1975; Crutcher 1975b). Towards $\zeta$ Oph Morton (1974) has derived $\delta_{\mathrm{Na}}^{-1} = 6$–10, $\delta_{\mathrm{K}}^{-1} = 6$–20 and $\delta_{\mathrm{Zn}}^{-1} = 1.7$–2.1; Lequeux (1975) found $\delta_{\mathrm{Na}}^{-1} \sim 10$; and Crutcher (1975a) obtained $\delta_{\mathrm{Na}}^{-1} \sim 5$ and $\delta_{\mathrm{K}}^{-1} \sim 8$. Cohen (1974) found that Na was depleted to a much greater extent in the interiors of dense shielded clouds compared to its depletion is diffuse clouds and Crutcher (1975b) also obtained this result. The above results appear to be consistent with both Na and K possessing an underlying depletion, due to refractory grain membership, of perhaps $\delta^{-1} \sim 2$–3. In diffuse clouds and the inter-cloud medium this then is the depletion that should usually be observed. The dense cloud towards $\zeta$ Oph is known to have a $\mathrm{H}_2$ density of $\gtrsim 10^3\,\mathrm{cm}^{-3}$ (Morton 1975; Jura 1975). At this density $n_{\mathrm{H}}/n_{\mathrm{H}_2} \sim 3 \times 10^{-2}$ according to Barlow & Silk (1976) and so differential depletion of Na, K and Zn should occur. The results for $\zeta$ Oph would appear to be consistent with these three elements being depleted by a factor of 2 due to adsorption, superimposed on an underlying depletion of about 3 for Na and K and no underlying depletion for Zn (consistent with the lower condensation temperature of Zn).

The remainder of the common metallic elements, which are listed in Table 3, should undergo differential depletion at all cloud densities, due to surface adsorption and trapping. The principal means of returning these adsorbed species to the gas phase is probably the sputtering mechanism described in Appendix A. There it is shown that for each elemental species M there exists a critical shock velocity $v_{\mathrm{crit}}(\mathrm{M})$, above which absorbed particles of the species are rapidly removed from the surface of a grain. Values of $v_{\mathrm{crit}}(\mathrm{M})$ for various elements M, along with their adsorption energies on graphite $E_{\mathrm{ads}}(\mathrm{M})$, are presented in Table 3. The larger of the two values of $E_{\mathrm{ads}}(\mathrm{M})$ for Ca is that for adsorption on silicate grains (the adsorption energies of Ti on graphite and silicates are the same). Data are also presented for Ar in Table 3, since the noble gases cannot be ejected from grain surfaces by hydride recombination. The adsorption energy of Ar on graphite is from Aannestad (1972) and is similar to its adsorption energy on silicates. The

**Table 3.** Adsorption energies and sputtering velocities for elements trapped on graphite grains.

| Element<br>M | $E_{\mathrm{ads}}(\mathrm{M})$<br>(eV) | $v_{\mathrm{crit}}(\mathrm{M})$<br>(km/s) |
|---|---|---|
| Ar | 0.1 | 4 |
| Li | 2.9 | 12 |
| Be | 5.0 | 16 |
| Mg | 3.1 | 17 |
| Ca | 3.4 | 22 |
| Al | 4.9 | 23 |
| Mn | 4.4 | 29 |
| Cu | 4.7 | 31 |
| Cr | 5.4 | 31 |
| Ti | 5.7 | 31 |
| Fe | 5.3 | 32 |
| V | 5.9 | 32 |
| Co | 5.4 | 33 |
| Ni | 5.4 | 33 |
| Ca | 7.7★ | 34 |

★ Adsorbed on silicates.

value of $v_{\mathrm{crit}}(\mathrm{M})$ for Ar is sufficiently low that this element should not be substantially depleted on to grain surfaces. He and Ne, with adsorption energies of 0.01 and 0.03 eV respectively (Aannestad 1972) will be prevented from accreting on to grain surfaces by ordinary thermal desorption.

We now review some observational results on the depletion of elements included in Table 3. For low-velocity gas ($v \lesssim 30$ km/s), minimum depletions appear to be observed in the inter-cloud medium and in H II regions. Hobbs (1976) finds $\delta_{\mathrm{Ca}}^{-1} \sim 10$–40 for stars observed through the inter-cloud medium while Stokes & Hobbs (1976) find minimum Ti depletions, $\delta_{\mathrm{Ti}}^{-1} \sim 10$–40. Morton (1975) has deduced that towards $\zeta$ Oph $\delta_{\mathrm{Al}}^{-1} \sim 50$–100 in the H II region compared to $\delta_{\mathrm{Al}}^{-1} \sim (1\text{–}3) \times 10^3$ in the H I region. Crutcher (1975a) deduces that towards the same star $\delta_{\mathrm{Fe}}^{-1} \sim 10$ and $\delta_{\mathrm{Mn}}^{-1} \sim 2$ in the H II region, compared to $\delta_{\mathrm{Fe}}^{-1} \sim 1000$ and $\delta_{\mathrm{Mn}}^{-1} \gtrsim 300$ in the H I region. Olthof & Pottasch (1975), from an analysis of Fe II and Fe III emission lines, have derived a gaseous abundance of iron relative to hydrogen of $2.5 \times 10^{-6}$ in the Orion nebula, corresponding to $\delta_{\mathrm{Fe}}^{-1} \sim 10$. D. G. York (quoted by Shull *et al.* 1977) has derived $\delta_{\mathrm{Fe}}^{-1} \sim 12$ for the average of eight unreddened stars. Thus underlying depletions due to refractory grain membership would appear to be $\delta_{\mathrm{Fe}}^{-1} \sim 10$, $\delta_{\mathrm{Mn}}^{-1} \sim 2$, $\delta_{\mathrm{Ca}}^{-1} \sim 10$–40, $\delta_{\mathrm{Ti}}^{-1} \sim 10$–40 and $\delta_{\mathrm{Al}}^{-1} \sim 50$–100. The magnitudes of circumstellar H II region shock velocities produced by stellar winds (Castor, McCray & Weaver 1975) seem sufficient to meet the values of $v_{\mathrm{crit}}(\mathrm{M})$ in Table 3 which are needed to sputter trapped adatoms, thus giving observed depletions in H II regions equal to the underlying depletions due to grain membership. In the inter-cloud medium, supernova remnants will be the main source of shocks. Upon adopting the same supernova parameters as in Section 3.6 of Paper I, it is found that a point in the inter-cloud medium will experience a shock with $v \gtrsim 30$ km/s once every $10^8$ yr. In an inter-cloud medium with $n = 0.16\ \mathrm{cm}^{-3}$ and $T \sim 5 \times 10^3$ K (Falgarone & Lequeux 1973) the mean time for an atom of atomic weight A to encounter a graphite grain with parameters given below will be $2 \times 10^8 A^{1/2}$ yr. Taking this as the depletion timescale, we see that there should be no significant depletion of atoms in the inter-cloud medium due to surface trapping and observed depletions should again correspond to the underlying depletions due to grain membership.

As discussed by Barlow & Silk (1977), the enhancement of Ca II/Na I ratios in cloud components moving with velocities $\geqslant 20\,\text{km/s}$ (Routly & Spitzer 1952; Siluk & Silk 1974) can be ascribed to the sputtering of adsorbed Ca atoms from the surfaces of grains, since from Table 3 $v_{\text{crit}}(\text{Ca}) = 22$ and 34 km/s for graphite and silicate grains respectively.

In the depletion model presented here and by Barlow & Silk (1977), the very large depletions of certain elements observed in some clouds are ascribed to the trapping of these elements on grain surfaces. Note that the total depletion of a given element will thus be the product of its underlying depletion due to grain membership and the depletion produced by surface trapping on grains. Thus Al for instance could have a larger underlying depletion than Ca, Ti or Fe, but the latter elements may undergo greater surface depletion than Al, due to their higher values of $v_{\text{crit}}(\text{M})$ and the extra depletion of Ca, Ti and possibly Fe on to silicate grains (Section 1).

From Mathis *et al.* (1977) one can derive a mean cross-section for graphite grains per unit volume equal to $1.1 \times 10^{-21}\,n/\text{cm}$, where $n$ is the number density of H nuclei. If each surface site on a grain has an area $\sigma = 10^{-15}\,\text{cm}^2$, the total number of surface sites per unit volume of interstellar space is equal to $4 \times 1.1 \times 10^{-21}\,n/10^{-15} = 4.4 \times 10^{-6}\,n$. This then is the total fractional abundance of heavy elements which can be accommodated in a monolayer on the surface of graphite grains. Iron/magnetite grains if they exist will contribute an additional surface area for depletion, as will silicate grains for the case of Ca, Ti and Fe atoms. Since the observations indicate underlying depletion factors $\delta^{-1} \geqslant 10$ for the metals in Table 3 we see that interstellar grains should be able to accommodate the remaining gas-phase atoms of these species. The condition found by Gilra (1972), that no significant coatings were allowed on graphite grains if the 2200 Å extinction feature was to survive, is thus also met, since no more than a monolayer of adsorbed particles is likely to be found on such grains. The hypothesis that metal hydride molecules trapped on grain surfaces give rise to the diffuse interstellar absorption bands is discussed by Barlow & Gilra (1977, in preparation).

Snow (1975) has proposed a model for the depletion of heavy elements in the interstellar medium in which the accretion rates of elements on to grains are determined by their first ionization potentials. In the model presented here on the other hand, the ionization state of an element is not expected to play a major role since positive ions approaching graphite or iron grains should be neutralized as they approach the grain if their ionization potential is greater than the work function of the grain material (4.4 eV for iron and 4.7 eV for graphite). Thus only K, Rb and Cs would perhaps adsorb as ions but once chemisorbed neutralization would be expected to take place. A possible means of discriminating between the model presented here and that of Snow would be comparison of the relative depletions of Li, Na and K. As discussed earlier in this section, K and Na appear to show similar depletions in interstellar space. Their first ionization potentials differ by 0.8 eV. The first ionization potentials of Li and Na differ by only 0.25 eV and so they should exhibit virtually identical depletions according to Snow's model.* The model presented here predicts that Li should show a larger depletion in clouds than Na, since Na will be ejected from grain surfaces by reactions of the type (12), whereas Li will not. The observational data on these two elements toward $\zeta$ Oph are ambiguous at present. Morton (1975) finds $\delta_{\text{Na}}^{-1} = 6$–$10$ and $\delta_{\text{Li}}^{-1} = 30$, but Audouze & Lequeux (1976) claim that the difference is less than this. More detailed investigation of Na and Li depletions would appear profitable. Clouds with $10 \leqslant n \leqslant 10^3\,\text{cm}^{-3}$ should be the most suitable regions for investigation since the low value of $v_{\text{crit}}(\text{Li})$ in Table 3 implies that Li will not be significantly depleted in

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[*] The underlying depletions of Li, Na and K should be the same since they have similar condensation temperatures.

regions where the depletion timescale (proportional to $1/n$) is longer than the interval between shocks with $v \geqslant 12$ km/s. A further point relevant to the correlation of first ionization potentials with depletion plotted by Snow (1975) is that in diffuse clouds Ca III/Ca II ~ 5 on average, although with wide variations (Stokes & Hobbs 1976). If the second ionization potential of Ca (11.87 eV) is plotted instead, the correlation is weakened.

Barlow & Silk (1977) have interpreted the near cosmic gaseous abundances of elements such as Si and Fe which are seen in high-velocity components (>40 km/s), as due to the destruction by sputtering of refractory grains containing these elements. They showed that the gas swept up by a supernova remnant which has decelerated from a high initial velocity to a velocity $v$ will exhibit a depletion $\delta = v/v_{\mathrm{sp}}$ for any element initially locked up in interstellar grains (i.e. ⩾90 per cent initially in grains). $v_{\mathrm{sp}}$ is the shock velocity above which the type of grain containing a particular element is completely destroyed. Implicit in this estimate of $\delta$ was the assumption that once the remnant expansion velocity has dropped below $v_{\mathrm{sp}}$, no further grain destruction takes place. However, as shown in Appendix B, incomplete grain destruction at velocities $v < v_{\mathrm{sp}}$ increases the value of $\delta$ which is predicted (i.e. decreases the depletion). As an example, consider Si or Mg, assumed mostly to be locked up in silicate grains, for which $v_{\mathrm{sp}} = 230$ km/s. For a current supernova remnant expansion velocity of 80 km/s equation (B6) of Appendix B predicts $\delta = 0.63$, compared to $\delta = v/v_{\mathrm{sp}} = 0.35$ predicted by the simple model. The grain sputtering model seems capable of accounting for the magnitudes of the observed depletions as well as the correlation of depletion with velocity plotted by Barlow & Silk (1977). The scatter about this correlation can be explained by two effects. (a) The radial component of velocity which is observed may be significantly less than the true velocity, in which case use of the observed velocity in equation (B7) will underestimate the depletion $\delta$. (b) Some high-velocity cloud components may not be due to decelerating supernova remnants. If the initial velocity of a cloud component was close to its observed velocity then the depletion $\delta$ will be given by equation (B4) of Appendix B and will be significantly less than predicted by equation (B6). For example, an initial shock velocity of 80 km/s will produce a depletion $\delta = 0.16$ compared to $\delta = 0.63$ predicted by the decelerating supernova remnant model.

## 3 The conditions required for the existence of mantles

In Section 1 of this paper it was concluded that non-metal atoms will be ejected from silicate grain surfaces in the form of monohydrides and will be ejected in the form of saturated hydrides from the surfaces of graphite and iron grains. Upon ejection these hydrides will rapidly be dissociated by the interstellar ultraviolet radiation field in regions of low shielding (Stief *et al.* 1972). Thus these elements will return to the surfaces of grains in the free atomic or ionic form once again, with subsequent ejection, as before. Not until sufficient shielding exists to prevent the dissociation of saturated molecules in the gaseous state will such molecules be able to stick to and remain on a grain surface without being ejected due to further recombination with H atoms. Such saturated molecules will be physically adsorbed. Thus the recombination and ejection process alone prevents the acquisition of mantles in regions of low shielding. In regions of higher shielding, where saturated molecules can exist in the gaseous state, molecular recombination on grain surfaces will no longer be operative and photodesorption will be the only process preventing mantle growth. The condition for the growth of a mantle will then be that the rate of sticking of molecules be greater than the rate at which they are photodesorbed from the surface (Watson & Salpeter 1972; Greenberg 1973). The rate of accretion of molecules by a grain of radius $a$ is given by

$$\frac{dn_a}{dt} = \pi a^2 n_a \bar{v}_a S_a \tag{15}$$

where $S_a$, $n_a$ and $\bar{v}_a$ are the sticking coefficient, number density and mean thermal velocity of accreting molecules. The rate at which molecules are lost from the surface due to photodesorption is given by

$$\frac{dn_a}{dt} = -\pi a^2 Y_{\text{pd}} G_0 \exp(-\tau_{\text{uv}}) \tag{16}$$

where $Y_{\text{pd}}$ is the photodesorption yield, $G_0$ is the local flux of ultraviolet photons in the 912–1900 Å region and $\tau_{\text{uv}}$ is the mean extinction over the 912–1900 Å region. Therefore accretion exceeds loss when

$$n_a \bar{v}_a S_a > Y_{\text{pd}} G_0 \exp(-\tau_{\text{uv}}).$$

If we assume typical parameters of $n_a = 10^{-3} n$, where $n$ is the number density of H nuclei, a mean molecular mass $m_a = 18 m_{\text{H}}$, a gas temperature of 10 K, a sticking coefficient $S_a = 1$ and take $Y_{\text{pd}} = 5 \times 10^{-3}$ and $G_0 = 1.7 \times 10^8 \text{cm}^{-2}$ from Section 3 of Paper II, we find the condition for mantle growth to be

$$n \exp(\tau_{\text{uv}}) > 8 \times 10^4 \text{cm}^{-3}.$$

Thus in a cloud of density $n = 10^3 \text{cm}^{-3}$, $\tau_{\text{uv}} = 4.4$ is required for mantle growth to commence. For the high ultraviolet albedo case of Barlow & Silk (1976), $\tau_{\text{uv}} = \tau_{\text{v}}$, implying $\tau_{\text{v}} = 4.4$. For the lower ultraviolet albedo case of Hollenbach, Werner & Salpeter (1971), $\tau_{\text{uv}} = 2.5\,\tau_{\text{v}}$, implying that $\tau_{\text{v}} = 1.8$. A density of $n = 10^4 \text{cm}^{-3}$ requires only $\tau_{\text{uv}} = 2.1$, implying $\tau_{\text{v}} = 2.1$ and $\tau_{\text{v}} = 0.85$ for the high and low albedo cases respectively. If hot stars are nearby then the extinction requirements will be increased.

These values of $n$ and $\tau_{\text{v}}$ are in the range inferred by Carrasco, Strom & Strom (1973) and Strom *et al.* (1975) for dense regions where mantle growth is implied by an increase in the ratio of total to selective extinction $R$ and an increase of the wavelength of maximum interstellar linear polarization. Fig. 2 of Carrasco *et al.* (1973) and Fig. 1 of Whittet & van Breda (1975) indicate that in the $\rho$ Oph cloud the value of $R$ increases with $A_{\text{v}}$ until it saturates at a maximum of $R \sim 4.3$ when $A_{\text{v}} \gtrsim 3.5$. Since $n \geqslant 10^3 \text{cm}^{-3}$ in the $\rho$ Oph cloud (Carrasco *et al.* 1973) the values of $A_{\text{v}}$ at which the onset of mantle growth is observed (i.e. when $R > 3.1$) are consistent with the range predicted above. The saturation of $R$ in the $\rho$ Oph cloud when $A_{\text{v}} \geqslant 3.5$ is consistent with all heavy elements having been accreted on to grain mantles (Carrasco *et al.* 1973; Whittet & van Breda 1975). Tucker *et al.* (1976) have found a linear correlation of $N_{^{13}\text{CO}}$ (the column density of $^{13}$CO) versus $A_{\text{v}}$ in the dark cloud L134, up to a value of $A_{\text{v}} \sim 3$–5, beyond which point $N_{^{13}\text{CO}}$ saturates. This can also be interpreted as being caused by all C and O atoms being locked up in grain mantles when $A_{\text{v}} \gtrsim 4$.

Mantles will remain on grains whilst the grains are shielded. Upon exposure to an unshielded ultraviolet radiation field the mantles will rapidly be destroyed by photodesorption. As derived in Section 3 of Paper II, the timescale for destruction of an ice grain of radius $a = 10^{-5}$ cm is $5 \times 10^4$ yr when exposed to the unshielded average interstellar radiation field. If an ice grain should find itself in a H II region the timescale for destruction will be even shorter, i.e. 130 yr when situated 2 pc from an O star emitting $3 \times 10^{49}$ ultraviolet photons per second with $\lambda < 1900$ Å.

The conclusion that ice mantles cannot exist in unshielded regions of interstellar space is in accord with the results of Gillett *et al.* (1975), who placed a very firm upper limit on the strength of any 3.1 $\mu$m ice absorption feature in the spectrum of the highly reddened star VI Cyg no. 12 ($A_{\text{v}} = 10$). They found $\tau_{(\text{ice})} \leqslant 0.02$, as compared to the strength of the ice absorption feature towards the Becklin–Neugebauer object of $\tau_{(\text{ice})} = 1.4$. Gillett *et al.*

find that the ratio of the strengths of the ice (3.1 $\mu$m) and silicate (9.7 $\mu$m) absorption features is given by $\tau_{(\text{ice})}/(\text{silicates})\ (\text{BN})/\tau_{(\text{ice})}/\tau_{(\text{silicates})}$ (VI Cyg no. 12) $\geqslant 15$, indicating a great disparity in the mass of ice grains (mantles) towards these two objects. This is understood in the present model as being due to the Becklin–Neugebauer object being situated in a dense, shielded molecular cloud, where the conditions for mantle accretion and retention are satisfied. On the other hand, the material towards VI Cyg no. 12, because of the lack of an observed molecular cloud, appears to be either dispersed over a long path length with low density or to be accumulated in an intracluster shell exposed to the intense ultraviolet radiation field of the entire OB cluster. For either of these conditions ice mantles would not be expected. Similarly, towards the Galactic Centre, for which $A_V \geqslant 28$, Soifer, Russell & Merrill (1976) have found $\tau_{(\text{ice})} < 0.25$, so that $A_V/\tau_{(\text{ice})} \geqslant 110$. Soifer *et al.* concluded 'Since the line of sight to the Galactic Center samples a 10 kpc path through mostly "normal" interstellar material, the conclusion that ices do not exist outside the shielded environment of molecular clouds is greatly strengthened'.

Ultraviolet processing of ice mantles into more complex molecules has been appealed to in order to explain the lack of a 3.1-$\mu$m absorption feature in unshielded regions of interstellar space (Donn & Jackson 1970; Greenberg & Yencha 1973). However, as discussed in Section 3 of Paper II, the rate of destruction of ice mantles by photodesorption is expected to be much faster than the rate at which they could be converted into more complex molecules by the UV radiation field. Moreover, practically all molecules containing H and C, N or O atoms exhibit strong stretching vibrational transitions in the 2–4 $\mu$m region of the spectrum. The 2–4 $\mu$m spectrum of VI Cyg no. 12 obtained by Gillett *et al.* (1975) shows a featureless continuum, and spectra of the 2 $\mu$m point source in the Galactic Centre, taken in the 1.4–2.7 $\mu$m region (Treffers *et al.* 1976) and in the 2–4 $\mu$m region (Soifer *et al.* 1976), show no trace of any interstellar absorption features. This objection also applies to the model of Hoyle & Wickramasinghe (1977) whereby grains composed of complex organic molecules are produced in prestellar molecular clouds and ejected into the interstellar medium; unless of course the range of organic molecules present in such grains was such that the absorption bands due to the various molecular species overlapped in such a way as to produce a featureless continuum in the 2–4 $\mu$m region.

The destruction of unshielded ice mantles is so rapid that in practically all regions of interstellar space the grain mixture should consist only of refractory grains, consistent with the almost invariant value of $R = 3.1$ found in diffuse interstellar regions (Turner 1976; Barlow & Cohen 1977) and the lack of an ice absorption feature in such regions. Refractory grain models have been proposed by Gilra (1971) and Wickramasinghe & Nandy (1971) in order to explain the interstellar extinction curve. Mathis, Rumpl & Nordsieck (1977) have produced a refractory grain model which fits the interstellar extinction curve whilst satisfying cosmic abundance limitations. It is thus concluded that ice mantles will be found only in dense shielded regions and that elsewhere the interstellar grain mixtures consists only of refractory grain species which have had their origin in circumstellar environments.

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## Appendix A: the sputtering of chemisorbed particles from grain surfaces

We here discuss a sputtering mechanism restricted to *chemisorbed* particles. Winters & Sigmund (1974) have shown that there are three contributions to the sputtering of such particles: (i) the direct knock-off contribution; (ii) the reflected incident particle contribution, where the incident particle is reflected by the underlying substrate material and knocks off an adsorbed particle on the way out; (iii) the sputtered atom contribution, where the incident particle sputters an atom of the underlying substrate material and the sputtered atom knocks off an adsorbed particle on the way out.

Processes (ii) and (iii) need only be considered at high incident particle energies and can be neglected at the energies in which we are interested here. From Winters & Sigmund (1974) the sputtering yield $Y$ due to mechanism (i) is

$$Y = \frac{N_{\text{ads}}(\text{k})}{\cos\theta} \int_{T=E_{\text{ads}}(\text{k})}^{\eta_{\text{ik}}E_{\text{i}}} d\sigma(E_{\text{i}}, T). \tag{A1}$$

$\eta_{\text{ik}} = 4m_{\text{i}}m_{\text{k}}/(m_{\text{i}}+m_{\text{k}})^2$, where $m_{\text{i}}$ is the mass of an incident particle and $m_{\text{k}}$ is the mass of an adsorbed particle. $E_{\text{i}}$ is the energy of the incident particle and $E_{\text{ads}}(\text{k})$ is the adsorption energy of the adsorbed particle. $N_{\text{ads}}(\text{k})$ is the surface number density of adsorbed particles ($\text{cm}^{-2}$). The cross-section $d\sigma_{\text{ik}}$ is given by

$$d\sigma_{\text{ik}} = C_{\text{ik}}E_{\text{i}}^{-p_{\text{ik}}}T^{-1-p_{\text{ik}}}\,dT. \tag{A2}$$

For low incident energies the cross-section is described by a Born–Mayer interaction and $p_{\text{ik}} = 0$. From Sigmund (1969) we have

$$C_{\text{ik}} = C_0 = \tfrac{1}{2}\lambda_0 a_0^2 \tag{A3}$$

where $\lambda_0 = 24$ and $a_0 = 0.219$ Å. Substituting (A3) into (A2); (A2) into (A1) and integrating, we obtain the sputtering yield

$$Y_{\mathrm{ik}}(E_\mathrm{i}) = \frac{N_{\mathrm{ads}}(\mathrm{k})}{2\cos\theta}\,\pi\lambda_0 a_0^2 \log\left\{\frac{\eta_{\mathrm{ik}}E_\mathrm{i}}{E_{\mathrm{ads}}(\mathrm{k})}\right\}. \qquad \text{(A4)}$$

For a grain of radius $a$ in an isothermal shock of velocity $v$, the rate at which adsorbed particles are sputtered by incident particles with gas-phase density $n_\mathrm{i}$ is given by

$$\dot{N}_{\mathrm{ik}} = -\pi a^2 n_\mathrm{i} v Y_{\mathrm{ik}}(E_\mathrm{i}). \qquad \text{(A5)}$$

The timescale for removal of the adsorbed particles by sputtering is

$$\tau_{\mathrm{ads}}(\mathrm{sp}) = \frac{16}{\pi^2 a_0^2 \lambda_0 \log\{\eta_{\mathrm{ik}}E_\mathrm{i}/E_{\mathrm{ads}}(\mathrm{k})\} n_\mathrm{i} v}. \qquad \text{(A6)}$$

Given relative abundances H : He : CNO = $1 : 10^{-1} : 10^{-3}$, it is found that He is always the most important species for sputtering adsorbed particles on grains. Sputtering will only be important when $\{\eta_{\mathrm{ik}}E_\mathrm{i}/E_{\mathrm{ads}}(\mathrm{k})\} > 1$ and it is found that when this condition is satisfied for incident He atoms, the sputtering timescale $\tau_{\mathrm{ads}}(\mathrm{sp})$ is always less than the slowing-down time of a grain due to viscous drag. Therefore we can define a critical shock velocity, $v_{\mathrm{crit}}(\mathrm{k})$, above which an adsorbed species will be removed from a grain surface by sputtering

$$v_{\mathrm{crit}}(\mathrm{k}) = \left(\frac{2E_{\mathrm{ads}}(\mathrm{k})}{m_\mathrm{i}\eta_{\mathrm{ik}}}\right)^{1/2} \qquad \text{(A7)}$$

where i = He. Values of $v_{\mathrm{crit}}(\mathrm{k})$ for various elements k adsorbed on graphite grains are tabulated in Table 3.

## Appendix B: the effect on elemental depletions of grain destruction in shocks

Barlow & Silk (1977) have shown that for a given grain material there exists a critical shock velocity $v_{\mathrm{sp}}$, above which complete destruction of a grain will take place. We make the approximation that for certain elements (e.g. Mg, Si, Fe) almost all ($\gtrsim 90$ per cent) of the atoms are locked up in grains. Consider an expanding supernova remnant of total mass $M$ and expansion velocity $v$. With the assumption of conservation of momentum we have

$$Mv = M_{\mathrm{sp}}v_{\mathrm{sp}} \qquad \text{(B1)}$$

where $M_{\mathrm{sp}}$ is the mass of the remnant when $v = v_{\mathrm{sp}}$. A given element is assumed to be locked up in some grain material with a critical destruction velocity $v_{\mathrm{sp}}$. For $v \geqslant v_{\mathrm{sp}}$ there will be no depletion of the element in the remnant, due to complete grain destruction, i.e. $\delta = 1$. When $v$ drops below $v_{\mathrm{sp}}$ newly swept-up grains will be incompletely destroyed, and the mean depletion factor $\bar{\delta}$ in the entire mass $M$ of the remnant will be given by

$$\bar{\delta} = \{M_{\mathrm{sp}} + (M - M_{\mathrm{sp}})\,\delta'\}/M \qquad \text{(B2)}$$

or

$$\bar{\delta} = v/v_{\mathrm{sp}} + (1 - v/v_{\mathrm{sp}})\,\delta'. \qquad \text{(B3)}$$

$\bar{\delta}'$ is the mean depletion factor in the mass swept up after $v$ has dropped below $v_{\rm sp}$. From equation (16) of Paper I the depletion factor $\delta(v)$ in a shock of initial velocity $v$ is given by

$$\delta(v) = 3c(v^2 - v_{\rm min}^2) - 3c^2(v^2 - v_{\rm min}^2)^2 + c^3(v^2 - v_{\rm min}^2)^3. \tag{B4}$$

Following Appendix A of Paper I $\bar{\delta}'$ is given by

$$\delta' = \left[\left\{3c(v_{\rm sp} - v) - c^2(v_{\rm sp}^3 - v^3) + \frac{c^3}{5}(v_{\rm sp}^5 - v^5) + (6c^2v_{\rm min}^2 + 3v_{\rm min}^4c^3)(v_{\rm sp} - v) \right.\right.$$
$$\left.\left. - c^3v_{\rm min}^2(v_{\rm sp}^3 - v^3)\right\} \Big/ \left(\frac{1}{v} - \frac{1}{v_{\rm sp}}\right)\right] - (3cv_{\rm min}^2 + 3c^2v_{\rm min}^4 + c^3v_{\rm min}^6) \tag{B5}$$

where $v_{\rm min} = 16H_{\rm s}^{1/2}$, $c = 5 \times 10^{-7} m_{\rm s}/H_{\rm s}$, $H_{\rm s}$ is the sublimation energy of the grain material (in eV) and $m_{\rm s}$ is the mass of a grain lattice particle, in units of the mass of a hydrogen atom.

For $v \gg v_{\rm min}$ we can simplify (B5) and substituting into (B3) we obtain

$$\bar{\delta} = v/v_{\rm sp} + [1 - (v/v_{\rm sp})]\left\{3c(v_{\rm sp} - v) - c^2(v_{\rm sp}^3 - v^3) + \frac{c^3}{5}(v_{\rm sp}^5 - v^5)\right\} \Big/ \left(\frac{1}{v} - \frac{1}{v_{\rm sp}}\right). \tag{B6}$$

Note that as $v$ approaches $v_{\rm min}$ the full form of equation (B5) must be used.