Silicon chemistry in PDRs

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Abstract. We consider the chemistry of silicon in photo–dissociation regions (PDRs), with special attention to the available observations of the Orion Bar. We focus on the "paradox" that fine structure emission of singly ionized silicon (Si^+) is known to be strong from such regions, whereas silicon in molecular form (and in particular SiO) is absent. We consider a number of possible explanations of this "paradox" and conclude that the most likely is that Si is in solid form at depths greater than roughly 3–4 magnitudes of visual extinction, relative to the ionization front, in regions such as the Orion Bar. We consider that direct photodesorption with a small yield is likely to be the process responsible for the ejection of a Si-containing mantle into the gas phase. Other possibilities, such as the Si being present as a component of grain ice mantles, are considered; we believe that they are less likely. We find that grain polar ice mantles are probably also destroyed in PDRs, through photodesorption, whereas thermal evaporation destroys the apolar component of ice mantles deep within the surrounding molecular cloud.

Key words: molecular processes – ISM: clouds – ISM: dust, extinction – ISM: H II regions – ISM: individual objects: Orion bar – ISM: molecules

1. Introduction

The form taken by interstellar silicon in molecular clouds is still a considerable puzzle. Ultraviolet observations (e.g. Sofia et al. 1994) have shown that a large fraction of the silicon is in solid form, even in diffuse clouds, in apparent contradiction with the timescale for destroying silicate grains in shocks in the diffuse ISM. This timescale is so short that the supply of such grains, through mass loss from late type stars, is inadequate to explain the fraction of silicon observed to be in the solid state (see McKee 1989, Jones et al. 1994, Draine 1995, Tielens 1998). A possible resolution of this discrepancy is that processes taking place in molecular clouds are responsible for refurnishing silicon–bearing grains. If this is the case, silicon that is taken up by a molecular cloud in gaseous form is ejected from the cloud in solid form: rather effective depletion of silicon must be taking

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place within the clouds. Gas phase silicon in molecular clouds is expected to be in the form of SiO (Herbst et al. 1989). However, the observed abundance of SiO is extremely low in some dense dark clouds, with typical upper limits to [SiO]/[H_2] of $3\,10^{-12}$ (e.g. Ziurys et al. 1989). If most of the gas phase silicon is in the form of SiO, then silicon is depleted on to grains to a surprising degree (to a much greater degree than C, N and O): the fraction of silicon remaining in the gas phase is less than 10^{-7}, on the above assumptions. One concludes that either the silicon depletion processes are surprisingly efficient, and/or the gas phase chemistry models are surprisingly wrong. A related question is: which form does the silicon take in the solid state?

While SiO "vanishes" in some molecular clouds, it reappears under certain circumstances. In particular, SiO has proven to be a good tracer of shocked gas in outflows (see e.g. Schilke et al. 1997, Pineau des Forêts and Flower 1997, Martin–Pintado et al. 1992, Gueth et al. 1998). The SiO abundance in the high velocity gas associated with young outflows is typically of order 10^{-7}; hence, an appreciable fraction of the "lost" silicon has reappeared in the form of SiO. In a previous study (Schilke et al. 1997), we considered the possibility that silicon reappears owing to the sputtering of grains in C-type shocks of speeds between 10 and 40 $km\,s^{-1}$. We found that 25 $km\,s^{-1}$ shocks with pre–shock densities of order 10^5 cm^{-3} were consistent with the observations. However, it was not clear from that study whether the silicon which returned to the gas phase originated in refractory material or in some form of "ice" in the grain mantle. In the latter case, the supposition was made that the Si-bearing material was present either as silane (SiH_4, see MacKay 1995, 1996) or as "dirt" mixed into other ice material (perhaps in the form SiO_2; an interesting by–product of the Schilke et al. study was the realization that SiO_2 can be the major gas phase form of Si for a considerable length of time in the post–shock material).

In order to decide which form silicon takes within molecular clouds, one clearly needs to study quiescent regions, where shocks do not confuse the chemistry. However, in cold quiescent regions, silicon seems usually to be absent from the gas phase. An alternative approach, which we shall pursue in this article, is to study the silicon chemistry in a PDR (Photon Dominated Region). PDRs are interstellar regions where the gas is predominantly neutral but the gas and dust are heated by UV (1000 Å) photons from neighbouring O-B stars (see the recent review of

Hollenbach and Tielens 1997). The dust temperature in PDRs can be as high as 100 K, and hence the evaporation of dust mantles becomes possible. On the other hand, the available evidence suggests that PDRs are quiescent regions: shocks, which might liberate Si from the solid form, are absent.

Detailed PDR models have already been constructed (Sternberg and Dalgarno 1995, Jansen et al. 1995) which include the silicon chemistry; these assumed steady state conditions, as well as a given abundance of gas phase silicon. The latter must be sufficiently high (of the order of 10 percent of the solar abundance of silicon) to account for the observations of the Si^+ fine structure line at 35 μm wavelength which now has been detected in several PDRs (eg Haas et al. 1986, Meixner et al. 1992, Stacey et al. 1995, Steiman-Cameron et al. 1997). It appears to be fairly certain that this line is emitted from a partially ionized (neutral) layer and not from the adjacent ionized gas (see the discussion in Sect. 4 below). There is in particular good evidence for this in the case of the Orion Bar where the spatial structure of the Si^+ emission is similar to that of other PDR tracers. The inferred Si^+ column density is of order $3\,10^{16}$ cm^{-2}.

The results for the Orion Bar represent moreover an interesting test case. Jansen et al. (1995) put an upper limit on the SiO abundance of [SiO]/[H] less than 10^{-10} (N(SiO) $< 6.5\,10^{12}$ cm^{-2}), which corresponds to less than $3\,10^{-6}$ of the solar abundance of silicon. However, in recent observations of the Orion Bar (Schilke et al. 1998), SiO has been detected with the IRAM 30-m telescope at levels consistent with the previous upper limits. For example, at the origin of the strip perpendicular to the ionization front discussed by Jansen et al. (1995), Schilke et al. detect a line (2 km s^{-1} width) of SiO(2-1) with intensity of order 0.1 K in the main-beam brightness temperature scale. The emission appears to be extended at roughly this level both parallel and perpendicular to the bar. We estimate that this corresponds roughly to N(SiO) of order $5\,10^{11}$ cm^{-2} or almost five orders of magnitude less than seen in Si^+. These results will be presented in detail elsewhere but it is clear that it is difficult to reconcile the SiO measurements with the column density inferred from the fine structure line.

The aim of the present study is to consider possible solutions of the paradox outlined above. We assume that Si is in a form other than gas phase SiO far from the HII region ionization front, which bounds the PDR on one side. We examine the consequences for the silicon chemistry of advection of material toward the ionization front from the adjacent molecular cloud. In Sect. 2 of this paper, we describe the computational scheme which we have adopted and, in Sect. 3, we present our results. Finally, in Sect. 4, we consider the extent to which the "silicon paradox" has been resolved and the implications for future studies.

2. Model

Our approach is similar to that adopted, for different purposes, by Elitzur and de Jong (1978) and, more recently, by Störzer and Hollenbach (1998). We consider a unit volume of gas which is "approaching" the ionization front of an HII region at a velocity

v_{IF} which is of order 1 km s^{-1} for a D-type ionization front (see the discussion of Störzer and Hollenbach). Thus, material is advected from deep in the molecular cloud to the PDR region. Advection can be of importance for species with large abundance gradients along the normal to the ionization front. The timescale for advection of a species with abundance x_i should be of order $t_i^{ad} = x_i/(v_{IF}\,dx_i/dz)$ and becomes comparable to chemical timescales for sufficiently large abundance gradients dx_i/dz. We expect large abundance gradients to be caused by processes, such as grain mantle evaporation, which have an exponential grain temperature dependence.

In this context, we solve the time dependent equations for the chemical abundances, in both the gas and solid phases, using a radiation field whose strength is determined by a time dependent extinction A_v. The latter is given by:

$$A_v = A_{v0}\,(1 - v_{IF}t/R_0). \qquad (1)$$

Here, we have supposed that the initial extinction is A_{v0} (which we have usually taken to be 10 magnitudes) and R_0 is the corresponding initial separation from the ionization front. The ratio A_{v0}/R_0 is taken to be $5.35\,10^{-22}\,n_H$. The rate coefficients for photoprocesses involving Si-bearing species were taken from Sternberg and Dalgarno (1995). Fits to the photodissociation rates of H_2 and CO as functions of A_v were obtained separately, using the steady state PDR model of Le Bourlot et al. (1993), with the same density and external radiation field. The resulting time dependent (ordinary) differential equations were solved by the Gear method.

The chemical network is similar to that used by Schilke et al. (1997) in their study of C-type shocks. Thus, we have in general (for exceptions, see below) adopted the rate constants for reactions involving Si-bearing species given in Table 2 of Schilke et al. (1997; this is available via anonymous ftp from cdsarc.u-strasbg.fr/cats/J/A+A/321/293). The network considers formation of SiO from either Si or Si^+ although the former dominates. It also includes build-up of silicon hydrides via reactions for example of Si^+ with H_2. We note, in particular, that we have used a rate coefficient for the Si(O_2, O)SiO reaction ($2.7\,10^{-10}\,(T/300)^{0.5}$ cm^3 s^{-1}) which derives from the room temperature measurement of Husain and Norris (1978) and which exceeds that measured by Swearengen, Davies and Niemczyk (1978) by more than an order of magnitude. Recent measurements of Le Picard et al. (1998) confirm the higher value of Husain and Norris. Le Picard et al. find that the rate coefficient for this reaction may be fitted by the form $1.76\,10^{-10}\,(T/298)^{-0.5}\exp(-17/T)$ cm^3 s^{-1}. We have, as a precaution, verified that the results presented below are essentially unmodified if the lower value of Swearengen et al. is adopted. The most critical reaction for the results presented in this paper is, in fact, the Si(OH, H)SiO reaction, for which we have adopted a rate coefficient of $2\,10^{-11}\,(T/300)^{0.5}$ cm^3 s^{-1}. Previous work (Langer and Glassgold 1990, Schilke et al. 1997) has assumed that the rate coefficient for this and analogous reactions is proportional to the population of Si atoms in the J = 1 excited fine structure state and consequently has an $\exp(-111/T)$ dependence. However, studies of analogous reactions involving

atomic carbon (Clary 1993, Husain 1993) show that the dominant long-range potential involves the polarizability and not the quadrupole moment of the atom (which is non-zero only for non-zero values of the total angular momentum J). We have therefore adopted a rate coefficient varying only with the thermal speed of the reactants.

The importance of the reaction of Si with OH has the consequence that the silicon chemistry in a PDR is sensitive to the OH abundance and consequently to the kinetic temperature variation with depth. We have adopted temperatures consistent with observations of molecular hydrogen in the Orion Bar (Parmar et al. 1991, Luhman et al. 1998). In our standard model, the temperature is assumed to vary with extinction according to the the formula $T = 1000/(1 + 2 A_v)$. Luhman et al. show that this profile is consistent with their NIR molecular hydrogen spectra towards the Orion Bar. We also consider constant temperature (500 K) models for comparison.

In contrast to the case of shocks, sputtering is expected to play no role in a PDR. Instead, we consider direct photodesorption (see below). Thermal evaporation of silicon–containing grain mantles occurs on a time scale τ_{ev}

$$\tau_{ev}^{-1} = \nu_0 \exp\left(-\Delta E/T_{gr}\right). \tag{2}$$

In the above, T_{gr} is the grain temperature and ΔE is the binding energy in kelvin of the Si-bearing ice to the grain surface (Watson and Salpeter 1972). ν_0 is a characteristic frequency given by:

$$\nu_0 = \sigma p_0 \left(2\pi M k T_{gr}\right)^{-1/2}, \tag{3}$$

where σ is the surface per molecule, of mass M, in the external layer of the grain mantle, and p_0 is the vapour pressure of the considered Si-bearing species at zero kelvin (Leger, Jura and Omont 1985). For SiO, we have adopted the vapour pressure of CO, which gives

$$\nu_0 = 3.8\,10^{15}\,T_{gr}^{-1/2}\,(s^{-1})$$

ΔE is an important but uncertain parameter. We have assumed that Si is present in the form of "dirt" and is a minor constituent of a solid but relatively volatile material. Thus, its evaporation rate is determined by that of the (presumed more abundant) volatile species. We attempt in the following to determine a reasonable value for ΔE by considering the available observations of Si$^+$ and SiO towards the Orion Bar PDR. For this purpose, we allow ΔE to vary between the binding energy for water ice ($\sim$ 6000 K) and that for ices consisting of non–polar species ($\sim$ 1000 K) (see Leger, Jura and Omont 1985).

Also critical in this procedure is the determination of the grain temperature T_{gr} as a function of depth in the PDR. We have chosen to adopt for this purpose the "Ansatz" of Hollenbach et al. (1991), who estimated the "secondary" heating due to hot grains within the PDR; a more realistic treatment would require consideration of different geometries. However, given the uncertainty in ΔE, a more accurate treatment of the dust temperature does not seem warranted.

The silicon which is assumed to be present as a minor constituent of of the grain mantles may also be phodesorbed. Estimates of the photodesorption yield Y (no of Si atoms ejected per incident UV photon) for different substances vary widely (see e.g. Draine and Salpeter 1979, d'Hendecourt et al. 1985). A more recent study of water ice by Westley et al. (1995) indicates, moreover, that the process is efficient only after the ice has been exposed to a certain amount of radiation. Thus, it appears that Y depends upon the processing of the ices, including the formation of radicals in the ice matrix, which makes it difficult to estimate the photodesorption yield in the situation of interest to us here. The rate of photodesorption of a Si atom (or SiO molecule) from a grain may be estimated from

$$k_{ph} = Y\,I_{UV}\,\gamma\,n_{gr}\,\sigma, \tag{4}$$

in cm^3 s^{-1}, where I_{UV} is the UV (912–2000 Å) photon flux, n_{gr} is the grain number density, $\sigma = \pi a^2$ is the photodesorption cross section and $\gamma = n(X)/(n_{gr}N_{site})$ is the fraction of sites occupied by species X. Setting the number of sites $N_{site} = 4\pi a^2/\delta^2$, where δ is the mean distance between adjacent sites in the ice mantle, which we take to be 2.6 Å, we obtain

$$\tau_{ph}^{-1} = Y\,I_{UV}\,\delta^2/4 \tag{5}$$

in s^{-1} for the inverse of the lifetime τ_{ph} of an atom or molecule against photodesorption. In this formula, I_{UV} is assumed to vary as $\exp\left(-2 A_v\right)$, and hence τ_{ph} increases rapidly with depth. We note that τ_{ph} is independent of the grain size distribution.

In the models of the following section, we set Y=0 when considering mantle evaporation. When photodesorption is included, we approximate the Westley et al. saturated rate by taking $Y = 0.0035 + 0.13 \exp -(336/T_{gr})$ in terms of the grain temperature T_{gr}. We assume the H$_2$O abundance in the grain mantles is $8.6\,10^{-5}$ that of hydrogen (Whittet 1993) and that the water molecules are ejected intact. The SiO photodesorption yield is taken equal to that of water. However, we also consider the case that silicon comes back into the gas phase due to photodesorption from a "more refractory" grain surface component (this could for example be the form of refractory Si which Tielens (1998) has postulated to explain the silicon depletion pattern). In this case, we put Y(Si) equal to a constant value of $5\,10^{-7}$. This yield has been deduced from the observations of Turner (1998) of SiO in translucent clouds. We find that this value of Y gives agreement with the fractional abundances of gas phase SiO, of the order of 10^{-10}, deduced by Turner from his observations, for the conditions (of radiation field, in particular) that Turner believes to be appropriate to these regions. The value of $Y = 5\,10^{-7}$ that we have derived is much larger than those listed by Turner.

3. Results

We adopt physical conditions believed to be appropriate to the Orion Bar and compare the column densities derived from the model with those observed. Thus, we assume the incident radiation field to be a factor of $\chi = 5\,10^4$ times the Draine (1978) interstellar UV field, and the hydrogen density n$_H$ to be $5\,10^4$ cm^{-3}(see Jansen et al. 1995, Hollenbach and Tielens 1997, Wyrowski et al. 1997, and Marconi et al. 1998 for estimates of these parameters). It is also important to realize that the

Table 1. Parameters and predicted column densities for models discussed in the text. All models assume a homogeneous PDR of nucleon density $n_H = 5\,10^4$ cm^{-3} and incident radiation field χ (in units of the interstellar field) $= 5\,10^4$. Models are distinguished (see Comment and Init. columns) by the initial form of Si and the form in which Si initially in the mantle reaches the gas phase. Thus in the Init. column, SiO(Ice) refers to models where SiO comes directly into the gas phase due to evaporation of the ice mantle and Si(sol) refers to models where Si from refractory material is photo-desorbed in atomic form. In the comment column, PE stands for models where thermal evaporation of ice mantles with a given binding energy ΔE in K (in parentheses) is considered and PD stands for models where direct photodesorption is considered. Models are also distinguished by the assumption made about the gas temperature variation and photodesorption yield (Y). In model 7, we assume a constant gas temperature of 500 K but in all other models we take the temperature to vary as T = $1000/(1{+}2\,A_v)$. For the photodesorption yield, a W in parentheses in the comments column implies use of the Westley et al. (1995) form for the photodesorption yield, whereas a C in parentheses means that a constant value of Y=5 10^{-7} was used. The last line of the table (Obs.) gives observed column densities of SiO and Si$^+$ towards the Orion Bar based on the results of Schilke et al. (1998) and Haas et al. (1986)

Model	Init.	Comment	N(SiO) cm^{-2}	N(Si$^+$) cm^{-2}	N(Si) cm^{-2}
1	SiO$_2$	Gas Phase	6.7 10^{15}	3.8 10^{16}	7.1 10^{14}
2	SiO(Ice)	PE(2500)	2.5 10^{16}	4.0 10^{16}	8.1 10^{14}
3	SiO(Ice)	PE(2800)	1.2 10^{15}	2.1 10^{16}	6.2 10^{13}
4	SiO(Ice)	PE(3000)	1.3 10^{13}	1.4 10^{16}	1.0 10^{12}
5	SiO(Ice)	PD(W)	8.4 10^{15}	3.7 10^{16}	3.6 10^{14}
6	SiO(sol)	PD(C)	7.7 10^{12}	1.7 10^{16}	2.7 10^{12}
7	Si(sol)	PD(C)(500)	4.0 10^{13}	1.7 10^{16}	5.7 10^{12}
8	Si(sol)	PD(C)	1.3 10^{12}	1.7 10^{16}	3.7 10^{12}
Obs.			5 10^{11}	3 10^{16}	

Orion Bar is not seen face–on, whereas we shall report column densities integrated along the normal to the face of the PDR. As the Bar inclination angle is poorly known (see the discussion of Marconi et al. 1998), it is difficult to correct for this projection effect, which may lead to the absolute column densities being underestimated by an order of magnitude.

The assumed fractional elemental abundances are consistent with the available Orion Bar observations. Thus [C]/[H] = 1.4 10^{-4} and [O]/[H] = 6.7 10^{-4}, whereas Si in various initial forms is assumed to have an abundance of 10 percent of the solar value (which gives [Si]/[H] = 3.6 10^{-6}), in accordance with the results of Haas et al. (1986, 1991; see also Stacey et al. 1995). Thus, 90 percent of Si is assumed to be in a highly refractory grain core.

We consider various possible forms in which Si might be "hidden" at large depth in the molecular cloud associated with a PDR and use the model to predict the evolution of chemical abundances as the gas and dust are advected towards the ionization front. Our first model considers purely gas phase processes and is intended to demonstrate that it is not possible to "hide" silicon without recourse to processes converting from solid to gas phase. Here, we suppose that the available silicon (i.e. that
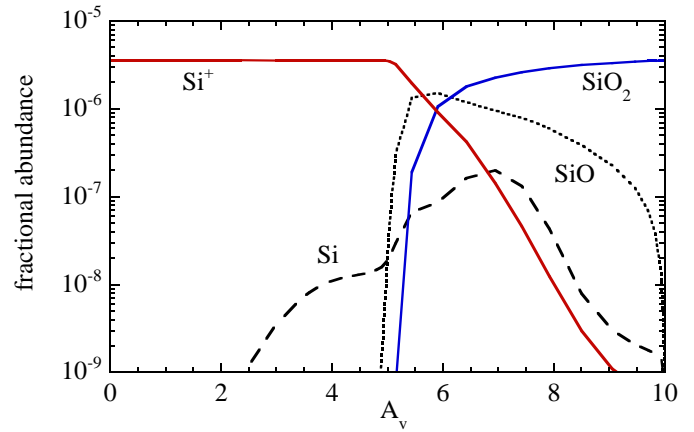
Fig. 1. Fractional abundances (relative to n_H) of Si bearing species plotted against visual extinction for model 1, where Si is initially in the form of gaseous SiO$_2$. The radiation field is incident on the left hand side and we begin the integration at a depth of $A_v = 10$. The full curves show the variation of gaseous SiO$_2$ at high extinction and Si$^+$ at low extinction. SiO is shown as the dotted curve and atomic Si as dashes.

which is not in refractory form) is present as gas phase SiO$_2$ at $A_v = 10$ mag. and follow the chemistry for the case of $v_{IF} = 1$ km s^{-1}. In models 2–4, we suppose that the available silicon is initially present as a "contaminant" in an ice mantle of binding energy ΔE. This mantle is allowed to evaporate according to the prescription in the previous section. In model 5, we also suppose silicon to be initially present in the ice mantle but allow transfer into the gas phase only by photodesorption (Eq. 4, using the Westley et al. data for the photodesorption of ice). Finally, in models 6–8, we consider a constant photodesorption yield of 5 10^{-7} with various assumptions about the gas temperature and the form in which silicon enters the gas phase.

In all these models, initial abundances for other than Si-bearing species have been obtained by solving the steady state equations. This procedure has the consequence that C, for example, is initially in the form of CO, whereas oxygen is divided between CO, O and O$_2$. For models 5–8 moreover, oxygen is initially also in the form of water ice which can be photodesorbed. In models 2–5, SiO is considered to be mixed with the evaporating (or photodesorbing) ice mantle. Otherwise, we do not consider possible "contaminants" in the solid phase.

Input parameters for the eight models are given in Table 1 where we also give the total column densities predicted by the models, as well as the SiO and Si$^+$ column densities measured towards the Orion Bar. The latter is an estimate which we have made based upon the results of Haas et al. (1986) and has a factor of 2 uncertainty. Table 1 also gives information on the assumptions made concerning the initial form of Si in different models.

In Fig. 1, we show the abundances predicted in model 1 as a function of depth (parametrized in terms of the visual extinction A_v). One sees that, as the ionization front is approached, SiO$_2$ is photodissociated, yielding SiO. This species is, in turn, photodissociated on a rather similar timescale to Si, and finally

Si is photoionized to Si^+. We note that the SiO abundance is non–negligible in this model, as in the steady–state models of Sternberg and Dalgarno (1995) and Jansen et al. (1995). Also, Si^+ becomes the main Si carrier at an extinction of $A_v \sim 6$ mag. from the surface. It is very difficult, in this type of model, to produce SiO column densities which are orders of magnitude smaller than that of Si^+. We find that the same conclusion holds when other choices are made (e.g. SiH_4) for the initial (gas phase) form of Si. One of the reasons for this is that atomic silicon can react with either O_2 or with OH to produce SiO (see discussion in the previous section):

$$Si + O_2 \rightarrow SiO + O$$

$$Si + OH \rightarrow SiO + H$$
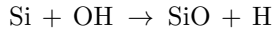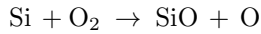
Thus, if either O_2 or OH is abundant in the layers of the PDR where atomic Si is produced by photodissociation of Si-containing species, SiO can form rapidly. A consequence of this is that our results are not very sensitive to the initial form assumed for gas phase silicon. Our calculations show that, whilst O_2 is photodissociated at depths beyond those at which atomic Si becomes important, OH is abundant at the high temperatures which occur close to the ionization front (see e.g. Sternberg and Dalgarno 1995) and plays an important role in the Si chemistry.

Let us now consider the models (2–4) where Si is initially in an ice mantle which is subsequently evaporated. We assume that the silicon is released as SiO but, again, our results are relatively insensitive to this assumption. In Fig. 2 (see also models 2–4 of Table 1), we show the computed abundances as functions of depth (visual extinction) in the PDR. Fig. 2 shows the sensitivity of our results to the binding energy (ΔE) of the grain mantle. In all three models, Si is supposed to be initially present (at A_v = 10 mag.) in the ice mixture in the form of SiO. In the upper panel (Fig. 2a), where ΔE = 2500 K, we see that solid SiO is instantaneously evaporated from the mantles, at a grain temperature of approximately 44 K. SiO is then photodissociated at A_v = 6 magnitudes, leading to an abundance profile similar to those found by Sternberg and Dalgarno (1995) and Jansen et al. (1995). In the middle panel (Fig. 2b), where ΔE = 2800 K, silicon remains in solid form to an extinction of 2.5 magnitudes, corresponding to a grain temperature of 48 K. At this point, it is suddenly transformed into Si^+. This transformation occurs irrespective of the form of Si in the ice mixture. We see also that the SiO abundance reaches 10 percent of the "available" silicon at A_v = 8 magnitudes but rapidly decreases at lower values of A_v due to photodissociation. In contrast, for ΔE = 3000 K (model 3), SiO reaches an abundance of only 10^{-3} of the available silicon prior to the onset of photodissociation. For a grain temperature of 45 K, at $A_v \sim 6$ mag., the evaporation rate (see Eq. 2) is very sensitive to ΔE. Thus, Fig. 2 demonstrates that, in this type of model, a situation can obtain in which Si^+ is the only gas phase form of Si with appreciable abundance.

One can attempt to determine a value of ΔE compatible with the current perception of the characteristics of the Orion Bar. For low values of ΔE, the Si-containing mantle is evaporated deep in the cloud, and an appreciable column density of SiO
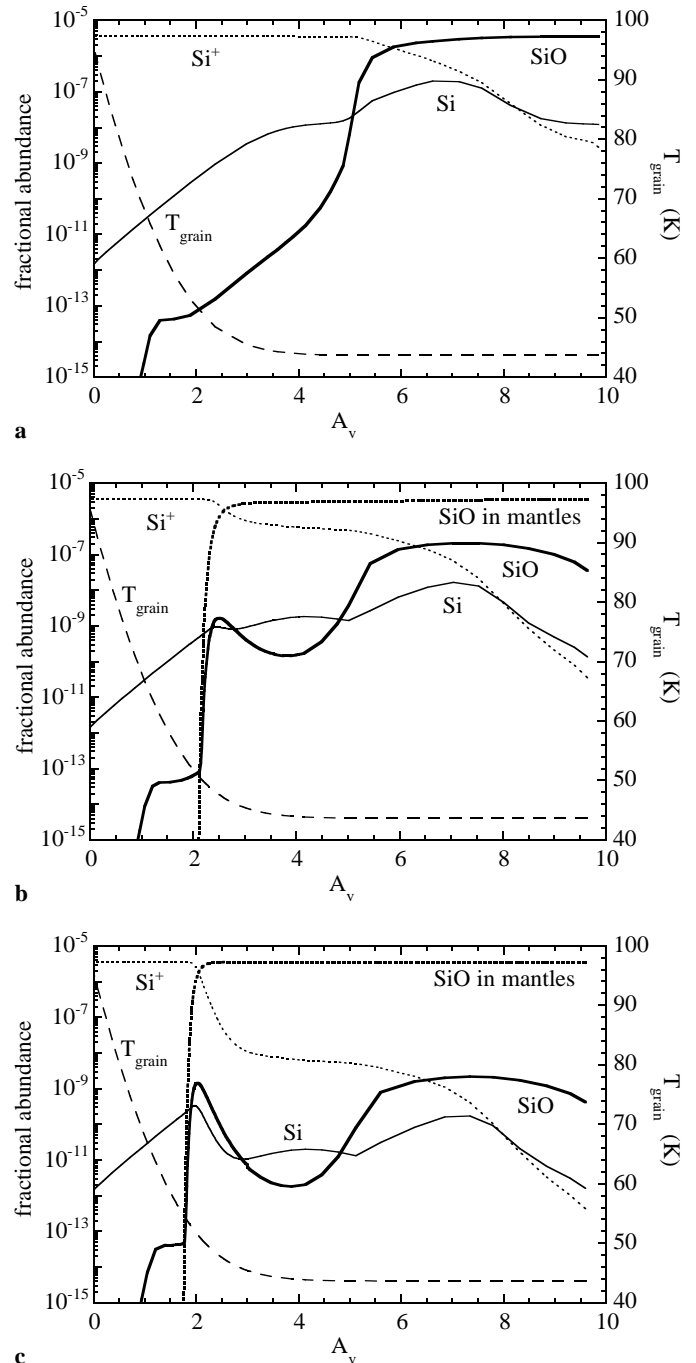
Fig. 2a–c. Fractional abundances (relative to n_H) of Si-bearing species as functions of depth for Models 2, 3 and 4. Si is supposed initially (A_v = 10) in solid form, immersed in an ice layer having binding energy ΔE = 2500 K **a**, 2800 K **b** and 3000 K **c**. The variation of grain temperature is shown as the dashed line on the three plots (see scale on right hand axis). The full curves on all three panels show SiO, the thin full curves Si and the light dots Si^+. SiO in solid (ice) form is shown as the bold dots in the bottom two panels; it disappears immediately for ΔE = 2500 K.

(comparable with that observed in Si^+) is to be expected. For high values of ΔE (6000 K, as expected for water ice), the ice survives its traversal of the PDR and is presumably destroyed in

the ionized gas. In this case, the Si^+ emission does not arise in the neutral PDR layer, and, furthermore, it is likely that silicon will be rapidly transformed into Si^{++} within the HII region. For intermediate values of ΔE, of order 3000–3500 K, there is an appreciable ($\sim 10^{16}$ cm^{-2}) column density of Si^+ but small amounts of Si-containing molecules such as SiO. We have examined the sensitivity of these results to the form (SiO or other) in which Si is ejected from the surface and find that this is of minor importance in general. We note also that comparison with observed FIR color temperatures towards the bar (~ 75 K, see Werner et al. 1976) suggests that our grain temperatures may be underestimates and hence that our estimate for ΔE is also too low. In fact, if the temperature is really so high, water ice evaporation would become possible. However, the Werner et al. observations were carried out with a 1$'$ beam which is not sufficient to resolve the bar and hence the observed color temperature is probably "contaminated" by hot dust within the ionized region. Moreover, as discussed below, we believe that direct photo-desorption is the dominant process causing the ejection of the water ice mantle into the gas phase.

We now consider the possibility (Models 5–8) that the photodesorption yield Y of Si-containing species is non-negligible and that this process rather than mantle evaporation accounts for the appearance of Si in the gas phase. We distinguish between Si mixed into the ice mantle and Si in a more refractory layer containing 10 percent of the cosmic Si abundance. In the former case (model 5), we use the Westley et al. (1995) data for the photodesorption yield and thus assume that the probabilities of photodesorption of water and SiO are the same. We also assume that the SiO molecule is not dissociated during the photodesorption process. In the case where we take Si to be in a more refractory layer, we adopt a yield of $5\,10^{-7}$ and assume that Si enters the gas phase in atomic form.

Fig. 3 shows that, for the conditions of model 5 (essentially the conditions of the Orion Bar), the ice mantles are photodesorbed at $A_v = 6$ mag. and SiO attains an abundance relative to H of $2\,10^{-6}$. The column densities (Table 1) are such that one would expect to observe both SiO and Si^+ in a region such as the Orion Bar. Thus, the observations exclude SiO as an important component of the water ice mantle. Moreover, photodesorption of water ice mantles is rapid starting at a depth corresponding to 7 magnitudes of extinction (Fig. 3b) and is is more important than thermal evaporation of H_2O ice under the conditions of the Orion Bar (the photodesorption occurs at a depth where the grain temperature is too low for evaporation as one sees in Fig. 2). Again we stress that ejecting silicon in a form other than SiO would not change our qualitative conclusions.

The situation is somewhat different in models 6–8, where we have adopted a considerably lower photodesorption yield for silicon. Moreover, in models 7 and 8, we assume that Si is ejected into the gas phase in atomic form. We show the dependence of abundance on depth in Fig. 4, where the top panel (model 8) shows results for our standard temperature profile, whereas the bottom panel shows results for a constant temperature of 500 K (model 7). One sees that, in models in which Si is photodesorbed in atomic form, the SiO abundance is sensitive to the presence
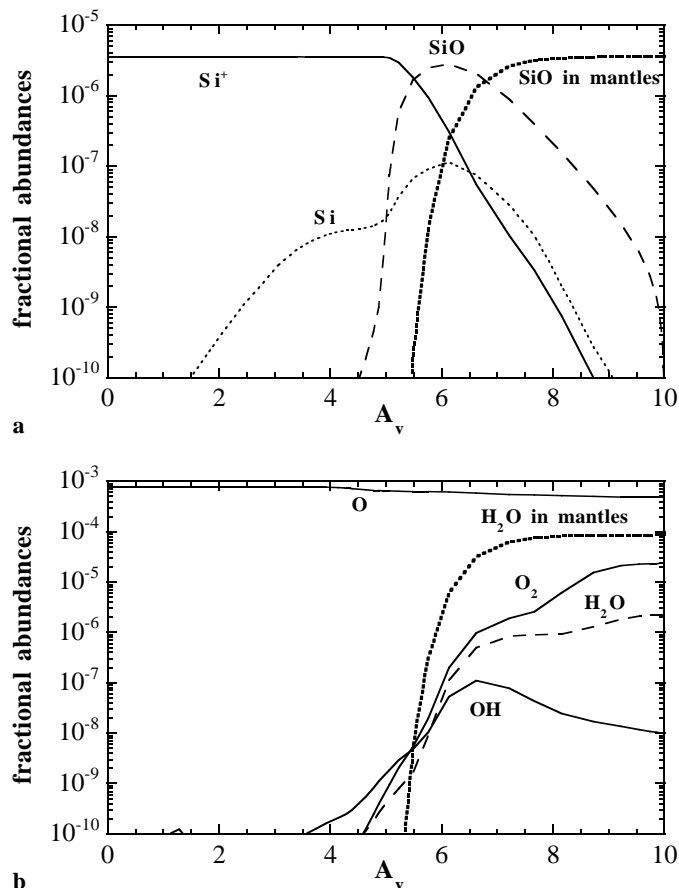
Fig. 3. a The *top panel* shows the abundances of Si-containing species as function of depth for Model 5, where we allow photodesorption of the water ice mantle (containing SiO) using the yield of Westley et al. (1995). The bold dotted line shows the variation of the abundance of SiO in solid form whereas the dashed line shows the variation of gaseous SiO. The full curve and light dots show ionized and neutral Si, respectively **b** The *bottom panel* shows the corresponding behaviour of water ice (bold dots) and gas phase water (dashes). The full curves give the results for atomic oxygen, molecular oxygen, and the hydroxyl radical.

of OH and hence to the gas temperature. Comparison of models 6 and 8 of Table 1 shows that, in this case, the SiO abundance is sensitive to the form in which Si enters the gas phase. We conclude that Si is most effectively "hidden" if it is ejected into the gas phase in atomic form and if, in addition, the temperature in the layer of Si ejection is sufficiently low that OH cannot form rapidly.

The most satisfactory model, from the viewpoint of consistency with the observations, is model 8 (top panel of Fig. 4), where we allow for the decrease of gas temperature with depth. In this case, the region where OH is abundant ($A_v \sim 7$) is sufficiently close to the ionization front ($A_v = 0$) that Si photoionization is a competitive process. The SiO abundance is of the order of 10^{-10} and is thus similar to the limit of Jansen et al. (1995) and a factor of a few larger than the recent measured value of Schilke et al. (1998). We conclude that photodesorption, with parameters similar to those adopted in model 8 (or
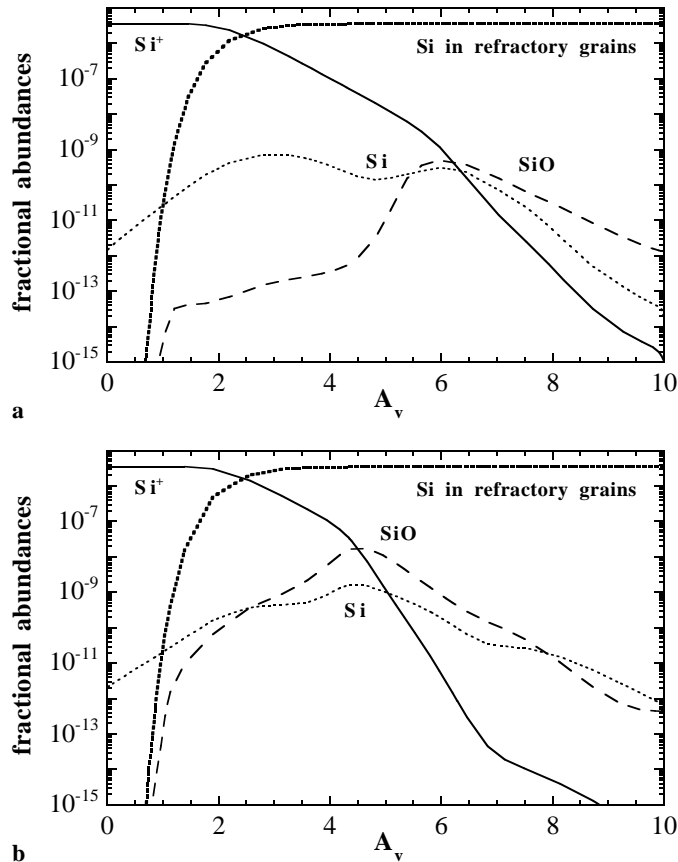
Fig. 4a and b. Abundances of Si-containing species as functions of depth for model 8 (*top panel*) and model 7 (*bottom panel*). Calculations were carried out for a constant photodesorption yield of $5\,10^{-7}$. The top panel shows results for our "standard" temperature profile $(1000/(1+2\,A_v))$, whereas the bottom panel shows results for a constant temperature of 500 K. Bold dots show the variation of the abundance of Si in "refractory form", whereas the dashed lines and the full curve show the variation of gaseous SiO and Si^+, respectively; the light dots indicate atomic silicon.

with a smaller photodesorption yield), is a possible explanation of the "paradox" discussed earlier. Put in other words, a photodesorption yield consistent with the observations of Turner (1998) can explain the observations of Si-containing species towards the Bar.

Finally, we note that the atomic Si column densities given in Table 1 are small in almost all circumstances, suggesting that it will be difficult to detect the [Si I] FIR fine structure lines in a PDR. In model 8 for example, the atomic Si column density is $2\,10^{-4}$ that of Si^+. Atomic Si is rapidly destroyed, either by photoionization or in its reactions with OH and O_2.

4. Discussion

In the previous section, we have attempted to throw light on what we have called the "silicon paradox", that is the weakness or absence of SiO in the molecular layers of PDRs, despite strong Si^+ emission from the neighbouring atomic layer. One might ask how certain it is that the observed Si^+ emission comes from the neutral gas, rather than from the HII region. We consider this question next and then summarize our conclusions on the silicon chemistry within a PDR.

4.1. Does the observed Si II emission originate in neutral gas?

An assumption which underlies all of the above discussion is that the observed [Si II] $35\mu m$ emission is produced in neutral gas (the PDR). However, one cannot entirely exclude the possibility that the $35\mu m$ emission originates within either the HII region or the ionization front separating the ionized and neutral material.

It is instructive, in this context, to compare with observations of iron. Unlike silicon, an iron-containing molecule has yet to be found in molecular clouds (e.g. Turner 1991). Iron is more depleted than silicon in diffuse gas, with a logarithmic depletion of 2.6 (relative to cosmic) in one of the ζ Oph components, as compared to 1.3 for Si (see Sofia et al. 1994). Therefore, it seems reasonable to suppose that silicon is deposited in a less refractory form than iron. On the other hand, [Fe II] lines are observed which peak in intensity close to the ionization front in the Orion Bar (see Marconi et al. 1998 and references therein). Iron is estimated to have an abundance of 20 percent of solar in the Orion HII region (Osterbrock et al. 1992). It seems plausible therefore that an iron-containing component of the dust is destroyed at the edge of the HII region. Whilst the precise composition of such a mantle is not known, it may reasonably be expected to contain Si as well as Fe and thus will be of importance for the Si abundance within the HII region.

However, we do not believe that the *main* contribution to the observed [Si II] lines comes from the ionized gas. The Stacey et al. $35\mu m$ [Si II] map and the Wyrowski et al. C91α map are quite similar, and the C I recombination line emission undoubtedly arises in neutral gas (based upon the line width). Thus, the coincidence in spatial distribution suggests strongly that an important fraction of the [Si II] emission is produced in the PDR. Both the [Si II] and the C I emission appear to come from a layer to the SE of the ionized bar (their spatial coincidence is confirmed by a more recent [Si II] map: Stacey, priv. comm.). Thus, we are convinced that Si in some form is released from the mantle within the neutral layer.

4.2. Si chemistry within the PDR

The models which we have presented are not exhaustive but they do contribute to resolving the "paradox" discussed above. Based on our understanding of the chemistry, we find that, in order that SiO should be currently unobservable in PDRs with large Si^+ column densities, silicon has to be ejected from the solid into the gas phase close to the ionization front. The models suggest that such a transformation occurs at depths corresponding to a visual extinction of around 2–3 magnitudes. In this case, any SiO produced is photo–dissociated rapidly. The most likely mechanism responsible for the ejection of Si into the gas phase seems to be photo–desorption, but there remains a large uncertainty in the yield, and laboratory studies would be very useful.

A sensitive issue in our analysis (as one sees comparing models 7 and 8) is the adopted temperature profile. This is critical for OH production and hence, in our model, for SiO. There is a well–known discrepancy between theoretical and observed temperature distributions in PDRs (Lis et al. 1997), in that temperatures inferred from molecular lines tend to be higher than model predictions. In view of the theoretical uncertainties, we have adopted the observed values, although these are not without their own internal contradictions. Our adopted distribution ($1000/(1 + 2A_v)$) is based on the recent spectroscopic results of Luhman et al.(1998). It is consistent, close to the ionization front, with the H_2 v=0 results of Parmar et al. (1991), who estimated a value of 1000 K at the front. At large depths (A_v of order 7 mag. for an edge–on geometry), where the gas becomes molecular, Hogerheijde et al. (1995) estimate a temperature of 85 K on the basis of formaldehyde observations, which is again roughly consistent with our adopted profile. On the other hand, at depths corresponding (for a H_2 density of $5\,10^4$ cm^{-3}) to A_v=5, Parmar et al. find much higher temperatures ($\sim$500 K) than predicted for this depth. Also, the measured ^{12}CO(6-5) brightness temperature of 175 K (Lis et al.) shows that some molecular gas is much hotter than estimated on the basis of formaldehyde measurements. The latter result and some of the H_2 data may be influenced by emission from hotter gas in dense clumps, but convincing evidence in favour of this view is lacking, in our opinion. We conclude that our adopted temperature distribution is reasonably consistent with current data and, if anything, tends to underestimate the kinetic temperature.

Another question that one might pose considering our results is the validity of our assumptions concerning the mode in which silicon comes into the gas phase. The comparison for example of models 6 and 8 shows that the ejection of Si in atomic form rather than as SiO causes the expected SiO column density to go down by more than a factor of five. On the other hand, we have considered variations of model 5 in which the silicon mixed with water ice is in a variety of forms (H_2SiO, SiH_4, SiO_2, SiH_3OH) and derive SiO column densities which differ by a factor of 2 or less from that given in Table 1. We conclude that the form in which Si comes back into the gas phase is not of great importance, although the most favorable case, from the viewpoint of reducing the expected SiO column density, is ejection as atomic Si.

Although our analysis suggests that silicon is probably not a significant constituent of ice mantles, our models 2–4 show that this possibility cannot be completely ruled out. We note that, in this case, the corresponding solid state spectral features might be observable in the infrared. However, the comprehensive ISO spectra of NGC 7538-IRS9 (Whittet et al. 1996) show no sign of any features other than those attributable to silicates. It has been argued that the so–called 'XCN' feature at 4.6μm might be due to SiH (Moore et al. 1991), but this proposal now seems unlikely to be correct (see Sandford 1996). On the available evidence, the column density of SiH ice towards sources such as NGC 7538-IRS9 is less than 10^{17} cm^{-2}(for an equivalent width less than 10 cm^{-1} and an absorption strength of 10^{-16} cm molecule $^{-1}$; Nuth and Moore 1988). The corresponding limit on the "Si-H"

abundance is 10^{-6}, which is a factor of 3 below that required to explain the fine structure line emission. Given the uncertainties, we cannot exclude the possibility that the evaporation of silane, associated with e.g. CO_2 ice, is responsible for the observed [Si II] line emission in PDRs, but we consider it to be unlikely. Alternatively, Si could be in the form SiO or SiO_2 in the ice mantles. In this case, one might hope to see a narrow feature at around 8μm due to the SiO stretch, although the nearby silicate feature would make detection difficult. Nevertheless, a narrow (10 cm^{-1}) feature might be detectable in ISO spectra awaiting analysis (Tielens, priv. comm.).

In our opinion, a more likely explanation of the "silicon paradox" is that Si is present in a somewhat more refractory form (e.g. Tielens 1998) in grain mantles which are partially destroyed by the UV photons incident upon the PDR. Our model 8, in which Si enters the gas phase in atomic form, is consistent with current observations; a detailed comparison with the results of Schilke et al. (1998) is however needed. We find that the SiO abundance as a function of depth is closely linked to the temperature profile, and it will be useful in the future to compare with the temperature dependence derived from tracers such as H_2. It is clear also that laboratory determinations of the photodesorption yield for Si-containing species are needed. The present calculations show that a rather small yield, of order $5\,10^{-7}$, can have important astrophysical consequences.

4.3. Ice mantles in PDRs

A by-product of the present investigation has been the clarification of the relative importance of various processes which destroy ice mantles within PDRs. Our results show, for example, that apolar ice mantles with binding energies of order 0.1 eV will evaporate far from the ionization fronts of regions such as Orion and M17. Thus, one can expect that, in such regions of high mass star formation, CO, N_2 and O_2 will be in the gas phase, even if water ice is still present. Furthermore, using the Westley et al. (1995) measurements of the photodesorption yield of water, we find that direct photodesorption can remove even polar ice mantles. For the polar component, photodesorption is more important than evaporation; this has implications for the structure of PDRs, as the abundances of water and other coolants then increase close to the PDR surface (at A_v of order 6 in the Orion Bar model).

5. Conclusions

Our main conclusion is that the Si$^+$ fine structure emission observed in many PDRs is likely to be a consequence of photo-erosion of grain mantles at depths corresponding to a few magnitudes of visual extinction. A small photodesorption yield ($5\,10^{-7}$), together with the assumption that silicon comes off in atomic form, suffice to explain the weakness of the emission from SiO in the Orion Bar and to account for the observed Si$^+$. Modest amounts of atomic Si (typically 0.001 of the ionized Si) are predicted by such models. An alternative explanation – that the silicon arises from the thermal evaporation of ice mantles

– cannot be excluded entirely but appears less likely. The high apparent degree of depletion of Si in dark dust clouds is thus likely to be due to efficient deposition of Si in a mantle which is more refractory than water ice and which has a small photodesorption yield. A by–product of our study is the conclusion that, in regions such as the Orion Bar, direct photodesorption of water ice is the main process causing the transition from solid to gas phase; this occurs at a depth where evaporation of water ice is unimportant.

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