THE ASTROPHYSICAL JOURNAL, 187:453-459, 1974 February 1 © 1974. The American Astronomical Society. All rights reserved. Printed in U.S.A.

# INTERSTELLAR ABUNDANCES: GAS AND DUST

**GEORGE B. FIELD** 

Center for Astrophysics, Harvard College Observatory and Smithsonian Astrophysical Observatory Received 1973 August 8

#### ABSTRACT

Data on abundances of interstellar atoms, ions, and molecules in front of  $\zeta$  Oph are assembled and analyzed. The gas-phase abundances of at least 11 heavy elements are significantly lower, relative to hydrogen, than in the solar system. The abundance deficiencies of certain elements correlate with the temperatures derived theoretically for particle condensation in stellar atmospheres or nebulae, suggesting that these elements have condensed into dust grains near stars. There is evidence that other elements have accreted onto such grains after their arrival in interstellar space. The extinction spectrum of  $\zeta$  Oph can be explained qualitatively and, to a degree, quantitatively by dust grains composed of silicates, graphite, silicon carbide, and iron, with mantles composed of complex molecules of H, C, N, and O. This composition is consistent with the observed gas-phase deficiencies.

Subject headings: abundances — interstellar matter

#### I. INTRODUCTION

The OAO-3 Copernicus ultraviolet satellite has provided important new data on the abundances of components of interstellar gas in the direction of several stars (Ap. J. [Letters], 181, L97-L127, 1973), while OAO-2 (Bless and Savage 1972) has earlier provided extinction curves over the range 1100-3600 Å which are relevant to interstellar dust. Together with ground-based work, these data constitute the basis for an analysis of the origin and composition of interstellar dust. In this paper we conduct such an analysis, based upon the interstellar spectrum of the reddened O9.5V star  $\zeta$  Ophiuchi.

#### **II. OBSERVATIONAL DATA**

Table 1 gives column densities of various gas-phase atoms, ions, and molecules in  $\zeta$  Oph. The column densities in table 1 for which error limits are not given are fairly accurate because the ultraviolet lines concerned lie on either the linear or the square-root portion of the curve of growth, while those having error limits are derived from ultraviolet lines on the flat portion. The result for B II is based on a single rocket observation. The column density of K I is based upon  $\lambda$ 7699, which has been resolved, although it is saturated; the same is true of H and K of Ca II. A number of molecules other than H<sub>2</sub> and CO (CH, CH<sup>+</sup>, CN) are seen in  $\zeta$  Oph, but with abundances which are negligible for the present purposes. Others (C<sub>2</sub>, CN<sup>+</sup>, CO<sup>+</sup>, CS, NH, NH<sup>+</sup>, NO, NO<sup>+</sup>, OH, H<sub>2</sub>O, MgH, MgH<sup>+</sup>, SiH, SiO) have been sought with negative results.

A number of species in table 1 (Li I, C I, Na I, Al I, and K I) are not the dominant ionization states in an H I region, so corrections for photoionization to undetected states are necessary. We have used the recombination coefficients computed by Seaton (1951),

Burgess,	Field,	and	Michie	(1960),	and H	Herbig	(1968),
adjusted	to $T =$	70°	K. The	photoio	onizat	ion coe	fficient

	TABLE	E 1		
COLUMN	DENSITIES	IN	ζ	OPHIUCH

		_	
Element	Species	Column Density Log N (cm <sup>-2</sup> )	References
Н	Нг	20.61	1
	$H_{2}$	20.61	1
Li	Liī	9.38	2
Be	Be II	< 10.92	3
B	Вп	< 13.15	4
C	Сі	14.50	5
	Сп	16.75 + 0.55	5
	ČŌ	14.66	6
N	Νı	$16.35 \pm 0.75$	5
	Νп	16.15 + 0.85	5
0	01	$17.25 \pm 0.35$	5
Na	Na 1	13.69	3, 7
Mg	MgI	$12.75 \pm 0.45$	5
	Mgu	15.40	5
Al	Alī	< 10.78	8,9
Si	Si 11	$16.15 \pm 0.65$	5
P	Рп	13.45	5
S	S I	13.20	5
+	Sп	$16.15 \pm 0.65$	5
Ar	Ar ı	15.05 + 0.65	5
Κ	Κı	11.81	10
Са	Ca I	9.67	11, 12
	Ca II	11.73	3, 13
Ti	Тіг	< 11.04	3
	Тіп	< 11.20	3
Mn	Mn II	$13.30 \pm 0.10$	5
Fe	Fe I	11.55	8.9
	<b>Fe</b> 11	$15.20 \pm 0.80$	5

REFERENCES.—(1) Spitzer *et al.* 1973; (2) Traub and Carleton 1973; (3) Herbig 1968; (4) Smith and Stecher 1971; (5) Morton *et al.* 1973; (6) Jenkins *et al.* 1973; (7) Hobbs 1969; (8) Bortolot 1972; (9) Shulman 1973; (10) Hobbs 1973; (11) White 1973; (12) Bortolot, Thaddeus, and Shulman 1971; (13) Marschall and Hobbs 1972.

454

Abundances of the Elements					
Number (1)	Element (2)		Abundance, $\zeta_2$ Oph log $N (\text{cm}^{-2})$ (3)	Abundance, Solar System log $N_s$ (cm <sup>-2</sup> ) (4)	$\log \left(\frac{N}{N_{\rm s}}\right)$ (5)
$ \begin{array}{c} 1\\ 3\\ 4\\ 5\\ 6\\ 7\\ 8\\ 11\\ 12\\ 13\\ 14\\ 15\\ 16\\ 18\\ 19\\ 20 \end{array} $	H Li Be B C N O Na Mg Ai Si P S Ar K C		$\begin{array}{c} 21.10\\ 12.03\\ < 10.92\\ < 13.15\\ 16.35 \pm 0.75\\ 17.25 \pm 0.35\\ 14.71\\ 15.40\\ < 13.32\\ 16.15 \pm 0.65\\ < 13.45\\ 16.15 \pm 0.65\\ 15.05 \pm 0.65\\ 13.77\\ 11.77\end{array}$	$\begin{array}{c} 21.10^{*} \\ 12.29 \\ 10.51 \\ 13.14 \\ 17.67 \\ 17.17 \\ 17.93 \\ 15.38 \\ 16.63 \\ 15.62 \\ 16.60 \\ 14.58 \\ 16.30 \\ 15.67 \\ 14.22 \\ 15.46 \end{array}$	$\begin{array}{c} 0.00^{*} \\ -0.26 \\ < 0.41 \\ < 0.01 \\ -1.32 \\ -0.82 \pm 0.75 \\ -0.68 \pm 0.35 \\ -0.67 \\ -1.23 \\ < -2.30 \\ -0.45 \pm 0.65 \\ < -1.13 \\ -0.15 \pm 0.65 \\ -0.62 \pm 0.65 \\ -0.45 \\ 2.60 \end{array}$
22 25 26	Ti Mn Fe		< 11.43 13.30 ± 0.10 $< 15.20 \pm 0.80$	14.04 14.57 16.52	< -2.61 -1.27 $\pm 0.10$ $< -1.32 \pm 0.80$

\* Abundances are normalized so that  $N_s(H) = N(H)$ .

 $\Gamma$  is set equal to  $\Gamma_0 G$ , where  $\Gamma_0$  refers to typical interstellar space and where G corrects for extinction in the cloud where the lines are formed. The value of  $\Gamma_0$ was taken from Seaton (1951), Herbig (1968), Bortolot (1972), or Brown (1972), where the radiation field approximated that of Habing (1968). The factor G was calculated from Habing (1968), using the albedo calculated by Gilra (1971) and the extinction determined for  $\zeta$  Oph by Bless and Savage (1972); its value ranged from 0.33 for Ca II/Ca III to 0.66 for K I/K II. Contributions to  $\Gamma_0$  by  $\zeta$  Oph itself were ignored; since the dominant velocity component in  $\zeta \text{ Oph}(-14.4 \text{ km s}^{-1})$  is seen in nine stars up to 20° from  $\zeta \text{ Oph}(\text{Herbig} 1968; \text{Marschall and Hobbs 1972}) and <math>\zeta \text{ Oph is 170 pc}$ distant, at least parts of the cloud must be more than 60 pc from  $\zeta Oph$ , where the contribution of  $\zeta Oph$  to  $\Gamma_0$  is <10 percent. Even the parts of the cloud which are as near as possible to  $\zeta$  Oph (15 pc, because of its H II region) would experience only a factor 3 increase in  $\Gamma_0$  (Herbig 1968)

From N(Ca I) and N(Ca II) we find  $n_e = 0.07 \text{ cm}^{-3}$ , compared with White's (1973) 0.13 cm<sup>-3</sup>, based upon a somewhat different  $\Gamma_0$ . The value 0.07 cm<sup>-3</sup> is expected for H I clouds heated by cosmic rays (Mészáros 1972). Using this  $n_e$ , we calculated the densities of Li II, C II, Na II, Al II, K II, and Ca III, and included them in the total column densities of atoms and ions in table 2. Column (4) of table 2 lists the column densities expected in  $\zeta$  Oph from the measured amount of H, together with the abundances in the solar system relative to H (Cameron 1973).

Here we comment on certain of the entries in table 2. *Carbon.*—The log N(C II) listed (16.35) is from the calculated C I/C II ratio in the H I region; no errors are given, because C I is well determined. The measured value of C II,  $16.75 \pm 0.55$ , may be contaminated by the H II region, where  $\log N(H) = 20.14$  according to Herbig. If the carbon in the H II region is about 60 percent graphite, as in the H I region (see below), one expects  $\log N(C II) = 16.23$  in the H II region. When this is added to the calculated C II in the H I region, the total  $\log N(C II)$  is 16.59, close to that observed.

Nitrogen.—Solar-system abundances in the H II region predict log N(N II) = 16.20, in agreement with observation. As N II is not expected in the H I region, and N would not be depleted on grains in the H II region, this indicates that the H II region contributes significantly, as postulated for carbon.

Sodium.—Na II dominates Na I by a factor 9.3. This estimate should be fairly accurate because it uses experimental cross-sections and a radiation field based upon measurement (Brown 1972).

*Phosphorus.*—The value quoted is that observed for P II. As the expected value in the H II region is  $\log N = 13.62$  if there is no depletion on grains there, a good fraction of the observed P II may be in the H II region, so the observed value is treated as an upper limit.

Sulfur.—The S II expected from the H II region, log N = 15.34, is considerably below the observed  $16.15 \pm 0.65$ . Probably most of the S II is in the H I region.

Calcium.—Ca II dominates Ca I and Ca III by factors of 100 and 10, respectively. Therefore, a large increase (up to 10 times) in the ionization rates would not affect N(Ca).

*Titanium.*—The value listed is the observed upper limit on Ti I + Ti II. As the ionization potential of Ti II is 13.57 eV, only 0.025 eV of spectrum is available to No. 3, 1974

ionize it in an H I region. This is probably inadequate to produce a significant amount of Ti III.

*Îron.*—If solar abundances apply in the H II region, one expects log N(Fe II) = 15.56. Even if Fe is depleted on grains, much of the observed Fe II could originate there. We therefore list N(Fe II) as an upper limit.

## **III. INTERPRETATION**

The striking deficiency of gas-phase heavy elements in the  $\zeta$  Oph cloud noted by Morton *et al.* (1973) continues to hold when the elements Li, Be, B, Na, Al, K, Ca, and Ti are included. As H I and H<sub>2</sub> are securely determined, it is very unlikely that the problem is an overestimate of N(H).

The missing heavy elements could be in the form of undetected ions. In the case of Ca, however, an increase in  $\Gamma$  by a factor greater than  $10^4$  is necessary to make  $N \sim N_s$ . This seems out of the question, as no more than a factor of 3 increase can be allowed, or  $N/N_s$  would exceed unity for Li and K. Such a factor would still leave unexplained the deficiency of the elements which are unnecessary to correct for ionization.

The possibility that the missing elements are in molecules is difficult to disprove conclusively. However, after H<sub>2</sub>, CO is the most abundant interstellar molecule among about two dozen detected, yet it accounts for only 0.1 percent of the expected carbon abundance in  $\zeta$  Oph. We conclude that molecules are unlikely to account for the missing elements.

The possibility that the observed deficiencies represent a real lack of the elements concerned can be dismissed, as Population I stars recently born from the interstellar medium usually have normal abundances, and the deficiencies in the  $\zeta$  Oph could seem to be typical of the interstellar medium generally (Morton *et al.* 1973).

We conclude that the most likely interpretation is that the missing elements are locked in dust grains, a possibility suggested by Routly and Spitzer (1952). This could result from collisions of atoms and ions with dust grains in the interstellar medium, as they should stick to the grains with high probability (Aannestad 1973). If the grains are negatively charged (Spitzer 1968), the rate at which an atom or ion is depleted by this process is proportional to  $(1 + 2.5Z)A^{-1/2}$ , where Z is its charge and A is its mass. The observed deficiency factors do not correlate with this quantity, however. Watson (1972) and Feuerbacher, Willis, and Fitton (1973) show that grains composed of insulators such as silicates should be positively charged in interstellar space as a result of photoemission. This would prevent depletion of ions such as C II, Mg II, Al II, and Ca II/Ca III, contrary to observation.

An alternative to accretion onto grains in interstellar space is condensation under nearly equilibrium conditions in cool stellar atmospheres (Hoyle and Wickramasinghe 1962; Kamijo 1963) or stellar nebulae (Dorschner 1968; Herbig 1970). In such models, one envisions a thermally stratified medium. At the points where the temperature is low enough, various solids condense out in thermal equilibrium. The condensation temperature for each element, defined as that temperature at which about half the atoms have condensed in one form or another, has been calculated by Larimer (1967), Anders (1968), Grossman (1972), Lewis (1972), and Cameron, Colgate, and Grossman (1973), for a mixture with solar-system abundances,  $N(O) \simeq 2N(C)$ . The results (table 3) are fairly insensitive to pressure; the value adopted (100 dyn cm<sup>-2</sup>) may be representative of a stellar atmosphere or nebula. From table 3 one sees that the most abundant condensable elements in a solar mixture, C, N, and O, would condense as ices of water, methane hydrate, and ammonia hydrate. The next most abundant group, Mg, Si, S, and Fe, should be present as enstatite ( $MgSiO_3$ ), forsterite (Mg<sub>2</sub>SiO<sub>4</sub>), troilite (FeS), and metallic iron.

Similar calculations have been carried out for carbon-rich atmospheres by Gilman (1969). For N(C) = 2N(O) and a pressure near 100 dyn cm<sup>-2</sup>, he finds that the abundant elements C, Si, and Fe condense as graphite (G), silicon carbide (SiC), and iron

 TABLE 3

 Condensation Temperatures

Stage	Temperature (° K)	Condensates	Elements Removed	
1	1400-1600	CaTiO <sub>3</sub> Mg <sub>2</sub> Al <sub>2</sub> O <sub>4</sub> , Al <sub>2</sub> SiO <sub>3</sub> , CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> CaMgSi O <sub>2</sub> , CaSiO <sub>2</sub> , CaSiO <sub>2</sub>	Ti Al	
2	1220–1320 1280	MgSiO <sub>3</sub> , Mg <sub>2</sub> SiO <sub>4</sub> , BeAl <sub>2</sub> O <sub>4</sub> Metallic Fe. Ni	Si, Mg, Be Fe Ni	
4	1210	MnSiO <sub>3</sub>	Mn	
5	970-1070	Alkali silicates	Na, K, Rb	
0 7	600-700	FeS, NaBO <sub>2</sub>	S, B	
8	120	$H_2 O$ NH <sub>2</sub> , H <sub>2</sub> O	U -	
9	75	CH <sub>4</sub> ·XH <sub>2</sub> O	Ĉ	
10	25	Ar (solid)	Ăr	

456

carbide (Fe<sub>3</sub>C); N, O, Mg, and S are still gaseous at the lowest temperature he considered  $(1270^{\circ} \text{ K})$ .

If grains condense in stellar atmospheres or nebulae, one might expect that abundance deficiencies of the elements would correlate with their condensation temperatures. Figure 1 is such a plot of the abundances in  $\zeta$  Oph against condensation temperatures calculated for an oxygen-rich atmosphere. Condensation temperatures were not available in the literature for Li and P. It was assumed that Li condenses along with Na, K, and Rb. It is believed that Ti condenses early and Ca late in stage 1, while Na condenses early and K late in stage 5.

A crude correlation appears in figure 1 between the observed deficiencies and the calculated condensation temperatures above 500° K, suggesting that the missing elements are in grains which condense under equilibrium conditions. The range of temperatures involved,  $500^{\circ}-1500^{\circ}$  K, is reasonable for a stellar nebula (e.g., Cameron and Pine 1973 give  $300^{\circ}-3000^{\circ}$  K for the solar nebula) or for the atmosphere of a cool star ( $T < 2000^{\circ}$  K). A possible—but not unique—interpretation of the correlation is that the grains condense in material flowing away from a star. Stage 1 occurs near the star, where the density is high, and the process goes nearly to completion. Later stages occur progressively farther from the star where the density is lower, and hence are less complete.



FIG. 1.—Logarithmic abundances of gas-phase elements in  $\zeta$  Oph, relative to solar-system values, plotted against the condensation temperature calculated for an oxygen-rich atmosphere (table 3). It is suggested that elements above 500° K condensed as cores in stellar nebulae or atmospheres, while those below 500° K condensed as mantles in interstellar space. The large deficiencies of C and Ca are consistent with the latter process.

The correlation does not apply below  $500^{\circ}$  K; we return to this point below.

## IV. DUST

Several of the condensates mentioned above have been considered in the literature as components of interstellar dust grains. A number of attempts have been made (e.g., Hoyle and Wickramasinghe 1969; Gilra 1971), using a mixture of condensates, to account not only for the broad-band extinction spectrum but also for specific features like the 0.21- $\mu$  bump. Here we consider such mixtures in the light of figure 1 and the theory of condensation, emphasizing the limitations imposed by the abundances of table 2. Our goal is to explain the extinction spectrum qualitatively, and the extinction at, say, the blue wavelength  $\lambda_B = 0.435 \,\mu$ , quantitatively; for simplicity, we assume spherical grains. As this is barely possible with the column densities given in table 2, we adopt the philosophy that each condensate should be utilized as efficiently as possible. To apply this procedure to  $\zeta$  Oph, we stipulate the quantitative constraint that  $A_B = 1.06$  mag (Bless and Savage 1972). The qualitative constraint imposed by the observed extinction spectrum  $A_{\lambda}$  of  $\zeta$  Oph can be summarized by three properties: (1) an increase in  $A_{\lambda}$  from  $\lambda^{-1} = 0.2$  to  $4 \mu^{-1}$ , with positive curvature in the infrared and negative curvature in the ultraviolet; (2) a bump at  $\lambda^{-1} = 4.75 \,\mu^{-1}$ , about 0.7  $\mu^{-1}$  wide; (3) a rapid increase from 6 to 9  $\mu^{-1}$ .

Gilra ascribed property (2) to small  $(a = 0.025 \,\mu)$ graphite grains. The mass of such small graphite grains needed to quantitatively explain property (2),  $\sigma =$  $5.6 \times 10^{-6}$  g cm<sup>-2</sup>, is independent of *a*; it consumes 62 percent of  $N_s$  (table 2) and produces  $A_B(G) =$ 0.27 mag.

By Gilman's theory (1969), graphite implies SiC. As we shall see, much of the graphite may have been deposited in interstellar space, so that 62 percent is an upper limit on the fraction of carbon condensed in carbon-rich atmospheres; we arbitrarily assume that 10 percent of the condensation occurred there. Of the total silicon abundance, 35 percent is in Si II (table 2). We assume that of the remaining 65 percent, 58 percent is in silicates and 7 percent is in SiC, in accordance with the above assumption. This yields  $\sigma(SiC) = 1.8 \times$  $10^{-7}$ ; and since Gilra adopted  $a(SiC) = 0.075 \,\mu$ to explain property (1), obtaining  $A_B/\sigma = 1.1 \times 10^5$ mag cm<sup>2</sup> g<sup>-1</sup>,  $A_B(SiC) = 0.02$  mag. (Gilra's much larger value was based upon using all the Si and assuming a larger abundance than is actually the case.)

Gilra tried to fit property (3) with small silicate particles ( $a = 0.045 \mu$ ), obtaining  $A_B/\sigma = 1.2 \times 10^4$ for a mixture in which Mg<sub>2</sub>SiO<sub>4</sub> dominates over MgSiO<sub>3</sub>. With our assumption that 58 percent of the Si is in silicates, the missing 94 percent of the Mg (table 2) will also be in silicates if 71 percent is in Mg<sub>2</sub>SiO<sub>4</sub> and 23 percent is in MgSiO<sub>3</sub>, giving  $\sigma$ (MgSiO<sub>3</sub> + Mg<sub>2</sub>SiO<sub>4</sub>) = 5.0 × 10<sup>-6</sup> and  $A_B = 0.06$ mag. From measurements on the 10- $\mu$  silicate band, No. 3, 1974

Gillett and Forrest (1973) found  $\sigma(\text{silicates})/A_v(\text{total}) = 5 \times 10^{-6}$ . Since  $A_v(\zeta \text{ Oph}) = 0.78 \text{ mag}$ , their data would indicate  $\sigma(\text{silicates}) = 3.9 \times 10^{-6}$ , in fair agreement with our  $5.0 \times 10^{-6}$ .

Iron may be condensed as metal, FeS, or Fe<sub>3</sub>C. As the metal absorbs quite efficiently, we assume that it is the dominant condensate. Wickramasinghe and Nandy (1971*a*, *b*) took  $a(Fe) = 0.02 \mu$  in order to fit property (3). For such small grains  $A_B/\sigma = 1.1 \times 10^4$ , independent of *a*. After subtracting the 5 percent of the Fe in Fe II (table 2), we obtain  $\sigma(Fe) = 2.8 \times 10^{-6}$ , so  $A_B(Fe) = 0.03$ .

This model, based upon graphite, silicon carbide, silicates, and metallic iron, agrees quantitatively with the 0.21- $\mu$  graphite bump and the 10- $\mu$  silicate band, and qualitatively with properties (1) and (3). Although it uses all of the Mg, Si, and Fe, and 67 percent of the C, the total extinction is  $A_B = 0.27(G) + 0.02(SiC) +$  $0.06(MgSiO_3 + Mg_2SiO_4) + 0.03(Fe) = 0.38$ , far less than the observed 1.06. The G, SiC, and Fe contribute optimally to  $A_B$ , but the silicate contribution would be increased 0.18 mag if  $a = 0.10 \mu$  rather than 0.045  $\mu$ . However, this would still explain only half of the observed extinction if only spherical grains are involved.

As often suggested, the remaining extinction may result from compounds of C, N, and O, all of which are deficient in the gas phase, C by more than can be accounted for by G and SiC. According to table 3, C, N, and O would condense as ices in stages 7–10 in oxygen-rich atmospheres, but the reduction of the observed deficiencies to nearly zero at stage 5 or 6 suggests that stages 7–10 do not proceed far toward completion. We therefore consider the possibility that C, N, and O accrete on the grains formed in stars after the grains enter the interstellar medium.

Graphite grains are negatively charged, so C (primarily C<sup>+</sup>) is attracted to them. As usual, C sticks to the surface, most of which is covered with H atoms. According to Donn (1965) and Watson and Salpeter (1972; hereafter referred to as WS) it either migrates to a growth edge, there to be incorporated as part of the graphite crystal, or it reacts with H to form CH<sub>4</sub>. However, the binding energy of  $CH_4$  on graphite is low (Aannestad 1972), and it can therefore easily be photoejected by stellar ultraviolet (WS). Similarly, N and O will collide, stick, and react with H to form NH<sub>3</sub> and  $H_2O$ . As their binding energies are also low, they are also photoejected. On the other hand, the few C atoms that do migrate to a growth edge cause the graphite grains to grow slowly. It is estimated that any parcel of interstellar matter remains outside of stars for at least 109 years (Salpeter 1970); and since graphite is very indestructible, this slow growth may continue for more than 10° years, providing a possible interpretation for the large mass of graphite (62 percent of all C) even though a relatively small percentage of matter is processed through carbon-rich systems.

Silicate grains are positively charged, and therefore

repel C II and other ions. However, N and O collide, stick, and react to form NH<sub>3</sub> and H<sub>2</sub>O. The binding energies of NH<sub>3</sub> and H<sub>2</sub>O on silicates are much larger than on graphite, so that photoejection is not efficient and a monolayer of these substances is expected to adhere to the silicate grains (Aannestad 1972). As WS show, NH<sub>3</sub> and H<sub>2</sub>O molecules subsequently resist photoejection from such a surface, as it has the same composition; and an ice mantle grows. When the mantle becomes thicker than  $10^{-6}$  cm (which takes 10<sup>6</sup> years in normal interstellar clouds), the photoelectrons produced by ultraviolet in the silicate core can no longer escape (Watson 1972); and as few are produced in the ice mantle, the grain becomes negatively charged. Carbon in the form of  $C^+$  is then attracted and sticks, reacting to form CH<sub>4</sub>. Whether carbon remains permanently depends upon the fate of the excited CH<sub>3</sub> produced when ultraviolet dissociates  $CH_4$ . On the one hand, it may be photoejected, thus preventing C from being incorporated permanently into the mantle. On the other hand,  $CH_3^* + H_2O \rightarrow$  $H_2CO + H_2 + H$  and other reactions are possible (WS), so that successive events of this kind can build up complex organic molecules which may be more strongly bound to the surface. Such ultraviolet processing also occurs deep in the grain, converting the C, N, and O compounds to complex molecules in about 10<sup>6</sup> years (Donn and Jackson 1970; Greenberg et al. 1972). According to Khare and Sagan (1973), the molecules produced include many of those observed in the gas phase by radio astronomers. Since the time scale for mantle growth is 10<sup>7</sup> years, only about 10 percent of the oxygen in the mantle will be unprocessed  $H_2O$ .

The result of accretion may therefore be the slow growth of graphite grains and the more rapid growth of a mantle on the silicate grains, composed of complex molecules of H, C, N, and O. From the dependence of interstellar accretion upon charge and mass (Mészáros 1972), one concludes that Ca collides about as frequently as C, so that if it is retained with about the same probability, it should be decreased by the same factor; this does not contradict figure 1. Other elements should be decreased by smaller factors, which are not inconsistent with figure 1. On the other hand, Li should be decreased by a factor of 16, rather than by the factor of 2 observed. This poses a contradiction if it cannot be explained, as N(Li) is well determined. A possible interpretation is that LiH, the saturated molecule formed on a grain, is intermediate between  $H_2$  in its ability to convert the energy released at formation into translational energy which can eject it from the grain (WS). Since the probability that CH remains is as high as 95 percent (WS), and since  $H_2$ almost always leaves (Hollenbach and Salpeter 1970), LiH could go either way.

Taking into account the atoms residing in N I, O I, silicates (with allowance for water of hydration), graphite, SiC, and C II, we find  $\sigma$ (CH<sub>4</sub> + NH<sub>3</sub> + H<sub>2</sub>O) = 2.4 × 10<sup>-5</sup>, which with a bulk density of unity gives

a mantle volume  $V_M = 2.4 \times 10^{-5} \text{ cm}^3$  in each cm<sup>2</sup> column. As the volume of the silicate core is  $V_C =$  $1.6 \times 10^{-6}$  cm<sup>3</sup> cm<sup>-2</sup>, the grain is larger than the core alone by the factor  $(1 + V_M/V_C)^{1/3} = 2.5$ , giving a radius of 0.11  $\mu$ . If we assume an index of refraction of 1.3, we obtain  $A_B/\sigma = 3.0 \times 10^4$  (Greenberg 1968), so that  $A_B = 0.72$  mag for the silicate-core-organicmantle grains. This is 0.66 mag larger than the contribution of the silicate cores alone, so the former value of  $A_B$  is increased to 1.04 mag, in fair agreement with the observed 1.06 mag.

The mantles we have described would not violate the observations of the 3.1- $\mu$  ice band. Gillett and Forrest (1973) found  $\sigma(H_2O)/\sigma(Mg_2SiO_4) = 0.29$  from the infrared bands in the Orion infrared source. Knacke, Cudaback, and Gaustad (1969) obtained upper limits on the strength of the ice band which are consistent with this. If all the oxygen remaining in  $\zeta$  Oph were in H<sub>2</sub>O ice, this ratio would be 3.6, about 10 times larger. Hence only about 10 percent of the O may be in H<sub>2</sub>O; this is consistent with ultraviolet processing as explained above. Field, Partridge, and Sobel (1967) predicted that absorption edges of  $CH_4$ ,  $NH_3$ , and  $H_2O$  at 1350, 1990, and 1570 Å should be observed if grains contain these compounds. That such edges are not apparent in the extinction spectrum of  $\zeta \text{ Oph}$  (Bless and Savage 1972) would also be explained by ultraviolet processing.

- Aannestad, P. A. 1972, Ph.D. dissertation, University of California, Berkeley.

- A-030-/2-206. Bortolot, V. J., Thaddeus, P., and Shulman, S. 1971, Bull. A.A.S., 3, 15. Brown, R. L. 1972, Ap. J., 173, 593. Burgess, A., Field, G. B., and Michie, R. W. 1960, Ap. J., 131, 529.

- Cameron, A. G. W. 1973, preprint. Cameron, A. G. W., Colgate, S. A., and Grossman, L. 1973, *Nature*, 243, 204.
- Cameron, A. G. W., and Pine, M. R. 1973, Icarus, 18, No. 3, 377.

- Donn, B. 1965, A.J., **70**, 320. Donn, B., and Jackson, W. M. 1970, Bull. A.A.S., **2**, 309. Dorschner, J. 1968, Astr. Nach., **290**, 171. Feuerbacher, B., Willis, R. F., and Fitton, B. 1973, Ap. J., 181, 101.
- Field, G. B., Partridge, R. B., and Sobel, H. 1967, in Interstellar

- Grains, ed. J. M. Greenberg and T. P. Roark (Washington: NASA SP-140), p. 207.
  Gillett, F. C., and Forrest, W. J. 1973, Ap. J., 179, 483.
  Gilman, R. C. 1969, Ap. J. (Letters), 155, L185.
  Gilra, D. P. 1971, Nature, 229, 237.
  Greenberg, J. M. 1968, in Nebulae and Interstellar Matter, ed. B. M. Middlehurst and L. H. Aller (Chicago: University of Chicago Press) chap. 6
- of Chicago Press), chap. 6.
  Greenberg, J. M., Yencha, A. J., Corbett, J. W., and Frisch, H. L. 1972, Mém. Soc. Roy. Sci. Liège, Ser. 6, 3, 425.
  Grossman, L. 1972, Geochim. Cosmochim. Acta, 36, 597.
  Habing, H. J. 1968, B.A.N., 19, 421.

In summary, the interstellar line and extinction spectrum of  $\zeta$  Oph can be understood if dust grains containing silicate and graphite cores and mantles of H, C, N, and O compounds use up substantial amounts of the available heavy elements. The cores condense in stellar atmospheres or nebulae under equilibrium conditions, while the mantles form in interstellar space.

Certain elements whose gas-phase abundances are still not precisely known should be found to be deficient by amounts which can be estimated from the arguments in this paper to be (in logarithmic notation):  $Be(\sim 1.3)$ , B(< 0.3), N(substantial), O(substantial), Al(>3.0), Si(~1.0), S(<0.3), Ar(substantial), Ti(>3.0), Cr(~1.0), Fe(~1.0), Co(~1.0), and  $Ni(\sim 1.0)$ . The deficiencies of N and O should be correlated with properties of the dust, such as  $A_V/N_H$ and particle size.

I am grateful to Dr. Lyman Spitzer, Jr., for preprints of the Copernicus results. This work was partially supported by the National Science Foundation under grant GP-36194X, and was completed at the Aspen Center for Physics at a workshop on interstellar physics supported by the National Aeronautics and Space Administration.

### REFERENCES

- Herbig, G. H. 1968, Zs. f. Ap., 68, 243.

- 53, 79.
- Hoyle, F., and Wickramasinghe, N. C. 1962, M.N.R.A.S., 124, 417.

- L122.
- Kamijo, F. 1963, Pub. Astr. Soc. Japan, 15, 440. Khare, B. N., and Sagan, C. 1973, in Molecules in Interstellar Environment, ed. M. A. Gordon and L. E. Snyder (New York: Wiley), p. 399.
- Knacke, R. F., Cudaback, D. D., and Gaustad, J. E. 1969,

- Knacke, R. F., Cudaback, D. D., and Gaussac, J. L. *Ap. J.*, **158**, 151. Larimer, J. W. 1967, *Geochim. Cosmochim. Acta*, **31**, 1215. Lewis, J. S. 1972, *Icarus*, **16**, 241. Marschall, L. A., and Hobbs, L. M. 1972, *Ap. J.*, **173**, 43. Mészáros, P. 1972, *Ap. J.*, **177**, 79. ——... 1973, *ibid.*, **180**, 381. Morton, D. C., Drake, J. F., Jenkins, E. B., Rogerson, J. B., Spitzer, L., Jr., and York, D. G. 1973, *Ap. J. (Letters)*, **181**. L103.
- Routly, P. M., and Spitzer, L., Jr. 1952, Ap. J., 115, 227.
  Salpeter, E. E. 1970, in *Interstellar Gas Dynamics*, IAU Symposium No. 39, ed. H. J. Habing (Dordrecht: Reidel), p. 221.
- Seaton, M. J. 1951, M.N.R.A.S., 111, 368.

- Seaton, M. J. 1951, M.W.A.A.S., HI, 500. Shulman, S. 1973, private communication. Smith, A. M., and Stecher, T. P. 1971, personal communication. Spitzer, L., Jr. 1968, *Diffuse Matter in Space* (New York: Wiley).

Spitzer, L., Jr., Drake, J. F., Jenkins, E. B., Morton, D. C., Rogerson, J. B., and York, D. G. 1973, *Ap. J. (Letters)*, 181, L116.

Traub, W. A., and Carleton, N. P. 1973, in preparation. Watson, W. D. 1972, *Ap. J.*, **176**, 103 and 271. Watson, W. D., and Salpeter, E. E. 1972, *Ap. J.*, **174**, 321 (WS). White, R. E. 1973, *Ap. J.*, in press. Wickramasinghe, N. C., and Nandy, K. 1971a, *Nature*, **229**, 81.

------. 1971b, M.N.R.A.S., 153, 205.