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ON THE FORMATION OF GRAPHITE PARTICLES IN THE ATMOSPHERES OF MIRA VARIABLES

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Summary

The observed molecular abundance ratios H_2O/H_2, CO/H_2, CN/H_2 in α-Orionis are explained on the basis of an equilibrium composition of the elements with atomic ratios $O/H \cong 10^{-4}$, $O/C \cong 1{\cdot}03$, $N/C \cong 0{\cdot}1$ and a total hydrogen density $\sim 6{\cdot}10^{15}\ \mathrm{cm}^{-3}$. Provided that $O/C < 1{\cdot}07$, $N/C < 1{\cdot}0$ and the total hydrogen density exceeds $\sim 10^{13}\ \mathrm{cm}^{-3}$, it is shown that the free carbon in an M star atmosphere becomes saturated with respect to bulk graphite at $T \cong 1800\,^\circ\mathrm{K}$. About 0·1–1 per cent of the total atmospheric carbon may condense into graphite flakes of radii $\sim 10^{-6}$ cm.

1. *Introduction.* Several observational data have recently become available which point to the presence of graphite particles in the atmospheres of M stars. Serkowski (**1**) has recently reported that many Mira variables exhibit a fluctuating intrinsic polarization with an approximately λ^{-1} type of wavelength dependence which is characteristic of small graphite flakes. Donn, Stecher, Wickramasinghe & Williams (**2**) have argued that all the observed features of this polarization are consistent with the hypothesis that graphite flakes of radii $\sim 10^{-6}$ cm condense in the stellar atmosphere and are aligned by stellar magnetic fields.

The cool flow of gas observed in several M giants including α-Orionis cannot be satisfactorily accounted for without invoking the presence of solid particles (**3**). It has already been pointed out (**4**) that the condensation of $\sim 0{\cdot}1$ per cent of the atmospheric carbon into solid particles of radii $\sim 10^{-6}$ cm would serve to maintain the observed steady flow of gas through the action of radiation pressure on grains.

Woolf (**5**) has reported an intrinsic reddening of Mira which indicates the presence of solid particles in this star. The early observations of Merrill (**6**) that the colour temperature of Mira variables estimated from the visible spectrum fluctuates more than that determined in the infrared also point to an intrinsic reddening effect.

If solid particles exist in the stellar atmosphere—as the observations strongly suggest—the question of their formation now demands serious attention. Previous discussions of the condensation solid particles in Mira variables (**4**) suffered from the lack of reliable relative abundance determinations for these stars. Particularly important is a good determination of the ratio O/C. If one assumes a solar value $O/C \simeq 1{\cdot}6$, equilibrium calculations of Hoyle & Wickramasinghe (**7**) reveal that, for gas densities in the range 10^{12}–$10^{15}\ \mathrm{cm}^{-3}$, condensation of particles of MgO, Fe, SiO_2 can occur at temperatures below $\sim 1500\,^\circ\mathrm{K}$. Since the boundary temperature in an M star atmosphere is probably $\sim 0{\cdot}57 T_{\mathrm{eff}}$ (**8**) it would appear unlikely that such particles can form to any appreciable extent, except in Miras of type later than M5 where the effective temperature may be expected to fall below $\sim 2300\,^\circ\mathrm{K}$ at minimum light.

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It is generally assumed that an O/C ratio exceeding unity, appropriate for the M stars, precludes the formation of graphite particles on account of the strong binding of the CO molecule. While this is undisputably true for a strong oxygen excess, e.g. $\mathrm{O/C} \simeq 1{\cdot}6$, it may not necessarily be true for a much smaller excess—e.g. if the oxygen exceeds the carbon concentration by only a few per cent. The total oxygen will then be insufficient to oxidize all the C as well as other competing elements such as Si. The possibility arises, in this case, that the competition of Si for the excess oxygen would have the effect of releasing appreciable quantities of carbon from CO. We shall show that precisely this situation arises in the case of the M stars. We obviously require a knowledge of the O/C ratio as well as the N/O, O/H, Si/H ratios in the atmospheres of these stars.

The object of the present paper will be to carry out molecular equilibrium calculations with a view to determining the atomic ratios in the stellar atmospheres, and also the conditions for the saturation of free carbon. We shall see in Section 2 that $\mathrm{O/C} \cong 1{\cdot}03$ is appropriate for most M stars, at any rate in the stellar atmosphere. Previous extensive molecular equilibrium calculations by Tsuji (**10**) unfortunately do not include this case. While Spinrad & Vardya (**9**) have calculated equilibrium abundances for a closely similar case $\mathrm{O/C} \cong 1{\cdot}05$, their paper does not discuss the distribution of free carbon atoms.

2. *Atmospheric abundances of the elements.* Spinrad & Vardya (**9**) analysing recent data on the strengths of various molecular bands deduce H_2O/H_2, CO/H_2, CN/H_2 ratios for several M stars. Their results for α-Ori and o-Cet are set out in Table I. It should be pointed out that the H_2O/H_2 and CO/H_2 figures are probably the best determined with an uncertainty of only a factor ~4. The CN/H_2 ratios are uncertain at least to within a factor ~10.

TABLE I

Star	Spectral type	T_{eff}	H_2O/H_2	CO/H_2	CN/H_2
o Cet (min)	M9e	2000	$1{\cdot}7 \times 10^{-5}$	$1{\cdot}7 \times 10^{-3}$	—
o Cet (max)	M6e	2500	5×10^{-6}	—	$1{\cdot}5 \times 10^{-10}$
α Ori (min)	M2Ib	3000	$1{\cdot}0 \times 10^{-5}$	10^{-4}	10^{-9}
α Ori (max)		3200			

For a particular star, with given values of T_{eff} and the total gas density, we could now estimate the relative abundances O : C : N : H which could reproduce observed molecular ratios. Equilibrium calculations of Spinrad & Vardya (**9**) over a range of permissible values of gas density and temperature indicate that a ratio O/C close to 1·05 is imperative for most M stars. However, these authors point out that the ratios N/O, O/H are less well defined being more sensitive to uncertainties in the appropriate photospheric temperature. For α-Ori they obtain a reasonable fit for the molecular ratios in Table I with $\mathrm{O/C} \cong 1{\cdot}05$, $\mathrm{N/O} \cong 2$, $\mathrm{O/H} \cong 10^{-3}$ at 3000°K; and with $\mathrm{O/C} \cong 1{\cdot}05$, $\mathrm{N/O} \cong 0{\cdot}1$, $\mathrm{O/H} \cong 10^{-3}$ at 3300°K. The second column of Table II gives their predicted molecular ratios for the former of these temperatures.

Although Spinrad & Vardya have stated that the high N/O ratio (~20 times solar value) might be *slightly* favoured, our attempt to fit the observed molecular ratios does not support such a claim.

In order to determine the appropriate atomic ratios as well as the conditions for carbon saturation we require a scheme to calculate the equilibrium composition

TABLE II

Molecular abundance ratios in α-Ori

	Observed	Model *S* and *V*	Present model
H_2O/H_2	1×10^{-5}	2.3×10^{-5}	1.6×10^{-5}
CO/H_2	1×10^{-4}	3.4×10^{-3}	6.1×10^{-4}
CN/H_2	1×10^{-9}	4×10^{-11}	1.8×10^{-8}

of a dissociating assembly of molecules. A computer program was set up to perform such a calculation involving ~80 molecular species consisting of C, N, O, H, Si, Mg, Fe, S, Ti, Zr and V. The principal molecular species included are listed in Table III. The procedure adopted is similar to that described by Tsuji (**10**). The molecular binding energies were taken from the JANAF Tables (**11**) and the vibrational and electronic partition function deduced from the data given by Herzberg (**12**), (**13**). The equations of equilibrium for all the reactions considered, together with the equations of constraint on the total concentrations of every atomic species involved were solved by the standard Newton–Rapheson iteration method.

TABLE III

Element	Principal molecular species competing for H, C, N, O
H	H, H_2, OH, H_2O, CH, CH_2, CH_3, CH_4, NH, NH_2, NH_3, HCN
O	O, OH, H_2O, O_2, CO, CO_2, SiO, SiO_2, MgO, FeO, TiO, TiO_2, VO, ZrO
C	C, C_2, C_3, CO, CO_2, CH, CH_2, CH_3, CH_4, CN, HCN
N	N, NH, NH_2, NH_3, CN, HCN, N_2
Mg	MgO
Fe	FeO
Si	SiO, SiO_2
Ti	TiO, TiO_2
V	VO
Zr	ZrO, ZrO_2

Assuming an effective temperature ~3000 °K and a total photospheric density 6.7×10^{15} cm^{-3} for α-Ori we tried to fit the observed molecular ratios (first column of Table II) by keeping the ratios Mg/H, Fe/H, Si/H, Ti/H, V/H, Zr/H at the solar values and varying O/H, O/C and N/O. It was found that a good fit with the observed values was possible with $O/H\cong10^{-4}$, $O/C\cong1.03$, $N/O\cong0.1$. The resulting molecular ratios are listed in the third column of Table II. Agreement with observations is seen to be quite favourable.

For o-Cet we obtained good agreement with the observed molecular ratios for a total density $\sim6.7\times10^{15}$ cm^{-3}, effective temperature ~2500 °K, $O/C\cong1.05$, $N/O\cong0.1$, $O/H\cong10^{-3}$. The predicted molecular ratios for this case are $H_2O/H_2\cong 2.3\times10^{-5}$, $CO/H_2\cong3\cdot10^{-3}$ and $CN/H_2\cong10^{-11}$.

These calculations bear out the general conclusion of Spinrad & Vardya (**9**) that the O/C is only very slightly in excess of unity for most M stars. It is also seen that the N/O ratio need not be greater than the solar value ~0.1. We shall see in the next section that these two features in conjunction would permit the saturation of carbon vapour in α-Orionis and also probably in most Mira stars.

3. *Carbon saturation.* Consider a stellar atmosphere with $O/H\cong10^{-4}$, $O/C\cong 1.03$, $N/O\cong0.1$ and a photospheric density 6.7×10^{15} cm^{-3}. In Fig. 1 we have

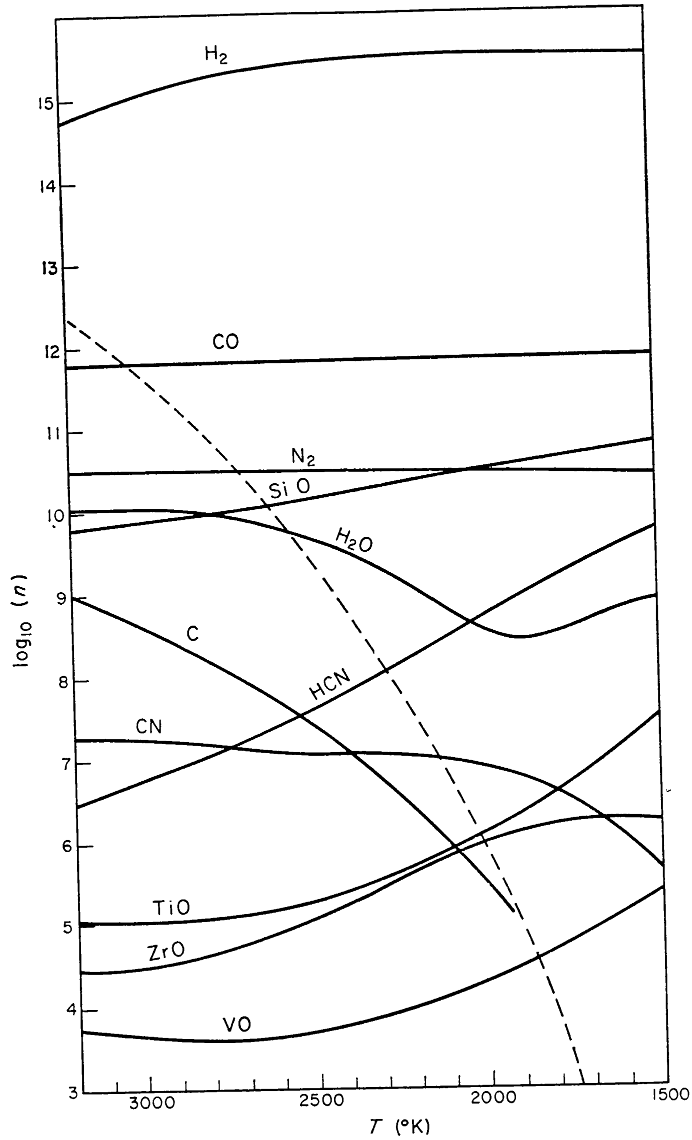

Fig. 1. *Abundances of principal compounds for a gas of density* $6{\cdot}7 \times 10^{15}$ *cm*$^{-3}$ *with a composition appropriate for α-Ori –* $O/C = 1{\cdot}03$, $O/H = 10^{-4}$, $N/O = 0{\cdot}1$, *the abundances of remaining elements relative to H kept at solar values. Dashed curve is the saturation vapour pressure of bulk graphite.*

plotted the number densities of several principal atomic and molecular specie including free carbon, for such an atmosphere as a function of T. The dashed curv is the vapour pressure of bulk graphite calculated from the thermochemical dat in the JANAF Tables. We see from Fig. 1 that the free carbon in the gaseou mixture becomes saturated with respect to the solid phase at $T \simeq 1900$°K. Th temperature is very close to the effective temperature at minimum phase of sever late type Miras including o-Cet (see Table I). It is therefore reasonable to conclu that graphite condensation takes place at, or very near to, the photospheric lev in these stars.

For α-Orionis, whose effective temperature is probably not less than ~ 3000° carbon saturation cannot take place at the stellar photosphere. The possibilit however, remains that saturation may occur at a higher level in the stellar atmo phere. In Fig. 2 we have plotted the partial pressure of free carbon (solid curv in an atmosphere with the same relative abundances as before, but with a total density $\sim 10^{14}$ cm^{-3}. The dashed curve is the vapour pressure of graphite. It is seen that the carbon vapour in this case reaches saturation at $T \simeq 1800$ °K. We repeated this calculation for other values of the total pressure in the region of $\sim 10^{14}$ cm^{-3}. It is found that the free carbon pressure is remarkably insensitive to changes in density by factors of $\sim 10^2$ in this region. Thus the saturation temperature remains close to ~ 1800 °K for the total gas density in the range 10^{13}–10^{15} cm^{-3}. The physical reason for this insensitivity has already been discussed by Tsuji (**10**).

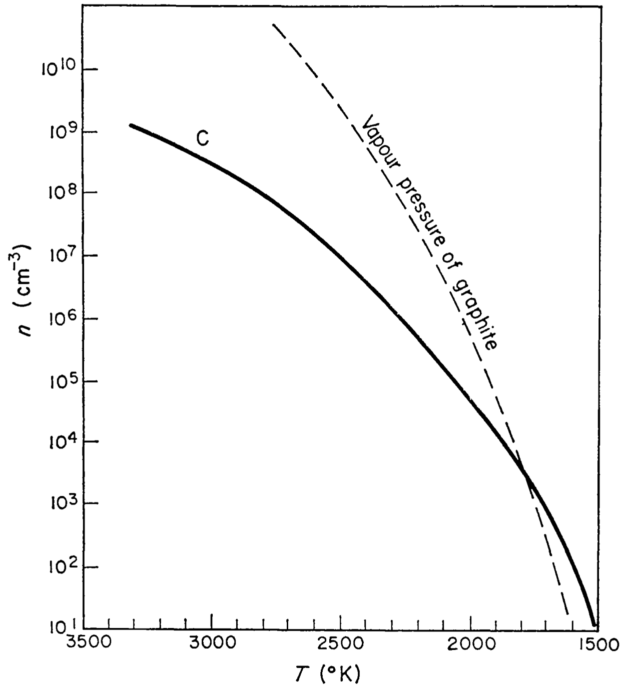

FIG. 2. *Solid curve is the number density of free carbon in α-Ori for a gas density in the range* 10^{13}–10^{15} *cm*$^{-3}$. *Dashed curve is vapour pressure of graphite in number density units.*

Although the solid curve of Fig. 2 was computed for $O/H \simeq 10^{-4}$, $O/C \simeq 1{\cdot}03$, $O/N \simeq 0{\cdot}1$ it was also found, by varying these quantities, that the free carbon pressure remains essentially unchanged provided:

$$10^{-3} > O/H > 10^{-4}$$

$$1{\cdot}07 > O/C > 1{\cdot}02$$

$$1{\cdot}00 > N/O > 0{\cdot}1.$$

As we have seen in the previous section there are strong indications that all these conditions are easily satisfied in the Mira variables. It was further found that the ratios Si/H, Mg/H, Fe/H, Ti/H, V/H, Zr/H may be increased or lowered by a factor ~ 10 from the solar values without changing the conclusions of the present section.

In the next section we shall discuss the conditions likely to exist in the atmosphere of a star similar to α-Orionis in relation to the carbon saturation. It should be borne in mind that the conditions prevalent in later type Miras would be even more conducive to the formation of graphite particles.

4. *Conditions in the stellar atmosphere.* The question now arises whether there exists a region of the stellar atmosphere where the temperature has fallen to $\sim 1800\,^\circ$K, while the gas pressure has not dropped by more than a factor $\sim 10^3$ below the photospheric value. An affirmative answer appears to emerge from the work of Tsuji (**8**), (**14**) on model atmospheres of M stars. In Fig. 3 we have reproduced the relation between the local temperature T and the optical depth $\bar{\tau}$ (defined in terms of the mean Rosseland absorption coefficient) given by Tsuji (**8**). This relationship may be assumed appropriate for M stars taking into account the effect of heavy line blanketing (**8**). The boundary temperature is $\sim 0{\cdot}57 T_{\mathrm{eff}} \cong 1700\,^\circ$K for α-Orionis. We also see that the value of the local temperature will be $\sim 1800\,^\circ$K at $\bar{\tau} \cong 10^{-3}$. The Rosseland mean absorption coefficient $\bar{\kappa}$, including molecular sources of opacity, has also been calculated by Tsuji (**14**). At $T \cong 1800\,^\circ$K it is found (**14**, Fig. 8) that $\bar{\kappa} \cong 10^{-6}$.

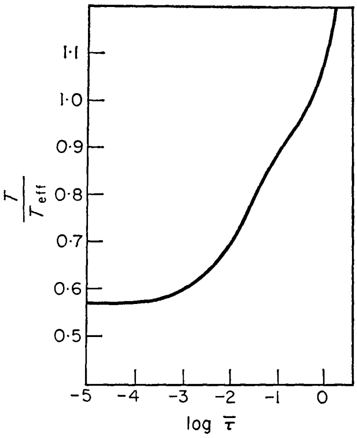

FIG. 3. *The relation between local temperature T and 'mean Rosseland' optical depth for an M star* (4, *Fig.* 8, *curve A*).

We can now estimate the local gas pressure P(dyne cm^{-2}) using the equatior of hydrostatic support:

$$\frac{dP}{d\bar{\tau}} = \frac{g}{\bar{\kappa}(T, P)}. \qquad (1$$

Here g is the surface gravity which is close to unity for the giant stars. From Tsuji's curves (**14**, Fig. 8) it would appear that $\bar{\kappa}$ is nearly independent of gas pressure fo $10^5 > P > 10^{-1}$. Under these conditions equation (1) integrates to give

$$P \cong \frac{g\bar{\tau}}{\bar{\kappa}}. \qquad (2$$

With $\bar{\kappa} \simeq 10^{-6}$, $\bar{\tau} \simeq 10^{-3}$, $g \simeq 1$ cm s^{-2} we have $P \simeq 10^3$ dyne cm^{-2}. Thus the ga density at the level of the atmosphere where $T \simeq 1800\,^\circ$K has not dropped by mor than a factor $\sim 10^2$ below its photospheric value. It is therefore reasonable t conclude that carbon saturation may occur over a considerable extent of the stella atmosphere.

A more realistic model of the stellar atmosphere would be desirable, whic takes into account the opacity due to solid particles as the condensation proceed

5. *Fraction of condensable carbon.* The equilibrium calculations may also b used to determine the fraction of carbon that could be condensed at any temperatu

below 1800°K. At $T \cong 1750$°K we set the partial pressure of free carbon equal to the vapour pressure of graphite, and re-solve the equilibrium equations omitting the constraint that the total amount of carbon in the gas phase is fixed. By subtracting all the C atoms which go into gaseous molecules from the given initial concentration of C we find that 5 per cent of the total carbon could remain condensed at this temperature, in the region of atmosphere where saturation is reached. If saturation occurs very close to the photosphere as in the late type Mira variables, the fraction of carbon in the *entire* atmosphere which could condense may be ~ 1 per cent. For α-Ori, where saturation occurs higher up in the atmosphere the fraction of carbon condensed may be $\sim 0{\cdot}1$ per cent. This low fraction which may be insufficient to produce strong optical effects suffices to provide the required mechanism for mass ejection in α-Ori (4).

6. *Concluding remarks.* Conditions for the nucleation and growth of graphite particles have been extensively discussed in relation to carbon star atmospheres (**15**), (**16**). At the densities appropriate to the M star case it may be estimated (**16**) that rapid exponential growth of condensation nuclei to thin flakes of radii $\sim 10^{-6}$ cm may take place in $\sim 3{\cdot}10^7$ s. For the carbon star atmosphere, it was further calculated (**15**), (**16**) that in order to maintain a formation rate of condensation nuclei $\sim 10^{-3}\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$ the required supersaturation ratio $P_\mathrm{C}/P_\mathrm{sat} \sim 2$. In the present case we have to condense ~ 5 per cent of the total carbon in a saturated region where the total hydrogen density is $\sim 10^{13}\,\mathrm{cm}^{-3}$. With the assumed C/H ratio $\sim 10^{-4}$, we thus require the condensation of $\sim 5 \times 10^7\,\mathrm{cm}^{-3}$ of carbon atoms into grains of radii 10^{-6} cm (containing $\sim 10^8$ atoms) within a typical pulsation period $\sim 3 \times 10^7$ s. This implies a nucleation rate of only $\sim 10^{-8}$. Since this rate is much less than what was required for the carbon star case we may conclude that the necessary supersaturation factor will be certainly less than 2. We would thus require a further drop in temperature by only a few degrees to accomplish the formation of grains.

We return finally to the close equality of the oxygen and carbon abundances which were obtained in Section 2. It is this remarkable feature that actually permits the condensation of graphite particles in the stellar atmosphere. It would appear unlikely that a nuclear reason exists for a O/C ratio very close to unity in M stars. On the other hand it appears more probable that an O/C ratio close to unity is maintained only in the stellar atmosphere, as a result of a process which selectively ejects more oxygen than carbon atoms. In this connection it may be relevant that most of the oxygen is in the form of H_2O (molecular weight 18), whereas the C is mostly in CO (molecular weight 28). On account of the very low surface gravity of the M stars it may well be that the lighter H_2O molecule evaporates faster than the heavier CO—resulting in a dimnution of the oxygen concentration. It is also probable, at any rate for the late M type stars, that radiation pressure on the H_2O molecule through infrared bands is more effective than on CO.

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