THE ASTROPHYSICAL JOURNAL, 350:L45–L48, 1990 February 20

THE FORMATION AND ANNEALING OF CIRCUMSTELLAR DUST, AS GAUGED BY *IRAS* LOW-RESOLUTION SPECTRA AND THE MICROWAVE MASER CHRONOLOGY

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Received 1989 October 13; accepted 1989 December 1

ABSTRACT

By comparing *IRAS* mean colors and LRS spectral differences in a large sample of Mira variables with the chronological sequence for development of microwave maser emission among such stars, it appears possible to describe a dust grain formation and annealing sequence. The early time spectra are dominated by aluminium oxides, which are then overrun by the emergence of silicates. Rather than the growth of silicate mantles on aluminate cores, we interpret this sequence as a simple result of the higher electron affinity of aluminum for oxygen, resulting in an initial abundance of AlO bonds in the underoxidized grains. Once all the Al becomes fully oxidized, the relative abundances of Al and Si dictate that the AlO signature will be swamped by the growth of the SiO stretching fundamental. The correlations among the proposed dust chronology, the increasingly thick circumstellar envelopes, and the light curve asymmetries of Mira variables are instructive for understanding the evolutionary changes occurring in such stars.

Subject headings: infrared: sources — interstellar: grains — masers — stars: circumstellar shells — stars: variables

I. INTRODUCTION

New data increasingly allow for understanding of the specific chemistry and dynamics of circumstellar dust. The *Infrared Astronomical Satellite* (*IRAS*: Neugebauer *et al.* 1984) provides colors and spectra for thousands of stars in late stages of their evolution, at times when mass-loss rates are large and significant compared to their nuclear time scales. One product of these new data is a recent study of 274 Mira variable stars by Little-Marenin and Little (1990, hereafter LML90) wherein six distinct classes of Miras were described. Similarly, radio astronomy has progressed sufficiently to allow Lewis (1989) to describe the chronological sequence for the development of SiO, H_2O, and OH masers in such stars. Finally, Onaka, deJong, and Willems (1989) have demonstrated a correlation among the asymmetry of the light curves of Mira variables, the amount of dust in the outflow, and the "appearance" of the 9.7 μm silicate feature. The purpose of this *Letter* is to draw an interesting connection between these results, a connection which has substantial implications for the formation, annealing, and outflow of newly formed circumstellar dust near Miras.

II. THE SEQUENCES

a) *Infrared*

As reported by LML90, the *IRAS* LRS spectra of 274 Mira variable stars can be divided into six groups, distinguished by shape of the 9–15 μm excess. See Figure 1. In addition to the featureless blackbody (no excess) and the 9.7 μm simple excess normally described as a "silicate" (Woolf and Ney 1969), the four other categories include (1) "Sil+," an asymmetric excess with primary and secondary maxima near 9.7 and 11 μm; (2) "Sil++," a broader asymmetric excess with nearly equal 10 and 11 μm maxima and a broad excess to longer wavelengths; (3) "3C," a broad, low-contrast excess with three more or less distinct maxima near 10, 11, and 13 μm; and (4) "Br," a broad, lower contrast excess with a poorly defined maximum between 11 and 13 μm. LML90 also noted the percentage of each class exhibiting certain microwave maser characteristics. We shall return to this point below. The significant aspect of these spectral groups is their mean [12]–[25] colors, defined as 1.56–2.5 log (f_{12}/f_{25}). Table 1 lists the mean properties.

Nuth and Hecht (1989) have proposed that the ratio of the flux in the region of the 10 μm silicate stretching fundamental, compared to the flux in the region of the 20 μm silicate bending fundamental, will decrease as grains "age." This proposal is based on numerous laboratory experiments in which simple silicate smokes were thermally annealed or underwent aqueous alteration. In each case, the ratio of 10 to 20 μm absorption by such smokes decreased as the processing increased. Listed in Table 1 are the 12/25 μm flux ratios which correspond to the mean colors of the LML90 LRS Miras. As can be seen, they monotonically decrease in the order Br, 3C, Sil++, Sil+, and Sil. This implies that the grains of Mira class "Br" are very young (nearly fresh condensates) and that the sequence 3C, Sil++, Sil+, and Sil represents increasingly processed grains, on average. The mean IR color reddens as the opacity increases. Hence, the dominant IR spectral signature from the shell is produced by even cooler, "older," and more processed

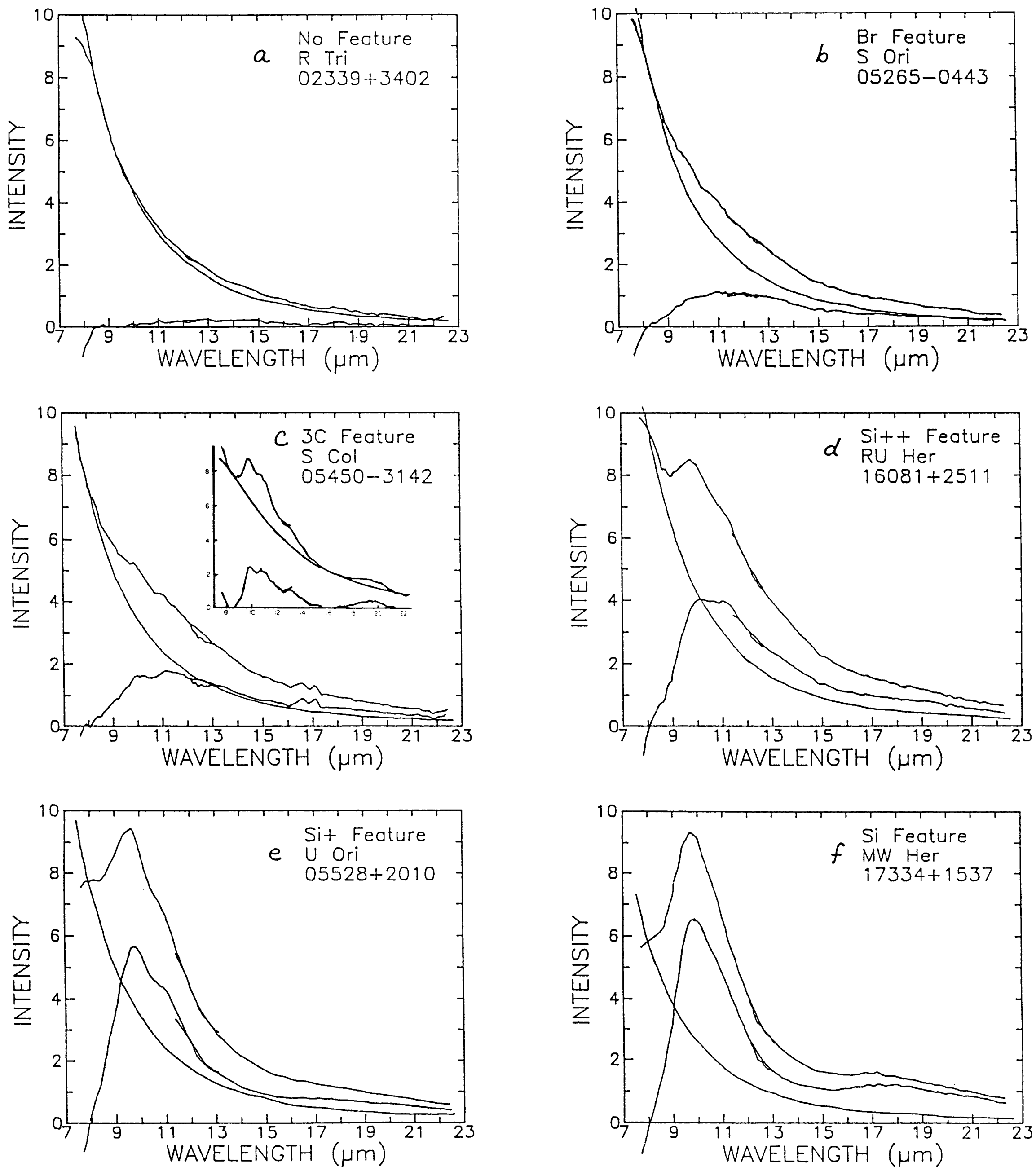

FIG. 1.—The six classes of LRS spectra of Miras, per LML90, arranged by increasing age and annealing of the dust. The three curves in each panel represent the LRS data as observed (*upper curve*), a smooth blackbody fit, and the difference (*lower curve*) which is due to the dust emission. The inset in panel *c* shows the three component features in the SRa variable W Hor.

dust as the shell thickens. We will discuss the detailed structure of the youngest grains, shortly.

Onaka, deJong, and Willems (1989) have shown, in a study of 109 Mira variables, that the amount of dust in the shells of Miras is inversely proportional to the asymmetry factor, f, in the light curves. This factor is defined by the ratio of the time from minimum to maximum light and the overall period. These authors have shown that the 9.7 μm silicate feature appears in Miras where $f < 0.44$ (asymmetric light curves), while γ alumina grains appear primarily in Miras with larger f (>0.44), the more symmetric light curves. The trend discussed by Onaka, deJong, and Willems can be seen clearly in the average f values listed in Table 1 for the various classes of emission features, ranging from 47 ± 4 for "Br" to 39 ± 4 for "Sil," paralleling the shift in the mean [12]–[25] color. Finally, these authors have shown that Mira sources in which the OH 1612 MHz maser emission is always observed have large silicate column densities. We will show in § IV that each of these observations is consistent with the chronology proposed in § III. Furthermore, the dust and maser chronologies indicate that the light curves of Mira variables become less symmetric as the stars increase their mass-loss rate. We will also argue that because the ratio of the 10/20 μm absorption bands changes as grains age, the inverse correlation of the Mira dust shell temperature with f, suggested by Onaka, deJong, and Willems, is uncertain.

TABLE 1

LML90 LRS Miras: [12]–[25] Color Median Values

Group	N	[12]–[25]	12/25	$\langle f \rangle$
Featureless blackbody	21	0.48 ± 0.06	2.70	46 ± 3
Broad feature (Br) (max 11–12 μm)	81	0.59 ± 0.11	2.44	47 ± 4
Three component (3c) (10, 11, 13 μm)	22	0.67 ± 0.16	2.27	42 ± 7
Sil++ (10 μm sil, strong 11.3 μm)	23	0.76 ± 0.14	2.09	43 ± 3
Sil+ (10 μm sil and 11.3 μm bump)	34	0.84 ± 0.21	1.94	39 ± 3
Sil (9.7 μm max)	93	0.87 ± 0.21	1.89	39 ± 4

b) *Microwave Masers*

Prior to the *IRAS* survey, it had already been recognized that SiO and H_2O maser sources were associated with optically identified stars, while the majority of 1612 MHz OH maser sources lacked optical associations. With the availability of the *IRAS* Point Source Catalog (PSC), it became possible to relate the observed maser characteristics with infrared colors and to place these in a sequence stretching from unreddened red giants to OH/IR stars and "planetary" nebulae. This chronological sequence of circumstellar masers has been proposed by Lewis (1989) who demonstrates that initially SiO, water, the OH main lines, and finally the 1612 MHz OH masers are added one by one as the circumstellar shell grows in thickness. Interferometric studies indicate a spatial relationship of the types of masers—SiO nearest the star, 1612 MHz OH most distant—that is consistent with this. The Lewis sequence is listed in Table 2.

Note that the chronology extends well beyond the Mira stages, into the so-called preplanetary and planetary nebula stages, where it is thought that the Mira has shed its envelope, but bearing no relationship whatever to planets. The [12]–[25] colors of these types of objects are much larger than any listed in Table 1, typically 1.5–2.5 (see Walker *et al.* 1989), corresponding to a 12/25 μm flux ratio of 1.1 to 0.42.

III. CORRELATION

As mentioned, LML90 also include mention of the percentage of each class of Miras exhibiting various types of microwave maser emission. Table 3 exhibits their numbers which we have ordered in terms of the Lewis chronology by comparing the relative detectability of each type of maser and assigning a "stage." There are unavoidable uncertainties concerning completeness and detectability. However, despite this normal limitation, the trends in the tables seem sufficiently compelling to merit the reader's further attention.

We assume, as does Lewis, that the OH masers are due to photoionization of H_2O by interstellar UV, and that this represents a relatively mature phase of the circumstellar envelope, namely, one that has been "filling up" and expanding for some time. Thus, stages 1–3 are in the order SiO, H_2O, OH. This suggests that the LRS sequence should be featureless, Br, 3C, Sil+, Sil. There is some ambiguity regarding the placement of the Sil++, due to the small number of masers observed for this group, either early (stage 2) or late (stage 7). All three Sil++ stars associated with OH masers show the main lines, but only one shows the 1612 MHz line. We thus favor stage 2 given the shape continuity between 3C and Sil+, along with its intermediate mean [12]–[25] values.

TABLE 2

Summary of Chronological Maser States

Stage	SiO	H_2O	OH(main)	OH(1612)	Notes
1	Y	N	N	N	
2	Y	Y	N	N	
3	Y	Y	Y	N	
4/5	Y	Y	Y	Y	
6	Y	Y	N	Y	
7	Y	N	N	Y	
8	N	N	N	Y	PPNs
9/10	N	N	Y	Y	
11	N	N	N	N	PNs

TABLE 3

Correlations of LRS Types and Masers: Percentage of Each Class Exhibiting Masers

LRS group	SiO	H_2O	OH	Stage
Featureless	60%	16%	8%	1
Br	62	43	13	2
3C	60	35	21	2–3
Sil++	67	18	23	2 or 7
Sil+	67	67	64	3/4/5
Sil	63	67	55	4/5/6

IV. DISCUSSION

Assuming the maser chronology is true, along with our ordering of LRS excess feature shapes, Table 3 implies a chemical processing sequence that begins with the development of a broad low-contrast feature which becomes three components, then two components, and finally dominated by the well-known, single 9.7 μm silicate feature.

Vardya, deJong, and Willems (1986) and Onaka, deJong, and Willems (1989) have argued that the appearance of a broad 12–13 μm feature in the LRS spectra of Mira variables with asymmetric light curves ($f < 0.44$) is due to absorption by alumina grains, and we agree with them on this point. However, we disagree with their assertion that this implies that alumina grains condense first, followed much later by the condensation of a silicate mantle around this alumina core. We argue instead that a better explanation can be found in an examination of the solid state chemical transformations which one would predict to occur following the condensation of a "chaotic silicate" (Nuth and Hecht 1989). Because a chaotic silicate forms rapidly from a supersaturated vapor containing metal atoms, SiO, AlO, and OH in a hydrogen atmosphere, Nuth and Hecht (1989) argued that the initial condensate will not be fully oxidized and that both aluminum and silicon will tend to reduce other metal oxides (e.g., FeO, Fe_2O_3, etc.) because both have a higher chemical reduction potential.

A comparison of the reduction potentials of Al and Si indicate that aluminum metal will reduce silica to produce aluminum oxide plus Si. In fact, this reaction was one method used to produce pure Si for laboratory experiments prior to the advent of the semiconductor industry and the need for large amounts of Si (Rochow 1973). In the interior of a chaotic silicate, where both Al and Si are less than fully oxidized and where oxygen itself might be scarce, the higher reduction potential of Al would initially act to produce AlO at the expense of SiO. Thus the stretching fundamental of solid (amorphous) AlO would initially grow at the expense of the 10 and 20 μm silica absorptions. However, after all available Al has become fully oxidized, either by reducing SiO to Si, or by reaction with O and H which has diffused into the grain, the Si and SiO components of the grain can begin to oxidize. This will increase the strength of the 10 μm silicate feature, and due to the fact that Si is roughly 10 times more abundant than Al, the 10 μm silicate absorption will eventually overwhelm the 12 μm alumina feature. As the Si oxidizes and polymerizes, the strength of the 20 μm bending fundamental grows faster than that of the 10 μm fundamental (Nuth and Hecht 1989) and the *IRAS* [12]–[25] colors, as defined above, should decrease as the grains are processed. The 3C, Sil++, and Sil+ features then represent intermediate stages between the alumina-dominated "Br" feature and the 9.7 μm silicate.

The conclusions of Onaka, deJong, and Willems are consistent with our model of increased grain processing for dust in older Miras. In particular, they show that the 1612 MHz OH maser occurs only in Miras with large silicate column densities: in the Lewis chronology, these are the oldest Miras and are thought to have the most silicate in their shells. Similarly, given that the broad alumina feature appears in stars with more symmetric light curves (average $f = 0.47$), this implies that the light curve of Miras apparently becomes increasingly asymmetric with age. This trend is demonstrated by the decrease of the average f values, from 47 (Br), to 42 (3C) and 43 (Sil++), to 39 (Sil+, Sil). This aging effect on the light curves is reinforced by the data of Onaka, deJong, and Willems which show that the mass of the shell is inversely proportional to the light curve asymmetry factor, f, and if we assume that Miras lose mass at a steadily increasing rate, the more massive shells will occur among the oldest stars.

Onaka, deJong, and Willems assumed that the optical properties of the grains which condensed in the outflow depend only on the composition, not on time, and thus assumed that once an alumina or magnesium silicate grain formed, its optical properties do not change. Nuth and Hecht, however, argue that this is not the case and that the absorption efficiency of circumstellar grains in the 20 μm region will increase relative to that at 10 μm. According to Onaka, deJong, and Willems, an increase in $Q_{abs}(20\ \mu m)$ relative to $Q_{abs}(10\ \mu m)$ of their model grains increases the temperature at the inner radius of the shell. They found that assuming constant optical properties for the silicate grains, the temperature of the grains at the inner radius of the dust shell decreases as f increases. However, we have shown above that the ratio of $Q_{abs}(20\ \mu m)/Q_{abs}(10\ \mu m)$ should be expected to increase as the grains age and f decreases. Thus an equally valid interpretation of this data might be that the temperature of the inner shell radius is nearly constant with f, but the change in optical properties of the dust changes the relative flux in the 10 and 20 μm regions.

V. CONCLUSIONS

1. We have shown that the maser chronology of Lewis (1989) is consistent with the assumption that the six categories of dust, as defined by the LRS spectra of Miras (Little-Marenin and Little 1990), are related in a specific age sequence, and also that the chronology is consistent with lab predictions by Nuth and Hecht (1989) that the ratio of 20/10 μm absorption strength increases as silicate grains age.
2. We have shown that if the age sequence implied by the LRS spectra is correct, then the light curves of Mira variables become more asymmetric with age.
3. We support the earlier conclusion of Vardya, deJong, and Willems (1986) that aluminum oxide is responsible for the broad 12–13 μm feature observed in the dust around young Miras.
4. We have shown that the sequence of spectra observed in Miras arises naturally as a consequence of the processing of freshly condensed chaotic silicates of cosmic composition.
5. Finally, 10 μm interferometric observations which suggest an "inner radius" of 10 stellar radii for the silicate dust shell and hence dust formation (Sutton *et al.* 1977) may have to be reconsidered if the bulk of the initial dust emission arises outside of the narrow 10 μm bandpass used in these studies.

We are delighted to acknowledge partial support of this work provided by NASA ADP grants JPL 957632 and NAG5-1214 to the University of Colorado. It is a pleasure to acknowledge exceptionally illuminating discussions with B. Murray Lewis.

REFERENCES

Lewis, B. M. 1989, *Ap. J.*, **338**, 234.
Little-Marenin, I., and Little, S. 1990, *A.J.*, submitted (LML90).
Neugebauer, G., *et al.* 1984, *Ap. J.*, **278**, L1.
Nuth, J., and Hecht, J. 1989, *Ap. Space Sci.*, in press.
Onaka, T., deJong, T., and Willems, F. 1989, *Astr. Ap.*, **218**, 169.
Rochow, E. G. 1973, in *Comprehensive Inorganic Chemistry*, Vol. **1**, ed. J. C. Bailar *et al.* (Elmsford, N.Y.: Pergamon), p. 1323.
Sutton, E., Storey, J., Betz, A., Townes, C., and Spears, D. 1977, *Ap. J. (Letters)*, **217**, L97.
Vardya, M., deJong, T., and Willems, F. 1986, *Ap. J. (Letters)*, **304**, L29.
Walker, H., Cohen, M., Volk, K., Wainscoat, R., and Schwartz, D. 1989, *A.J.*, in press.
Woolf, N., and Ney, E. 1969, *Ap. J. (Letters)*, **155**, L183.

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