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The chemical composition of luminous stars: Problems or opportunities?

ABSTRACT

The surface chemical composition of a luminous star changes as the star evolves. Spectroscopic definition of the changes may be used to test stellar evolutionary models. This essay discusses some of the observed and predicted changes in three different groups of luminous stars: hot massive stars, yellow supergiants, and luminous asymptotic giant branch stars.

INTRODUCTION

The atmosphere of a luminous star may be losing mass at a high rate, pulsating with attendant shock waves, greatly extended so that it can no longer be considered plane-parallel, so cool and tenuous that local thermodynamic equilibrium is a grossly inadequate assumption and ..... the list of deterrents could be continued. Is the list so terrifying that a stellar spectroscopist with a penchant for abundance analysis ought to retreat down the HR diagram and select less difficult stars? In this essay, I show that the luminous stars despite the evident problems do provide opportunities to apply knowledge of their atmospheric chemical compositions to important unsolved problems in stellar evolution and nucleosynthesis.

One may readily identify two broad reasons for obtaining accurate data on the compositions of luminous stars. The first reason exploits the stars' great luminosity: these stars may be used to establish many observational facts about the chemical evolution of our and other galaxies - one key item is the abundance gradient across our Galaxy from centre to edge. The second reason and the focus of this essay is that the composition is a tracer of the evolutionary history of a star and, of course, a prerequisite for detailed modeling of the stellar atmosphere and its wind or circumstellar shell.

On reflecting on the challenge implicit in the invitation to present this review, I decided to present a collage of abundance analyses for hot and cool massive luminous stars and for cool less massive luminous stars. Time and space finally dictated that my initial list for the collage be pared considerably. I elect to discuss three topics of current interest:

- the appearance of H-burning products at the surface of hot massive stars;
- the Na enrichment of the atmospheres of yellow supergiants;
- luminous asymptotic giant branch (AGB) stars and the dredge-up of material from the He-burning shell.

Each sketch alludes to at least one fundamental problem and highlights at least one valuable opportunity.

HOT MASSIVE STARS

Stellar evolution at the most simplistic level is the tussle between gravity's desire to engineer a collapse against the opposition fed by the energy released through nuclear reactions. If we are to understand fully this tussle, we surely need to analyse the changes of chemical composition effected by the nuclear reactions. Since the high temperatures required for nucleosynthesis exist only in the deep interior, the changes are not immediately observable at the surface. To render them observable, a star must experience either deep mixing by thermal convection or by rotationally induced currents, and/or severe mass loss by a wind or explosive ejection or, if the star belongs to a binary system, undergo mass transfer on a large scale to the companion star. Hot massive stars illustrate these opportunities for examining the products of nucleosynthesis and the processes that rendered them observable.

The Wolf-Rayet stars are stellar cores laid bare by severe radiation-driven winds: the WN stars have been stripped to the former H-burning shell where C and O were transmuted to N by the CNO-cycles, and the WC stars have been stripped to the former He-burning shell. I comment on less striking examples of stars with atmospheres enriched in material from a H-burning layer.

Of stars

The Of stars include the most massive stars in our and other galaxies: *e.g.*, the well-known O4f star ζ Pup has a mass M ~ 45 $M_\odot$. Quantitative spectroscopy of the photospheres and of the extensive winds that are fed from the photospheres has advanced remarkably - see the fine review by Kudritzki and Hummer (1990). Non-LTE analysis of the photospheric Balmer lines, He I and He II lines, yields the basic parameters T_{eff}, g, and the helium abundance. Most of the Galactic Of stars analysed to date have a 'normal' helium abundance y = n(He)/(n(H) + n(He)) = 0.09 where an uncertainty of ± 0.02 is quoted; unless I state otherwise abundances are taken from the above review or from Kudritzki (1991). Several stars including ζ Pup have He-rich photospheres; *e.g.*, y = 0.17 ± 0.03 (ζ Pup) and 0.20 ± 0.03 (HD 34656, O7IIf). The distinctive characteristic of the He-rich stars, which span the mass range (20-120 $M_\odot$) appears to be that they have evolved further from the zero age main sequence (ZAMS).

While there are now 'unified' models of the photosphere and wind with an impressive measure of self-consistency (*i.e.*, the wind is predicted given T_{eff} and g and is not added to the photosphere through a set of free parameters), there has not been the same unification of atmosphere and interior. Mass loss via the wind has apparently not stripped the star to its He-rich layer: the current mass loss rate for ζ Pup, which is 'only' $10^{-5.6}$ $M_\odot$ yr^{-1}, is predicted to have increased over the 10^6 yr spent evolving from the ZAMS, but that mass loss has removed no more than about 1 $M_\odot$ from the 45 $M_\odot$ star. Kudritzki (1991) supposes that the He enrichment is due to combinations of mass loss, convection, and rotationally induced mixing. Spectroscopy of Of stars is now challenging theoreticians interested in stellar interiors to acocunt quantitatively for the observed He enrichment.

OBN stars

Challenges persist to lower masses and luminosities. Spectral classification puts OBN and OBC stars close to the ZAMS. A non-LTE abundance analysis of four OBN and two normal OB stars has brilliantly confirmed long-held suspicions that the strengthening of N lines signalled a N overabundance caused by the mixing of CNO-cycled material into the photosphere (Schönberner *et al.* 1988). Table 1 gives abundances for θ Car (OBN), τ Sco (a very similar but normal B star), and the Sun: θ Car is very C- and slightly O-poor, and N and He-rich.

Table 1.

Quantity	θ Car	τ Sco	Sun
He/H	0.20	0.11	0.11
N/C	50	0.63	0.28
N/O	2.0	0.32	0.13
ΣCNO[a]	9.2	8.8	9.0

[a] $\Sigma CNO = \Sigma \log[n(X)/(n(H) + 4n(He))]$ for X = C, N, O.

The relative abundances of the catalysts C, N, and O reflects a basic property of the CNO-cycles: the CNcycle consumes H about 1200 times faster than the ON-cycle and, hence, one expects severe C depletion, but a modest O depletion, as observed. As often happens with the appearance of CNO-cycled products at a stellar surface, the nucleosynthetic origins of the contaminants are readily recognizable, but the means of transporting the products to the surface is an open question. This question applies to the OBN stars with the intriguing rider - why are so few selected for OBN membership? Schönberner *et al.* proposed that OBN progenitors were very rapidly rotating ZAMS stars in which severe rotationally-induced mixing kept them approximately chemically homogeneous with CNO-cycled products transported to the surface and with an evolutionary track in the HR-diagram that was intially to the left of the ZAMS. When rotational braking through a stellar wind was complete, the stars could no longer maintain a chemically homogeneous interior and the evolutionary track turned to the right and crossed the ZAMS. Then the fact that the OBN stars appear just to the right of the ZAMS is an accident; these stars are more highly evolved than appears at first sight. As for the Of stars, this proposal awaits quantitative confirmation. Other proposals - the OBN stars are evolving to the blue from the red supergiant region or are binaries in which severe mass transfer has occurred - also call for a more thorough observational scrutiny.

B Supergiants

There are indications that He enrichment may be common among the more evolved OB stars. Here, I draw on preliminary results given by the Munich group (Lennon *et al.* 1990) for the supergiants ε and κ Ori (B0Ia and B0.5Ia respectively) with $M \sim 40\ M_{\odot}$. Non-LTE analysis provided the results shown in Table 2. Lennon *et al.* give the abundance uncertainties as about ± 0.1 dex for elements represented by several lines: C and Mg are represented by one feature each and O by the most lines. Helium appears to be appreciably enriched in these supergiants, but curiously N is *underabundant* relative to the Sun, many B main sequence stars (*e.g.*, τ Sco), and the Orion nebula. Another odd result, one remarked upon by Lennon *et al.*, is the metal (Si,Mg) deficiency of ε and κ Ori. Lennon *et al.* comment that "the most likely explanation for this is that there is a systematic error in all the non-LTE calculations for the metal lines" and the error may be in the adopted model atom and/or in the model atmosphere (Lennon *et al.* suggest neglect of line blanketing as a possible cause).

Table 2.

Quantity[a]	κ Ori	ε Ori	Sun
He/H	0.25	0.25	0.11
log ε′(C)	-4.54	-4.16	-3.55
log ε′(N)	-4.44	-4.80	-4.10
log ε′(O)	-3.49	-3.81	-3.22
ΣCNO	-3.41	-3.62	-3.02
log ε′(Mg)	-4.80	-5.11	-4.57
log ε′(Si)	-4.84	-4.79	-4.60

[a] $\log \varepsilon'(X) = \log [n(X)/(n(H)+4n(He))]$

I would note here that the C II 4267 Å feature, the sole indicator of the C abundance in Lennon *et al.*'s analysis, offers an instructive reminder of the fallibility of non-LTE calculations. The first non-LTE analysis of the C^+ ion (Lennon 1983) found the non-LTE (and LTE) equivalent width of the 4267 Å feature to be much stronger than observed in OB stars. Recent non-LTE calculations (Eber and Butler 1988) used by Lennon *et al.* matched the observed equivalent widths for a roughly solar C abundance. Why did the 1983 NLTE study fail to predict even the sense of the change to the LTE equivalent width for the 4267 Å line? Eber and Butler remark "there is no simple explanation for the different results of the current calculations compared with those of Lennon.... It would seem that the increased complexity of our model atom, compared to that of Lennon, is responsible for the improved results". Lennon's model C^+ atom consisted of 14 levels. Eber and Butler include about 100 levels. This example is offered as a cautionary tale and is not necessarily a fair measure of the potential reliability of non-LTE abundance analyses. If the C abundance in B stars is the goal, it should be derived from some of the many other C II lines that are much less sensitive than the 4267 Å line to non-LTE effects.

Could it be that similar systematic errors remain in the N II and O II analyses so that the expected N-enrichment and possible O-deficiency are masked? Or is the He enrichment itself the result of a systematic error? Lennon *et al.*'s preliminary analysis shows, I suggest, apparent inconsistencies when the abundances are checked against our rational expectation that He and N enrichments must be correlated. Of course, there is at least one radical alternative: H II regions such as the Orion nebula and/or the stars that form from these gas clouds may have non-solar abundances. Certainly, there is a long record showing that Orion and other local H II regions are O-poor relative to the Sun. However, it is very difficult to imagine that this alternative can account for internal He-enrichment without substantial N-enrichment.

YELLOW SUPERGIANTS

Rho Cas and HR8752 are among the most luminous stars of spectral type F and G in the Galaxy. Their atmospheres are complex environments, as Jan Smolinski's review here makes quite clear - see also Sheffer and Lambert (1986, 1987). The complexity - the problem - is balanced by the prospect - the opportunity - that the yellow supergiant's atmosphere has had its chemical composition altered as a result of mixing and mass loss in preceding stages of evolution, *i.e.*, the O-B star and/or the red supergiant. Here, I comment on just one monitor of this mixing - the Na abundance.

Na enrichment in F-K supergiants

Boyarchuk and Lyubimkov (1985) presented a fairly comprehensive abundance analysis of ρ Cas. This LTE analysis using standard plane-parallel atmospheres uncovered a remarkable overabundance of Na that was attributed to a combination of operation of the NeNa cycle in the interior and mixing of the cycle products to the surface. Since the atmosphere of a star like ρ Cas is tenuous and relatively cool, non-LTE effects are a likely candidate for strengthening the Na lines and leading to a spurious Na overabundance in a LTE analysis. This suspicion was dismissed by Boyarchuk *et al.* (1988) who reanalysed Boyarchuk and Lyubimkov's Na I equivalent widths using a 19 level model Na atom: the Na abundance was decreased by only 0.17 dex and the non-LTE overabundance [Na/Fe] $\simeq$ +0.67 continued to point to synthesis of Na.

Drake (1991) has done an independent non-LTE calculation with a 47 level Na atom and confirmed that the corrections for non-LTE effects are small. Plez (1990) has shown that the derived Na abundance is affected only slightly ($\lesssim$ 0.05 dex) when the assumption of a plane-parallel layered atmosphere is replaced by the more realistic geometry of spherically symmetric layers. There may remain questions about the effects of inhomogeneities (granulation) and of the wind on the derived Na abundance. Boyarchuk and Lyubimkov included Ca I lines in their analysis. Since Ca and Na should respond similarly to these effects, the Na/Ca ratio may be a more reliable measure of Na overabundance than the Na/Fe ratio: [Na/Ca] $\simeq$ +0.9 from Boyarchuk and Lyubimkov's LTE analysis. Drake's analysis of less luminous stars show that this ratio is little changed when non-LTE analyses are substituted for the Na I and Ca I lines. In short, Na appears overabundant in ρ Cas.

Boyarchuk *et al.* (1988) collated Na abundances for 6 F supergiants to show that the Na overabundance increases with stellar mass from [Na/Fe] $\simeq$ +0.4 at M ~ 7 $M_\odot$ (α Car, α UMi) to +0.7 at M ~ 40 $M_\odot$ (ρ Cas). These are non-LTE estimates for Na; the corrections for departures from LTE are small. The LTE Na overabundances in these luminous supergiants are generally confirmed by other investigators: *e.g.*, Luck and Lambert (1985) give [Na/Fe] = +0.53 (α Car = Canopus), +0.57 (ι Car), +0.59 (α Lep), and +0.27 (α Per), and the several studies of Canopus are in good agreement: [Na/Fe] = +0.35 (Lyubimkov and Boyarchuk 1982), +0.41 (Desikachary and Hearnshaw 1982), +0.53 (Luck and Lambert 1985), and +0.42 (Spite, Spite, and François 1989. In general, the overabundance persists, if [Na/Ca] is taken to be a measure that is less sensitive to the adopted model atmosphere; however, [Na/Ca] = 0.12 (α Per) and +0.15 for Canopus (according to Spite *et al.* 1989).

Na overabundances have been reported for cooler supergiants (also, M ~ 10 $M_\odot$), and even for low mass giants. I comment here only on the supergiants. Luck (1977) found [Na/Fe] = +0.48 and [Na/Ca] = +0.39 in the mean for 14 G and K Ib supergiants - see also Luck (1978). (He also found Al to be overabundant: [Al/Fe] = +0.52 (Luck 1977). Note Spite *et al.* (1989) give [Al/Fe] = +0.23 for Canopus.) Wallerstein, Pilachowski, and Harris (1984) determined Na, Al, Si, Ca, and Fe abundances for the Cepheid variable X Cyg: the mean abundances over the 16 observed phases are [Na/Fe] = +0.22 and [Ca/Fe] = 0.00 (note: [Al/Fe] = +0.20). All of these estimates are from LTE analyses. Recently, Drake (1991) has obtained high S/N spectra of several Na I lines in 6 of the supergiants previously analysed by Luck (1977). A preliminary non-LTE analysis of the Na I, Ca I lines (see Drake and Smith [1991] for a description of the Ca model atom), Fe I, and Fe II (see Gigas [1986] for model atoms) gave the results summarized in Table 3: the [Na/Ca] ratios are reduced and, except for ε Gem and 1 Pup, Na is not measureably overabundant. The large Na overabundances found for the F supergiants are not a common feature of these cooler Ib supergiants.

Table 3.

Star	$\left[\frac{Fe}{H}\right]$	$\left[\frac{Ca}{Fe}\right]$	$\left[\frac{Na}{Fe}\right]$	$\left[\frac{Na}{Ca}\right]$	$\left[\frac{Na}{Ca}\right]^a$
μ Per	+0.1	+0.1	+0.1	0.0	+0.4
ξ Pup	+0.2	+0.3	+0.2	-0.1	+0.2
ε Gem	+0.3	+0.2	+0.5	+0.3	+0.7
η Per	+0.2	+0.2	+0.3	+0.1	+0.3
145 CMa	+0.1	+0.1	+0.3	+0.2	+0.4
1 Pup	0.0	0.0	+0.4	+0.4	+0.4

[a] Luck (1977)

There is, in principle, a straightforward explanation for the Na overabundance - see admirably clear discussions by Denisenkov and Ivanov (1987) and Denisenkov (1988, 1989). Temperatures in the central parts of the convective core of the OB progenitor are sufficiently high that Na is synthesized by proton capture from the more abundant ^{22}Ne: $^{22}Ne(p,\gamma)^{23}Na$. This is one step of the NeNa cycle invoked by Boyarchuk and Lyubimkov (1985), but the central temperatures during H-burning are too cool to drive the other reactions of the cycle and the Na that is produced is very largely preserved. The Na is confined to the convective core. When the star evolves to become a red supergiant, a deep convective envelope engulfs the outer layers of the (now dead) convective core and some of the synthesized Na is entrained within the convective envelope. Hence, the Na abundance of the envelope is increased. A red supergiant's convective envelope leads to other more well publicized changes of surface composition: *e.g.*, a reduction of the C/H abundance and the $^{12}C/^{13}C$ ratio and an increase of the N/H abundance. A Na overabundance is a natural accompaniment to these changes caused by the CNO-tricycle.

The predicted increase of Na depends primarily on two factors: (i) the degree of overlap between the OB star's convective core and the red supergiant's convective envelope, and (ii) the initial ^{22}Ne abundance. Other factors to be considered include convective overshoot and mass loss. Severe mass loss during H-burning reduces the H-rich envelope and enhances the surface enrichment produced by the convective envelope. Convective overshoot in the H-burning core results in a larger Na enrichment in the post-red supergiant. If the overshooting is very severe, the red supergiant does not evolve back to the blue and, hence, does not become a yellow supergiant. Since the F-type supergiants have the CNO abundances expected of post red supergiants (Luck and Lambert 1985), they have most probably evolved from the red and not directly from the blue and, hence, such severe overshooting may be ruled out. Convective overshooting has a negligible effect on the red giant's envelope and the dredge-up (Matraka, Wassermann, and Weigert 1982). Denisenkov (1989) shows that overshooting near the maximum allowed will increase the Na enrichment by only about 20% over the standard case. The predicted Na enrichment is insensitive to the reaction rate for $^{22}Ne(p,\gamma)^{23}Na$ because the generally adopted rate leads to the essentially complete destruction of ^{22}Ne before H is exhausted in the core.

Observations and predictions are compared in Figure 1. The former comprise [Na/Fe] for the F supergiants (ρ Cas, γ Cyg, α Car, and α UMi) as given by Boyarchuk *et al.* (1988) and the average [Na/Fe] and [Na/Ca] for the G-K Ibs in Table 3. Since Na and Ca respond more similarly than Na and Fe to changes/errors in the adopted model atmospheres, [Na/Ca] may be a more reliable monitor of the Na enrichment. Use of either Fe or Ca serves to minimize effects of differences in the overall metallicity and also changes in the H mass fraction of the atmosphere which are, however, predicted not to exceed 10%. Predicted Na enrichments taken from Denisenkov (1989) and Dearborn (1990) are in fair agreement.

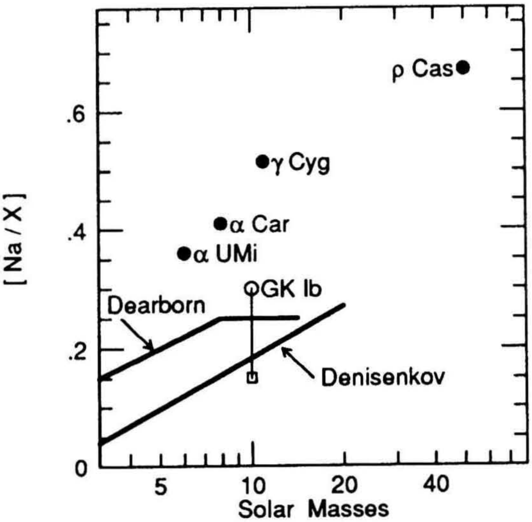

Fig. 1: Sodium overabundances in supergiants. For the F supergiants (filled circles), the reference element is Fe (≡ X). For G-K Ib supergiants in Table 3, the reference element is Fe (open circle) and Ca (open square). Two predictions for standard models are shown: Dearborn (1990) and Denisenkov (1989).

Inspection of Figure 1 shows that observation and prediction are in reasonable agreement for the G-K Ib stars. A firmer statement requires deeper understanding of the difference between [Na/Fe] and [Na/Ca]; note that the non-LTE abundance analysis is a preliminary one. Agreement between theory and observation does not extend to the F supergiants. This disagreement has been emphasized by Denisenkov and Ivanov (1987), and Denisenkov (1988,1989) whose preferred explanation is that the stars' initial ^{22}Ne abundance was about 3 times higher than is given in the standard compilations of 'solar' abundances (Cameron 1982, Anders and Ebihara 1982, Anders and Grevesse 1989).

The ^{22}Ne Abundance

Anders and Grevesse (AG) give the ^{22}Ne abundance as 2.34 x 10^5 on the usual meteoritic scale where Si = 10^6 and then the $^{22}Ne/^{23}Na$ ratio is 4.1. AG's ^{22}Ne abundance is based on an elemental abundance, log $\varepsilon(Ne) = 8.11 \pm 0.10$ where log $\varepsilon(H) = 12.0$. The isotopic ratio $^{20}Ne/^{22}Ne = 13.7$ is obtained from measurements of the solar wind. (^{21}Ne is a minor species.) The elemental Ne abundance is based on measurements of solar energetic particles (SEPs) and a correction of 0.65 dex (the FIP = first ionization potential effect) required to transform the SEP measurements of Ne to the photospheric Ne abundance. Meyer's (1989) thorough review of Ne, and particularly the Ne/O ratio, confirms that the local (Sun, B stars, H II regions) Ne abundance is close to AG's value. Meyer remarks that Simpson *et al.* (1986) used infra-red emission lines from the Orion nebula and obtained an unsually high Ne/O ratio, but Simpson *et al.*'s Ne abundance is log $\varepsilon(Ne) = 8.1$ (*i.e.*, AG's value) and they remark that their O abundance, log $\varepsilon(O) = 8.60$, is rather uncertain. In short, the Ne abundance for the yellow supergiants was most probably not as high as log $\varepsilon(Ne) \simeq 8.6$, which with the assumed ratio $^{20}Ne/^{22}Ne$ = 14, is needed to account for the enhanced Na abundances.

Denisenkov (1988,1989) pointed out that the $^{20}Ne/^{22}Ne$ ratio is lower in galactic cosmic rays (GCRs) than in the solar wind: $^{20}Ne/^{22}Ne \simeq 2.2$ is inferred for the GCR *source*, but the inferred source ratio $^{22}Ne/^{23}Na \simeq 5.0$ is within the uncertainties equal to AG's value (Webber *et al.* 1990). Since the GCR source abundances show a roughly solar-like FIP effect when compared with local solar/stellar abundances, the $^{22}Ne/^{23}Na$ ratio for the stellar(?) reservoir feeding the GCR source may have $^{22}Ne/^{23}Na \sim 5.0 \times 10^{0.65} \sim 22$, a ratio adequate to account for the observed Na overabundances.

Identification of this $^{22}Ne/^{23}Na$ ratio with the ratio initially present in the main sequence progenitors of the yellow supergiants demands another key assumption: the GCRs originate from stars that will evolve into yellow supergiants. If, on the other hand, the GCRs come from evolved stars such as the Wolf-Rayet stars, their abundances are *not* those that should be adopted for the interpretation of yellow supergiants. In particular, ^{22}Ne is expected to be overabundant at the surface of a Wolf-Rayet star containing material previously in the He-burning zones. Indeed, Silberberg and Tsao (1990) analyse GCR source abundances and claim that WC stars make the "predominant contribution" to the ^{22}Ne abundance. Then, the ^{22}Ne enrichment in the GCRs is irrelevant to the issue of Na in the yellow supergiants.

Direct measurement of the $^{20}Ne/^{22}Ne$ ratio in stars or nebulae will not be easy. High resolution spectra of Ne I lines in sharp-lined B stars such as τ Sco may just yield a detection of ^{22}Ne. Isotope shifts ^{20}Ne-^{22}Ne for Ne I lines at 6000-7000 Å are about 30 mÅ (Odintsov 1965)!

Na and other anomalies

If the Na abundances in the F supergiants cannot be ascribed to a high initial ^{22}Ne abundance, one must look elsewhere for an explanation. Among other abundance anomalies, I note the low $^{12}C/^{13}C$ ratios found for many G-K Ib supergiants (Tomkin, Luck, and Lambert 1976): $^{12}C/^{13}C \sim 20$ is predicted for a post-red supergiant, but $^{12}C/^{13}C < 10$ is frequently observed. Denisenkov and Ivanov (1987) pointed out that the $^{12}C/^{13}C$ and Na overabundances are roughly correlated. This correlation may not indicate a causal connection because at the high temperatures needed to synthesize Na, both ^{12}C and ^{13}C are destroyed and the surface $^{12}C/^{13}C$ ratio will be only slightly affected by greater mixing with material exposed to high temperatures - see Denisenkov (1989). One is hesitant to suggest that some Na synthesis has occurred through ^{22}Ne enrichment during

He-burning and a subsequent exposure to hot protons. This radical idea seems unlikely to account for the apparent Al overabundance in these supergiants. Clearly, more needs to be done at the telescope and in the office!

LUMINOUS AGB STARS

Thermal pulses and dredge-up

On the exhaustion He in the core, the giant of M(ZAMS) < 8 $M_\odot$ ascends the asymptotic giant branch. The core of primarily C and O is supported by degenerate electrons. The AGB star obtains its luminosity from a H-shell and a He-shell that are in close proximity to the C-O core. Such a double-shell source is unstable and experiences a series of 'thermal pulses' in which the He-shell is ignited and burns for a (relatively) short period, but is otherwise quiescent with all nuclear energy contributed by the H-burning shell near the base of the star's deep convective envelope. On ignition, the He-shell is predicted to be briefly convective before He-burning is confined to the base of the He-shell. H-burning stops when the He-shell has been ignited and, then, the H-rich deep convective envelope may extend into the top of the He shell which, when convection was occurring, was enriched in products of He-burning and associated reactions so that freshly synthesized products are mixed into the deep envelope and so into the observable atmosphere. This episode of mixing, which may be repeated each thermal pulse, is known as the third dredge-up. After He burning has progressed quiescently for a while, the He-shell ceases to generate nuclear energy and H-burning resumes. The third dredge-up ceases just prior to reignition of H-burning which continues for a (relatively) long time (the interpulse period) until the ashes of H-burning have increased the mass and the temperature in the He shell is raised to the ignition point when He burning recommenced such that convection covers most of the He-shell.

This cycling between H and He-burning may be repeated many times. He-burning increases the mass of the C-O core. The AGB's star luminosity increases with increasing core mass. The limiting luminosity ($M_{bol} \simeq -7.1$) is that corresponding to a C-O core having the Chandrasekhar mass of 1.4 $M_\odot$. If the AGB star attains this limiting mass, further evolution will result in a supernova. Mass loss prior to and especially on the AGB probably controls the relation between ZAMS mass and limiting luminosity as an AGB star.

Repeated applications of the third dredge-up are expected to convert the initially O-rich giant into a C-rich one. Iben's (1975) models of intermediate mass AGB stars (say 3-8 $M_\odot$) predicted that cool carbon stars would be found over a range of luminosities with $M_{bol} \simeq -7.1$ as a natural upper bound. Such a prediction, which cannot be easily tested using samples of Galactic carbon stars, was tested against a sample of carbon stars in the Magellanic Clouds - see Blanco, McCarthy, and Blanco (1980). Luminous carbon stars were *not* found: the mean $M_{bol} \simeq -4.8$ for carbon stars suggested that the progenitors of the carbon stars were low rather than intermediate mass stars (IM). The questions concerning low mass AGB stars that are raised by this suggestion are not discussed here, as my focus is on the luminous AGB stars that *may* be of intermediate mass.

Luminous AGB stars

The absence of luminous carbon stars provoked several hypotheses that attempted to reconcile the predictions and the observations:

• the luminous AGB stars do not exist because severe mass loss terminates AGB evolution.

• severe mass loss leads to a very dusty and, hence, opaque circumstellar shell that obscures the luminous carbon-rich star.

• luminous AGB stars in the interpulse phase develop a H-burning layer in direct contact with their deep convective envelope such that carbon added at each third dredge-up is converted to nitrogen and the atmosphere and envelope are maintained as O-rich. Such stars are said to possess a hot-bottomed convective envelope (HBCE).

On occasions, it would seem that the observational evidence on the very existence of AGB stars between the luminosities of the carbon stars and the limit $M_{bol} \simeq -7.1$ was not fully appreciated. There is now irrefutable evidence that the Magellanic Clouds have AGB stars extending up to $M_{bol} \simeq -7.1$ and that many (all?) of these stars are S stars, *i.e.*, O-rich and enriched in s-process products which are attributed to the He-burning shell. (It remains to be shown that the ^{12}C from the He-shell has been converted to ^{14}N to preserve the O-richness of the envelope.) The seminal paper on these S stars was written by Wood, Bessell, and Fox (1983, here WBF) who surveyed long-period variables (LPVs) in the Clouds and obtained low resolution spectra, bolometric magnitudes, and the periods.

Our spectroscopy of WBF's stars has been pursued at the Cerro-Tololo Inter-American Observatory with the cassegrain echelle spectrometer at the 4m telescope. I summarize here the key findings reported by Smith and Lambert (1989, 1990) and by Lambert (1991) who previews unpublished findings relating to the operation of the s-process in the Cloud and Galactic AGB stars.

At the spectral resolution (about 0.3 Å) provided by the CTIO spectrometer, we found it easy to confirm that stars identified by WBF as having enhanced ZrO bands are S stars: see Smith and Lambert (1989) for comparisons of Fe I and Zr I lines in Galactic M and S stars and two WBF stars from the SMC. The He-core burning supergiants, even those only just more luminous than the limit $M_{bol} \simeq -7.1$, show no s-process enrichments. This obvious difference between stars having almost identical atmospheres is proof that the S stars are s-process enriched. The s-process overabundances appear quite similar to those of Galactic S stars. Unquestionably, the third dredge-up has operated in these luminous AGB stars. It remains to be proven whether the third dredge-up continues to operate.

Lithium-rich AGB stars

Confirmation that WBF's luminous AGB stars were S stars did not come as a surprise. *The* surprise came at the telescope where immediate inspection showed that these S stars were Li-rich: the Li I 6707 Å resonance doublet was as strong as in the rare examples of Galactic Li-rich S stars such as T Sgr (Boesgaard 1970). Our survey suggests that *all* the LPVs in the Clouds with periods longer than 300 days and with $M_{bol} \simeq -6$ to -7 are Li-rich. Supergiants with $M_{bol} \gtrsim -7$ are not Li-rich. LPVs with $M_{bol} \gtrsim -6$ are not Li-rich; $M_{bol} \simeq -6$ is the upper luminosity limit for the cool carbon stars. However, few AGB stars fainter than $M_{bol} \approx -6$ have been observed to-date; giants with $M_{bol} > -6$ are faint for high-resolution spectroscopy with 4m telescopes. The presence in the Clouds of a class of red giants, all of which are Li-rich, stands in seemingly stark contrast with the rarity of Li-rich stars among magnitude-limited samples of Galactic S stars. We presume that Li-rich Galactic stars are also stars with $M_{bol} \simeq -6$ to -7 and the sample is dominated by less luminous stars. The inability to determine accurate luminosities for Galactic red giants is legion. This discovery of the identity of Li-rich giants in the Clouds shows once again the opportunities afforded us by these stellar systems.

Synthesis of Li in red giants has long been ascribed to 'the ^7Be transport mechanism' (Cameron and Fowler 1971): $^3He(\alpha,\gamma)^7Be(e^-,\nu)^7Li$ where the ^3He was synthesized through the initial steps of the pp-chain in the main sequence progenitor. The HBCE of a luminous red giant appears to have the appropriate conditions for the ^7Be-transport mechanism to operate efficiently (Scalo, Despain, and Ulrich 1975): the synthesized ^7Be and

^7Li must be swept quickly to low ($T < 3\ 10^6$ K) temperatures to avoid destruction by protons. Scalo *et al.* predicted that the threshold luminosity for appearance of a HBCE is $M_{bol} \simeq -5.4$, a limit in accord with our observations. A more precise comparison requires more physically consistent models computed for the non-solar compositions of the two Clouds.

With today's improved models of AGB stars and superior computers, it should be possible to marry the observations and the nucleosynthesis of Li to gain novel insights into the structure of a HBCE. The challenge is to synthesize ^7Li to the observed levels in the face of two possibly major constraints: the supply of ^3He is most probably fixed once the star evolves off the main sequence ($Z(^3He) \sim 10^{-3}$, Dearborn 1990), and, as the material in the envelope is circulated through the hot base, some of the existing ^7Li will be destroyed. Scalo *et al.*'s calculations showed that the ^7Li abundance in a HBCE increases initially, reaches a maximum and then declines as the ^3He supply is exhausted and the synthesized ^7Li is destroyed by protons at the base of the convective envelope. For envelopes of a constant base temperature T_b, the maximum ^7Li abundance was predicted to increase with T_b, but the time for retention of ^7Li is shortened as T_b increases. Furthermore, Scalo *et al.* pointed out that during a thermal pulse, T_b may drop so that synthesis of ^7Li is interrrupted, but not so low that destruction of ^7Li is inhibited. In short, it should be obvious that the surface (envelope) abundance of ^7Li is a senstive and complex indicator of conditions at the base of the envelope. This indicator deserves continued observational and theoretical attention.

The problem of ^7Li synthesis is worthy of pursuit. Our discovery that *all* luminous LPVs in the Clouds are Li-rich may be combined with some plausible assumptions to show that ejection of the Li-rich envelopes is possibly the major factor controlling the ^7Li enrichment of a galaxy from an initial value, $\log \varepsilon(Li) \simeq 2$ set by the Big Bang, to $\log \varepsilon(Li) \simeq 3$ in the case of our region of the Galaxy (Smith and Lambert 1990; Lambert 1990). If the evidence of substantial galactic enrichment of ^7Li by red giants can be strengthened, the red giants will provide an opportunity to define the nature of the Big Bang more closely.

Spectroscopic signatures of IM-AGB stars

A calculation of the yield of synthesized Li by luminous AGB stars is dependent on the masses assumed for the Li-rich stars and, in particular, on the masses assumed for the Li-rich convective envelopes that must shortly be shed. Of course, other factors, also quite uncertain, enter into the estimate of the yield. Initially, we supposed that these most luminous AGB stars must be the most massive expected by standard calculations, where 'standard' here implies 'no mass loss'. This supposition led us to identify the Li-rich stars as IM-AGB stars, say $M \sim (4\text{-}10)\ M_\odot$ with the higher masses being more representative.

Our prejudice for IM-AGB stars was set in part by the requirement that these luminous stars must have a high core mass and by WBF's mass estimates based on fits to the luminosity-period relation of these LPVs. On the assumption that the LPVs pulsate in their fundamental mode, WBF's calculations give $M_{AGB} \sim (4\text{-}10)\ M_\odot$ for the observed Li-rich stars, where M_{AGB} is the current mass and ($M_{ZAMS} - M_{AGB}$) is the (unknown) mass lost at all prior stages of evolution. New calculations (Wood 1990) suggest $M_{AGB} \sim (3\text{-}6)\ M_\odot$ for the majority of our sample. The core mass may be estimated from the luminosity (WBF): $M_{core} \sim (0.9\text{-}1.4)\ M_\odot$. Stars with $M_{ZAMS} \gtrsim 4\ M_\odot$ reach the AGB with $M_{core} > 0.9\ M_\odot$. Stars of lower M_{ZAMS} may reach $M_{core} > 0.9\ M_\odot$ during AGB evolution. (When WBF wrote their paper, it was disputed whether the LPVs pulsated in their fundamental (Willson 1982) or their first-overtone mode (Wood 1981). This controversy appears to have been resolved with Wood (1990) conceding that "the Mira variables are indeed fundamental mode pulsators". If the Cloud LPVs are first-overtone pulsators, pulsation theory gives $M_{AGB} \sim (2\text{-}6)\ M_{\odot}$ according to WBF, and apparently M_{AGB} would be reduced slightly with the new calculations reported by Wood (1990).)

Since $M_{ZAMS} > M_{AGB}$, we felt encouraged to identify the Li-rich stars with 'standard' IM-AGB stars. One of the marks distinguishing IM-AGB from LM-AGB models is that, in the former, the s-process in the convective He-shell of a thermal pulse is run by neutrons from the reaction $^{22}Ne(\alpha,n)^{25}Mg$, the ^{22}Ne neutron source. In standard IM-AGB models, the ^{22}Ne n-source is ignited if the core mass exceeds $M_{core} \simeq (0.9\text{-}1.0)\ M_{\odot}$ (Iben 1991). The Li-rich stars meet this condition. In standard LM-AGB models of low core mass $M_{core} \lesssim 0.9\ M_{\odot}$, the temperature in the He-shell is too low to ignite the ^{22}Ne n-source and neutrons are considered to be provided by the reaction $^{13}C(\alpha,n)^{16}O$. A second distinguishing mark is that the neutron density at the time of s-processing by the ^{22}Ne n-source is predicted to be so high in IM-AGB stars that the s-process abundances will differ from solar s-process abundances for nuclides affected by neutron-density sensitive branch points along the s-process path. Predictions of the neutron density achieved by the ^{13}C n-source are subject to greater uncertainties at present, but it certainly appears possible that the neutron densities may be as low as those needed to account for the solar abundances ($N(n) \sim 3 \times 10^{8}\ cm^{-3}$) - see Käppeler *et al.* (1990). One uncertainty is the ^{13}C mass fraction in the He-shell at ignition of the ^{13}C n-source. The equivalent uncertainty is largely absent for IM-AGB models because the ^{22}Ne abundance is set by the model's initial mass fraction of C, N, and O because this trio is processed to ^{14}N during H-burning and to ^{22}Ne via ^{18}O by α-capture prior to ignition of the ^{22}Ne n-source.

These two distinctive marks lead to observable differences in surface composition:

• Operation of the ^{22}Ne n-source has been predicted to lead to a non-solar mix of Mg isotopes in the atmosphere of an IM-AGB star (Truran and Iben 1977; Scalo 1978; Malaney 1987): *e.g.*, a star with $M_{core} = 1.2\ M_{\odot}$ and s-process elements enriched by a factor of 10 at the surface is predicted to have $^{24}Mg:^{25}Mg:^{26}Mg$ = 17:15:68 instead of the solar (initial) ratios of 79:10:11 (Malaney and Lambert 1988). Such a distortion of the isotopic Mg abundances may be searched for among lines of the MgH A-X system at 5000-6000 Å;

• Along the s-process path in the valley of stability, a competition occurs at a few relatively long-lived nuclei between decay and neutron capture. These nuclei serve as branch points in the s-process path. At each branch point, there is a critical value of the neutron density $N(n)_{cr}$: if $N(n) << N(n)_{cr}$, the nuclide at the branch decays but, if $N(n) >> N(n)_{cr}$, the unstable nuclide captures a neutron. Two branches are available for use with AGB stars: a branch at ^{85}Kr determines the abundance of Rb (= $^{85}Rb + ^{87}Rb$) relative to Sr and Y, and a branch at ^{95}Zr controls production of stable ^{96}Zr. Standard IM-AGB models predict that the atmospheres should have significantly higher Rb/Y and $^{96}Zr/Zr$ ratios than LM-AGB stars where the neutron density *may* be as low as that required to account for the solar abundances. The Li-rich Cloud stars are, on account of their known high luminosities, and, hence, their core masses, expected to ignite the ^{22}Ne n-source and, if they resemble standard models, should have the signatures of high Rb/Y and $^{96}Zr/Zr$ ratios. On the other hand, the luminosities of individual Galactic S stars are unknown and these spectroscopic signatures may be used to identify counterparts of the standard IM-AGB and LM-AGB models.

Our search for the distinctive marks of IM-AGB models among the Li-rich stars of the Clouds has only just begun. An earlier search of Galctic S stars and their relatives the Barium stars was unsuccessful at finding IM-AGB stars (Smith and Lambert 1984,1986; Tomkin and Lambert 1979,1983; Malaney and

Lambert 1988; Smith 1988; see also papers in preparation that are previewed in Lambert 1991).

The three tests (^{i}Mg, Rb, ^{96}Zr) could not always be made on every star; for example, some S stars and all Barium stars are too warm for the ZrO bandheads to be detectable. In many cases, 2 of the 3 tests were applied and gave a consistent result - the expected signatures of a standard IM-AGB model were not found. The Galactic sample contains few Li-rich stars. HR 8714 has a similar Rb/Y ratio to other S stars and T Sgr (a super Li-rich S star) shows no excess ^{96}Zr relative to similarly cool S stars. Both stars contain Tc and, hence, are thermally pulsing AGB stars. If the predicted high neutron densities of standard IM-AGB models are valid, the few Li-rich Galactic stars examined to-date may be declared to be LM-AGB or non-standard IM-AGB stars. At present, our preliminary analyses of the Li-rich AGB stars in the Clouds show no enhancement of their Rb abundance and no evidence for ^{96}Zr. We have been as yet unable to test these stars for excess aundances of ^{25}Mg and ^{26}Mg.

Although the limited sample size and the preliminary nature of some of the spectroscopic tests must be kept in mind, it would appear that Li-rich AGB stars are not well represented by standard models of IM-AGB stars. Observation and theory can possibly be reconciled by recognizing that mass loss may reduce the envelope masses such that conditions in the He-shell during a thermal pulse mimic those of a standard LM-AGB model. Certainly, there is evidence that the luminous AGB stars in the Clouds are losing mass at rates so high that many evolve early off the AGB; *e.g.*, the luminosity function of Hughes and Wood (1987) suggests that between $M_{bol} \sim -6$ and -7 stars are leaving the AGB due to mass loss. A similar or even earlier termination is likely for the more (relative to the Clouds) metal-rich Galactic IM-AGB stars. However, the rate of mass loss must, if the stars are otherwise standard IM-AGB (*i.e.*, $M_{bol} < -6.0$) stars, be so crafted that the core reaches $M_{core} \gtrsim 0.9\ M_{\odot}$ and sufficient thermal pulses and third dredge-ups occur to convert the M to a S star. Clearly, it would be of interest to investigate the nature of thermal pulses in stars with the degenerate cores of IM-AGB stars, but with envelopes of reduced mass: can a thermally pulsing AGB star achieve $M_{core} \gtrsim 1\ M_{\odot}$ and enrich its envelope in s-process elements by an order of magnitude without violating the observable constraints on the ^{25}Mg and ^{26}Mg, Rb, and ^{96}Zr abundances?

Perhaps we should not yet exclude the possibility that the apparent disagreement between models and observations may result from errors in the adopted nuclear reaction rates. Arnould (1991) reviewed the measurements of several key rates and, in particular, noted that Wolke *et al.*'s (1989) analysis of the ^{22}Ne(α,n)^{25}Mg rate gave "lower and upper limits on that rate that differ by as much as a factor of $\approx$ 1000 at the temperatures ($T \approx 3.5 \times 10^{8}$ K) that are generally considered as typical for the operation of ^{22}Ne(α,n)^{25}Mg." Arnould also notes that Wolke *et al.* claim that the competing ^{2}Ne(α,γ)^{26}Mg rate is faster than previously assumed. Iben (1991), recognizing the uncertainties discussed by Arnould, writes: "The actual cross section may be such that the ^{22}Ne source is not activated in any AGB stars; it could equally well be large enough that ^{22}Ne acts as a strong neutron source also in AGB stars with core masses much smaller than 1 $M_{\odot}$. Or, the standard rate may be correct. In any case, the results of Wood, Bessell, and Fox (1983) tell us that some neutron source is acting in real AGB stars with core masses larger than 1 $M_{\odot}$, and ^{22}Ne remains the most likely source." Recent measurements (Drotleff *et al.* 1991) of the ^{22}Ne(α,n)^{25}Mg rate at low energies confirm that the previously adopted rates (Caughlan *et al.* 1975) was essentially correct and may have been underestimated at $T \lesssim 0.5\ 10^{9}$ K. In short, the ^{22}Ne n-source probably operates as described by published standard IM-AGB models.

These models are built around an electron degenerate C-O core. Stars in the range $M \sim (8\text{-}10)\ M_{\odot}$ burn C in their cores before developing an electron degenerate O-Ne-Mg core (Nomoto 1984,1987). These very luminous AGB stars ($M_{core} \sim (1.1\text{-}1.43)\ M_{\odot}$) experience thermal pulses in the He shell, but detailed calculations of the pulses and dredge-up have not been published. Novae with large overabundances of O, Ne, and Mg in their ejecta attest to the existence of stars that leave behind their O-Ne-Mg cores as white dwarfs. Among the most luminous of the Cloud AGB stars may be some with O-Ne-Mg cores. Predictions of the s-process in the He shell and the synthesis by the HBCE are awaited with interest.

CONCLUDING REMARKS

This review of three different classes of stars near the Humphreys-Davidson limit is intended to show that the chemical compositions of luminous stars holds many of the keys to understanding their evolution. As I indicated at the beginning, the atmospheres of these stars are complicated and variable structures that present the quantitative spectroscopist with severe problems. Since the chemical compositions provide so many otherwise unavailable opportunities to probe stellar evolution of luminous and massive stars, we shall not be deterred from pursuing these fascinating stars. In the week before the Colloquium, I picked up Marianne Moore's *Collected Poems* and the book fell open at page 178 (Moore 1982) at a poem that encapsulated the determination not to be deterred by atmospheric intricacies:

I May, I Might, I Must

If you will tell me why the fen
appears impassable, I then
will tell you why I think that I
can get across it if I try.

Marianne Moore
1887-1972

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