The Chemical Composition of Stars

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Abstract

This essay discusses how recent and continuing advances in astronomical spectrometers are providing novel opportunities for stellar spectroscopists to address a wide variety of problems of stellar nucleosynthesis and evolution

1. *Introduction*

Thirty years ago, Bengt Strömgren (1958) delivered The Halley Lecture in the University Museum in Oxford on the topic "The Composition of Stars and their Ages". His lecture sketched the theoretical principles, observational practices, and his initial goals for that system of photoelectric narrow-band photometry now universally known as Strömgren photometry. As Professor Strömgren was enlightening his learned audience on May 27, 1958, I may have been nearby as my first delightful year as an undergraduate reading Physics at Oxford was coming to an end. Although my curiosity about astronomy and, in particular, about stellar evolution and nucleosynthesis, had been piqued a year earlier by reading Fred Hoyle's *Frontiers of Astronomy*, I did not attend Bengt Strömgren's Halley Lecture.

Here, as in my talk in Copenhagen at the Niels Bohr Institute, I shall attempt to convey the excitement that now envelopes pursuit of the determination and interpretation of the chemical composition of stars. Although, in contrast to Strömgren's Halley lecture, I shall concentrate on spectroscopic rather than photometric methods of attack, a common thread connects these two lectures given 30 years apart. Strömgren referred in his lecture to exploratory studies of his photometric system using the 36 and 82-inch reflectors of the W.J. McDonald Observatory in West Texas. Observations obtained at this observatory with the 82-inch and the 107-inch reflectors will illustrate several of my topics. Emphasis in my essay on spectroscopic methods and neglect of photometric methods of abundance determination reflects a personal enthusiasm but certainly not astrophysical myopia. There is a critical need for a thorough review of the intimate connections between spectroscopic and photometric methods of abundance determination; the common view that the former is the preferred and secure basis for calibrating the latter deserves to be challenged. Perhaps, another occasion can be found to elaborate on this theme that, I suspect, would have provoked original ideas and suggestions from Professor Strömgren.

My initial ruminations on the instructions to address questions of "Recent Progress and Future Possibilities" led me to isolate three major themes:

(i) Interesting and important astrophysical problems whose solution is dependent on accurate data on stellar chemical compositions.
(ii) The stellar spectra that are basic ingredients with which an abundance analysis commences.
(iii) The methods and associated tools of the abundance analysis that are applied to the stellar spectra and other observations (e.g. photometry) to obtain the abundances. The tools include model stellar atmospheres and a library of atomic and molecular data.

Today's exciting expansion of our knowledge of stellar chemical compositions is occurring in large part because substantial, often dramatic, advances are occurring in all of the fields spanned by the above three themes. Larger telescopes with more sensitive and versatile spectrometers provide high quality stellar spectra over broader spans of the electromagnetic spectrum. Concurrently, advances are occurring in the key components of abundance analysis: model stellar atmospheres, spectral line formation including thorough treatments of the departures from Local Thermodynamic Equilibrium (LTE), and the library of atomic and molecular theoretical and experimental data. This happy conjunction of high quality stellar spectra and refined analytical tools is providing the imaginative observer with novel opportunities to tackle outstanding unresolved astrophysical problems.

To set the stage, I conclude this introduction with a few brief remarks on each of my three major themes.

Astrophysical Problems. The truly challenging problems may be defined succinctly: what was the origin, structure, and evolution of the Universe, the galaxies (including our Galaxy), the stars, and the solar system? A stellar spectroscopist who gathers the appropriate measures of stellar chemical compositions may probe almost any aspect of this question. Specific topics that follow in this essay are primarily devoted to questions of stellar evolution and nucleosynthesis. As a reminder that the potential scope of inquiry is very broad, I draw attention to just one recent focus of great interest: the discovery by Spite and Spite (1982) that Population II dwarfs have a measureable lithium abundance, ($\log \varepsilon(\mathrm{Li}) \simeq 2$ on the usual scale where $\log \varepsilon(\mathrm{H}) = 12$), has led to a flurry of claims and counterclaims about the yield of lithium from the primordial fireball, the nature of the fireball and alternative cosmologies, and theoretical ideas on the ways in which the surface Li abundance of Population I and II stars may be modified with age and reassessments of schemes for ^{7}Li synthesis by stars. The Spites' discovery has also led to a revival of observational studies of lithium in stars. Current studies seek to delineate not only how stars destroy lithium but also how a few stars may synthesize lithium in copious amounts.

Stellar Spectra. Recent and continuing advances in the tools of the trade include more large telescopes, more efficient spectrometers, and expanded spectral coverage. Further advances including the European Southern Observatory's Very Large Telescope are imminent, at least to observers with the long-term visions of a Bengt Strömgren. Such advances translate to the following enhanced opportunities for the observer to extend or to initiate programmes involving:

- fainter stars
- large samples of stars
- higher resolution spectra
- access to a preferred wavelength interval
- higher signal-to-noise (S/N) spectra
- higher temporal resolution

Often, outstanding advances towards the solution of fundamental problems will call for combinations of these opportunities. In the main body of my essay, I endeavour to illustrate, through a variety of examples drawn from the recent literature and our own work at the McDonald Observatory, the potential of these opportunities.

Methods of Abundance Analysis. The raw ingredients are astronomical observations (stellar spectra and photometry), model stellar atmospheres, and basic atomic and molecular data. Today, these ingredients are whipped together in a suite of computer codes that represent an increasingly sophisticated representation of the physics of stellar atmospheres.

Since Dimitri Mihalas reviews model atmospheres elsewhere in this volume, I limit my remarks to noting that, in the context of "Recent Progress and Future Possibilities", serious exploration of atmosphere construction is commencing in which the basic assumptions previously adopted are being modified or discarded. The 'new' atmospheres are beginning to impact our studies of stellar chemical compositions. The basic assumptions to which I refer involve questions of geometry, LTE, and hydrostatic equilibrium. A brief selective discussion of how the basic assumption pertaining to geometry is being modified must suffice to convey the scope of 'future possibilities' in the field of model atmospheres. Several studies have now been reported in which the basic assumption of homogeneous plane-parallel, semi-infinite layers is modified. Atmospheres for luminous cool stars with thick atmospheres have been computed from the same basic assumptions except that the sphericity of the thick atmosphere is recognized (e.g. Bessell *et al.* 1989). The assumption of homogeneity has been discarded in a few exploratory studies; e.g., Nordlund's (1982) modelling of solar granulation through numerical solutions of the hydrodynamic and radiative transfer equations. Other exploratory discussions of inhomogeneity have drawn attention to thermal instabilities that may arise when abundant molecules such as CO and SiO in O-rich stars exert a major influence on the radiative equilibrium of a star's upper atmosphere. The extreme sensitivity of such molecular opacity to temperature can lead to a 'bifurcation' of the solutions that satisfy the condition of radiative equilibrium (Muchmore 1986); i.e., a 'hot' column can coexist with a 'cool' column. Theoretical exploration and empirical testing is just beginning for these and other modifications of the basic assumptions that are the foundation of the various grids of model atmospheres in wide use for abundance analyses.

In the following sections, I aim to illustrate through specific examples how rapid and startling progress is being made towards the solution of a variety of astrophysical problems. My emphasis is unashamedly on the recent improvements in the quality and diversity of observed stellar spectra.

2. *Stellar Spectra in the 1980s*

In the Introduction, I listed six enhancements of the opportunities now open to the stellar spectroscopist relative to the more limited opportunities available less than a generation ago when telescopes with apertures larger than 100 inches were available only to a select few and serious spectroscopy was restricted to a narrow spectral interval recorded on photographic plates. Here, I amplify the discussion of the enhanced opportunities.

2.1 *Exploration of the Magellanic Clouds*

Perhaps the most dramatic exploitation of these opportunities is presently being made through moderate to high-resolution spectroscopy of faint stars and especially those in the Magellanic Clouds, the Galaxy's globular clusters, and the distant parts of our Galaxy's disk and central bulge.

Spectroscopy and photometry of Magellanic Cloud field and cluster stars have in recent years provided a stream of new results about stellar evolution. My focus here is on the red giants that belong to the asymptotic giant branch (AGB). The most evolved of AGB stars are predicted to experience He-shell flashes followed by the possibility of a mixing of products from the He-burning shell into the deep convective envelope and, hence, the spectroscopically accessible atmosphere. The principal products are ^{12}C from He via the 3α-process and heavy elements (e.g. Sr and Ba) synthesized by successive neutron captures (the s-process) from abundant lighter 'seeds' such as the iron-peak elements. The neutron source is considered to be ^{22}Ne$(\alpha,n)^{25}$Mg in the most massive AGB stars (say $M \simeq 3 - 8M_\odot$) and ^{13}C $(\alpha,n)^{16}$O in the less massive stars. This mixing (or third dredge-up) converts O-rich M giants into S stars and finally into C-rich N-type giants. Since bright Galactic S and N stars exist in great numbers and their chemical compositions may be analysed in detail from high-resolution spectra, it might appear that the much fainter AGB stars of the Magellanic Clouds play nothing more than a supporting rôle in the testing of the theory of the AGB stars and the third dredge-up. In fact, the rôles of principal and supporting player are reversed because reliable estimates of absolute luminosity are obtainable for Cloud members but not for the bright Galactic AGB stars. In short, one 'knows' from their location in the H-R diagram whether candidate AGB stars in the Clouds are or are not AGB stars, and, a closer comparison with theoretical expectations provides estimates of the stellar masses. The best that one can do for the Galactic stars is to estimate their luminosity from statistical parallaxes; a very few stars may belong to open clusters. As an extreme reflection on the uncertain estimates of luminosity, I note that just 10 years ago two authorities speculated on an alternative explanation for the Galactic stars: "Perhaps the simplest explanation of S stars and of many N-type carbon stars is that the surface composition characteristics originate during a helium [core] flash of an infrequently occurring nature" (Iben and Truran 1978). Although the possibility of He core flashes of "an infrequently occurring nature" may be retained as an explanation for peculiar rare stars, surveys of the Clouds have uncovered the general pattern of evolution on the AGB and the place of the S and N stars in that pattern.

The observed pattern provided one early surprise. Predictions that dredge-up of ^{12}C and s-process was the sole prerogative of intermediate-mass AGB stars were first shaken and then shattered by surveys of cool carbon stars in the Magellanic Clouds. The luminosity function of C stars in the Clouds peaks at $M_{bol} \sim -4.8$ or $\log L/L_{\odot} \sim 3.8$ (Cohen *et al.* 1981; Richer 1981). Carbon stars are not found with $\log L/L_{\odot} > 4.3$ (Cohen *et al.* 1981; Wood, Bessell, and Fox 1983 hereafter WBF; Wood 1987); this luminosity was the predicted *lower* limit for carbon star production by intermediate mass stars. The observed luminosity range is consistent with an identification of cool carbon stars as thermally pulsing *low* mass AGB stars. Between the observed upper limit ($M_{bol} \sim -6$) for cool carbon stars and the maximum luminosity for an AGB star ($M_{bol} \sim -7.1$), a limit set when the degenerate core reaches the Chandrasekhar limit, the AGB stars in the Clouds are oxygen-rich. This sample defined first by WBF contains S stars. WBF speculate that H-burning at the base of the convective envelope may through the cycling of C to N reconvert the carbon-star to an oxygen-star heavily enriched in nitrogen. The H-burning necessary to accomplish this conversion of C to N is predicted to occur at the base of the deep convective envelope of the most luminous AGB stars (Iben 1973; Scalo, Despain and Ulrich 1975; Renzini and Voli 1981). Other explanations for "The Carbon Star Mystery: Why Do the Low Mass Ones Become Such and Where have the High Mass Ones Gone?" (Iben 1981) are reviewed by Iben (1989).

These and other conclusions about the evolution of AGB stars in the Clouds are founded almost entirely on low resolution spectra and photometry. That this was possible is due to the controlling rôle of the CO molecule in the dissociation equilibrium of carbon and oxygen with the result that spectra of cool stars with an abundance ratio C/O < 1 (oxygen-rich) are readily distinguishable at even low resolution from spectra of cool stars with C/O > 1 (carbon-rich). In addition, enrichment of cool oxygen-rich stars with s-process elements is detectable through a strengthening of bands of metal-oxides such as ZrO and YO; i.e., S stars can be distinguished from M stars without access to high resolution spectra. But to retrieve finer details of the chemical composition, high resolution spectra must be obtained and analysed.

High resolution spectroscopy is now being undertaken of Cloud AGB and other stars in the upper part of the H-R diagram including OB stars, F supergiants and AGB stars. One goal of such analyses is to define differences in the stellar and interstellar (i.e., H II region) abundances and to relate these differences (e.g. N enrichment of a star) to mixing and mass loss by the star. These analyses have assumed an especial significance with the explosion of Supernova 1987A. If that explosion occurred in a star evolving to the blue after a period as a red supergiant, the envelope would have been enriched in N and indeed, there is evidence for such enrichment. Examination of C, N, and O abundances in a sample of OB stars should reveal the frequency of N enrichment and, hence, an upper limit on the fraction of stars that are evolving to the blue. Since N enrichment of the surface may also result from extensive mass loss near the main sequence or by mass exchange in a binary, it may not be a simple matter to isolate the post-red giant stars from such imitators. Studies of F supergiants reported by Spite *et al.* (1989) and Russell and Bessell (1989) have focused on determining the abundances for a wide variety of elements that sample the major sites of stellar nucleosynthesis. Comparison of the abundances in the Small and Large Magellanic Clouds with those in the Galactic stars of the same metallicity is expected to yield clues to the chemical evolution of these three galaxies.

High resolution spectra of the AGB stars in the Clouds promise to provide answers to some obvious questions as well as surprises that raise additional questions. It is with a surprise that I close this section. Recently, we (Smith and Lambert 1989) obtained spectra of five AGB stars in the Small Cloud. The stars were taken from WBF's list of O-rich AGB stars that are more luminous than the carbon-rich AGB stars and were classified as S stars because ZrO bands were detected on low resolution spectra. Our spectra from 5470-7900 Å at a resolution $\lambda/\Delta\lambda \simeq 20{,}000$ were obtained with CTIO's 4m telescope, the Cassegrain echelle spectrometer and a GEC CCD detector.

Two key questions may be answered with our spectra:

(i) Are these luminous massive AGB stars enriched in the s-process elements as WBF supposed from the appearance of the ZrO bands?

(ii) Is there evidence in the compositions for the presence of a hot-bottom convective envelope (HBCE) that converts the freshly synthesized C dredged from the He-shell into N?

The answer to the first of these questions is unambiguous. In Figure 1, I show a strip of spectrum near 7555 Å for two SMC stars and the Galactic stars δ Vir (a normal M giant) and HD 35155 (a S star). Inspection of the spectra shows that the

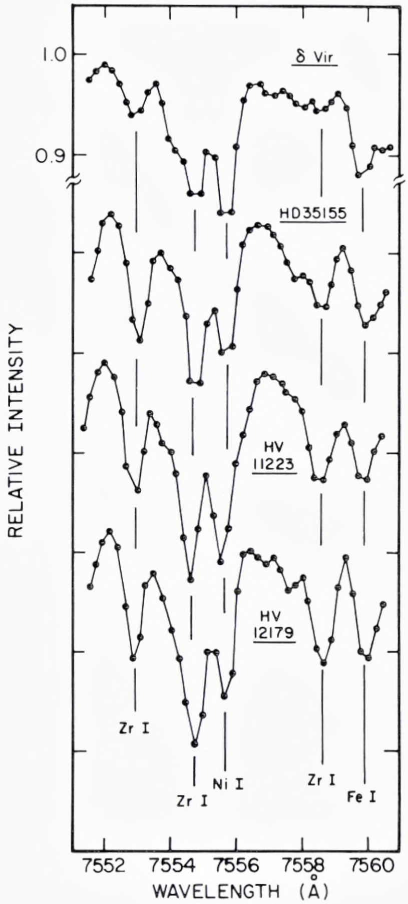

Fig. 1. Spectra showing the increased strengths of the Zr I lines in the SMC red giants relative to the normal-abundance red-giant δ Vir. The SMC giants are similar to the Galactic S-star HD 35155.

Zr I lines that are a monitor of the s-process products are enhanced (relative to δ Vir) in both SMC stars and the S star HD 35155. All 4 SMC stars show the s-process enhancements. Inspection of other wavelength intervals shows enhancements of other s-process elements. Since the enhanced equivalent widths of the s-process lines of the SMC and Galactic S stars are similar, we conclude that WBF's most massive AGB stars are enriched in the s-process, i.e., the predicted third dredge-up has occurred in these stars. Our abundance analysis confirms this conclusion.

Occurrence of the third dredge-up, as betrayed by the s-process enrichments, must add carbon to the envelopes of these stars. Indeed, these intermediate-mass stars were predicted by Iben (1975) in a series of pioneering calculations to evolve into carbon stars. However, as noted above, there are no luminous carbon stars in the clouds. Several obvious explanations have been advanced for their absence; e.g., evolution on the AGB is terminated by severe mass loss prior to transformation of the envelope from oxygen-rich to carbon-rich; severe mass loss shrouds a carbon-rich star in a thick graphite dust shell; a HBCE converts C to N to maintain an oxygen-rich envelope.

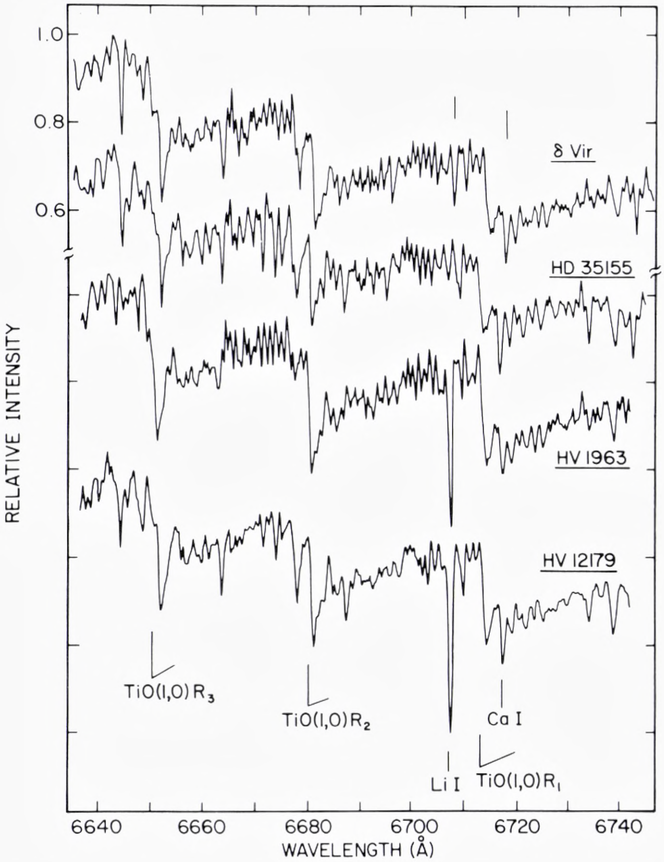

Fig. 2. Sample spectra illustrating the Li I resonance doublet. An entire echelle order is shown: note the very strong Li I feature in the SMC stars (HV 1963 and HV 12179) as compared to the two Galactic red giants. Note also that this region is blanketed by TiO absorption.

The presence of a HBCE may be signalled by the surprise provided by our spectra:

the great strength of the Li I resonance doublet at 6707 Å – see Figure 2 where it is shown that the Li I doublet is prominent in the SMC stars but very weak in δVir and HD 35155. Galactic counterparts of the Li-rich SMC stars are known but rare. The handful of Galactic examples have been gathered from surveys of two or more hundred cool giants. By contrast, each of the five SMC stars, a sample chosen randomly from the luminous AGB stars listed by WBF, is Li-rich with Li abundances within the range reported for the Galactic Li-rich stars, i.e., Li abundances of 10^2 to 10^4 higher than those found in normal red giants. In the latter, Li is diluted by a factor of about 50 below the abundance of the parental interstellar cloud. Reduction (destruction, diffusion, mass loss) of surface Li prior to evolution onto the first giant branch may have further reduced the Li abundance of some red giants. Lithium abundances are not yet available for SMC giants at a stage prior to the onset of thermally pulses on the AGB. Observations of the F and later type main sequence stars in which Li is expected to be seen are beyond the range of today's telescopes. A clue to the interstellar Li abundance in the LMC is provided by the upper limit, $\log \varepsilon(\mathrm{Li}) \lesssim 2$, derived from the nondetection of the Li I 6707 Å interstellar line in the near maximum spectrum of SN 1987A (Baade and Magain 1988; Sahu, Sahu and Pottasch 1989) – see, however, Malaney and Alcock (1989) who argue that a more realistic upper limit is $\log \varepsilon(\mathrm{Li}) < 3.6$. If $\log \varepsilon(\mathrm{Li}) \lesssim 2$ is appropriate for the SMC's interstellar gas, the Li abundances of the 5 SMC AGB stars range from about the primordial value to up to almost 100 times larger. Since, however, the reference Li abundance for the AGB stars should be the lower (diluted) value expected for the pre-AGB red giants (i.e. $\log\ (\mathrm{Li}) \lesssim 0.3$), the SMC AGB stars with $\log \varepsilon(\mathrm{Li} \simeq 2.2$-$3.8$ must surely have synthesized the Li now observed in their atmospheres. Synthesis of Li has been previously proposed to account for the rare ($\lesssim 1$ % of red giants, Scalo 1976) Li-rich Galactic giants. By contrast, Li appears to be enhanced in perhaps all of the most massive (4-8$M_\odot$) SMC AGB stars. We do not yet have spectra for less massive/luminous SMC AGB stars but we suspect that they will exhibit the low (diluted) Li expected for normal red giants. If this suspicion is confirmed, it will encourage the identification of the Galactic Li-rich giants as massive AGB stars. Their rarity is then a direct result of the bias of the Initial Mass Function toward low masses and the more rapid evolution of high mass stars along the AGB.

The possibility that ^{7}Li may be synthesized in red giants was recognized by Cameron and Fowler (1971) who proposed the "^{7}Be-transport mechanism" in which ^{7}Li is created via the sequence $^3\mathrm{He}\ (\alpha,\gamma)\ ^7\mathrm{Be}\ (e^-, \nu)\ ^7\mathrm{Li}$ in a convection zone where the ^{3}He is a product of prior H-burning and the ^{7}Li (and ^{7}Be) is transported by the convection to cooler layers of the red giant and so avoids destruction by protons. Luminous AGB stars are predicted to develop convective envelopes with high temperatures ($T_b \simeq 20$-60×10^6K) at their base where the ^{7}Be-transport mechanism and H-burning will occur. Theoretical studies suggest that, under certain conditions, ^{7}Li may be created and mixed to the surface of luminous AGB stars (Iben 1973;

Sackmann, Smith and Despain 1974; Scalo, Despain, and Ulrich 1975). Scalo *et al.* (1975) predict that a HBCE develops in AGB stars with $M_{bol} \lesssim -5.4$. Since our SMC stars have $M_{bol} \simeq -6$ to -7 and their Li abundances are within the (uncertain) range predicted by Scalo *et al.*, we associate the Li-rich SMC stars with the occurrence of a HBCE.

A part of the fascination for these massive AGB stars is their betrayal of the secrets of internal nucleosynthesis including the subtle mechanisms needed to synthesize and transport Li to the surface. Another reason for interest in these stars is their potential rôle as a leading producer of ^{7}Li within a galaxy. A firm calibration of the yield of ^{7}Li from Li-rich AGB stars may terminate the vigorous debate on the primordial ('big-bang') Li abundance in favour of the value observed in Galactic Pop. II dwarfs ($\log \varepsilon(\mathrm{Li}) \simeq 2$) rather than the value ($\log \varepsilon(\mathrm{Li}) \simeq 3$) seen in the youngest Pop. I stars.

Our observations suggest that the Li rich stars are massive AGB stars. Although our sample is small, the fact that all are enriched in Li suggests that all AGB stars in this mass range synthesize and retain substantial amounts of Li. Observations of less luminous AGB stars are needed to determine the lower mass limit for Li enrichment. With some simple assumptions, we may estimate whether mass loss from the Li-rich AGB stars results in a progressive enrichment of the interstellar ^{7}Li abundance. Let the Li-rich stars of mass 4 to $8 M_\odot$ have an abundance $\varepsilon(\mathrm{Li})_s$ and their ejected mass be equal to the inital stellar mass less about 1 $M_\odot$, the mass of the white dwarf remnant. The ejecta of lower mass stars are depleted in Li by a factor of about 50. If the initial mass function follows the form, $\phi(m) \propto m^{-2.35}$, interstellar Li will increase as long as

$$\varepsilon(\mathrm{Li})_s \gtrsim 5\varepsilon(\mathrm{Li})_0$$

where $\varepsilon(\mathrm{Li})_0$ is the prevailing interstellar abundance. Our results suggest that $\varepsilon(\mathrm{Li})_s$ satisfies this condition. Our identification of the most massive AGB stars as an important source of galactic ^{7}Li confirms Scalo's (1976) conclusion based on crude estimates of mass loss from Li-rich AGB stars.

The hypothesis that Li production is a consequence of a HBCE would seem to demand that the atmospheres of the Li-rich AGB stars contain the products of H-burning that must also occur at the base of the convective envelope; i.e., the atmospheres should be N-rich. Unlike Li that may be eventually destroyed throughout the convective envelope, the N enrichment is seemingly a permanent signature of a HBCE. Brett (1989) used low-resolution near-infrared and infrared spectra plus spectrum synthesis of molecular bands to estimate the C, N and O abundances of a sample of luminous SMC AGB stars that included two of our stars. He concluded that the stars are not as extremely N-rich as would be expected for a HBCE and that these AGB stars have experienced the third dredge-up but have not developed a HBCE. Analysis of CN lines in our spectra does suggest, however, that the N abundances in these SMC stars probably exceed both the C and O abundances, thus these red giants might actually be quite N rich. A full analysis of the CN lines requires knowledge of the C abundance, thus, a proper CNO analysis must await improved spectra of the infrared vibration-rotation CO bands. Since Scalo *et al.*'s (1975) calculations suggest that the timescale for ^{7}Li-production is significantly shorter than for ^{14}N production, the Li-rich stars may be identified as having just developed a HBCE and, if the HBCE is maintained for long enough, these stars may later develop a N-rich and Li-poor atmosphere.

This discussion of the composition of massive AGB stars in the SMC is but a beginning of detailed spectroscopic exploration of the AGB stars in the Clouds. Much can be done with existing equipment. A list of key questions to be answered at the telescope would surely include: Is Li production restricted to the most massive AGB stars? Are these stars maintained as O-rich by a HBCE that converts C into N? Is there spectroscopic evidence for the predicted neutron source – ^{22}Ne(α, n)^{25}Mg – in these stars? Did this source operate in the He-shell at the predicted neutron densities? Are there systematic differences between the s-process enrichments and abundance patterns in high and low mass AGB stars as the neutron source is expected to change from ^{22}Ne(α,n) ^{25}Mg to ^{13}C(α,n) ^{16}O? How do the abundance patterns change for S and N type stars (i.e., with metallicity) between the Galaxy, the LMC and the SMC? Do the cool supergiants with masses above the limit for AGB stars have the expected low (diluted primordial) Li abundance?

2.2 *Statistical Spectroscopy of Red Giants*

With today's telescopes, spectrometers and computing facilities, it is possible to execute observing programs that are designed to search large numbers of stars for extremely rare examples of an abundance anomaly. In this section I discuss two programs of 'statistical spectroscopy' completed recently at our McDonald Observatory.

2.2.1 *Lithium in G and K Giants*

Lithium is expected to be destroyed in all but the outermost layers (1-2 % by mass) of a main sequence star. On ascent of the red giant branch, a deepening convective envelope dilutes the remaining lithium and so reduces the surface (i.e. observable) lithium content by a large factor. G and K giants are expected to have a low lithium abundance. This expectation can be expressed quantitatively. Currently, the lithium abundances in the local interstellar gas and in those young stars believed to retain the primordial abundance is $\log \varepsilon(\mathrm{Li}) = 3.1 \pm 0.2$. Although the interpretation is not without its critics, the current Li abundance appears to have grown from the level $\log \varepsilon(\mathrm{Li}) = 2.0 \pm 0.2$ seen at the surfaces of unevolved Population II stars with $[\mathrm{Fe/H}] \leqslant -1$. A compilation of Li abundances in unevolved stars (Rebolo, Molaro, and Beckman 1988) suggests how the abundance may have grown with metallicity. This suggested trend describes the *maximum* Li abundance at the surface of a main sequence star. In general, the cooler stars exhibit significantly lower Li abundances.

Iben's (1967) models predict the dilution at the tip of the red giant branch to amount to a factor of between 60 at 3 $M_\odot$ to 28 at 1 $M_\odot$. Therefore red giants of near solar metallicity are expected to have Li abundances of $\log \varepsilon(\mathrm{Li}) \approx 1.3$ at 3 $M_\odot$ to ≈ 1.7 at 1 $M_\odot$, assuming that their main sequence progenitors retained the primordial lithium over the shallow layer predicted by standard Iben models. However, since many main sequence stars show significant lithium depletion, these predictions surely refer to the *maximum* expected in a red giant. In short lithium in red giants should not exceed an abundance $\log \varepsilon(\mathrm{Li}) = +1.5 \pm 0.2$ and a majority of giants are expected to show a Li abundance below this maximum value.

Wallerstein and Sneden's (1982) discovery of an apparently ordinary K-giant with a nearly cosmic Li abundance challenged the simple picture of Li destruction, depletion, and dilution: the giant HD 112127 (spectral type K2 III: CN+3) has a Li abundance $\log \varepsilon(\mathrm{Li}) = 3.0 \pm 0.2$. A detailed analysis of the spectrum of HD 112127 demonstrated that the spectral type assignment is accurate; the atmosphere parameters are those of a giant. Finally, the star evidently is a giant with a deep convective envelope because the ^{13}C content is enhanced ($^{12}\mathrm{C}/^{13}\mathrm{C} \approx 22$).

Stars as Li-rich as HD 112127 are extremely rare and all previously known examples have other striking abundance anomalies. Lithium abundances for the weak G-band G and K giants range up to the cosmic abundance of $\log \varepsilon(\mathrm{Li}) \simeq 3$ but their atmospheres are severely contaminated with the products of H-burning CN-cycling: i.e., $^{12}\mathrm{C}/^{13}\mathrm{C} \sim 3$, and a low ^{12}C with a high ^{14}N abundance such that ^{12}C plus ^{14}N is conserved. By contrast, HD 112127 has the ^{12}C, ^{13}C and ^{14}N abundances expected of normal giants on the first ascent of the giant branch. The Li-rich S and C stars discussed in the preceding section are much more highly evolved than giants like HD 112127.

The significance of HD 112127 to our picture of stellar evolution depends on the answer to the question: Is HD 112127 a very peculiar, even unique star or is it a representative of a rare subclass of G and K giants? To answer this question, we conducted a survey of the Li I 6707 Å doublet in 644 bright giants (Brown *et al.* 1989).

Our spectra were obtained with the coudé spectrograph of the 82-inch telescope at the McDonald Observatory. The Reticon detector recorded 95 Å around the Li I doublet at a resolution of 0.3 Å and a high S/N ratio (> 150). The Li abundance was extracted by spectrum synthesis.

The results of our survey are conveniently displayed as a histogram (Figure 3). All but a handful of the 644 giants have a Li abundance within the predicted range for giants having a deep convective envelope, i.e., $\log \varepsilon(\mathrm{Li}) \lesssim 1.5$. The lower histogram in Figure 3 is compiled from observations of main sequence stars. As expected, the two histograms are similar but that for the giants is displaced by a factor of about

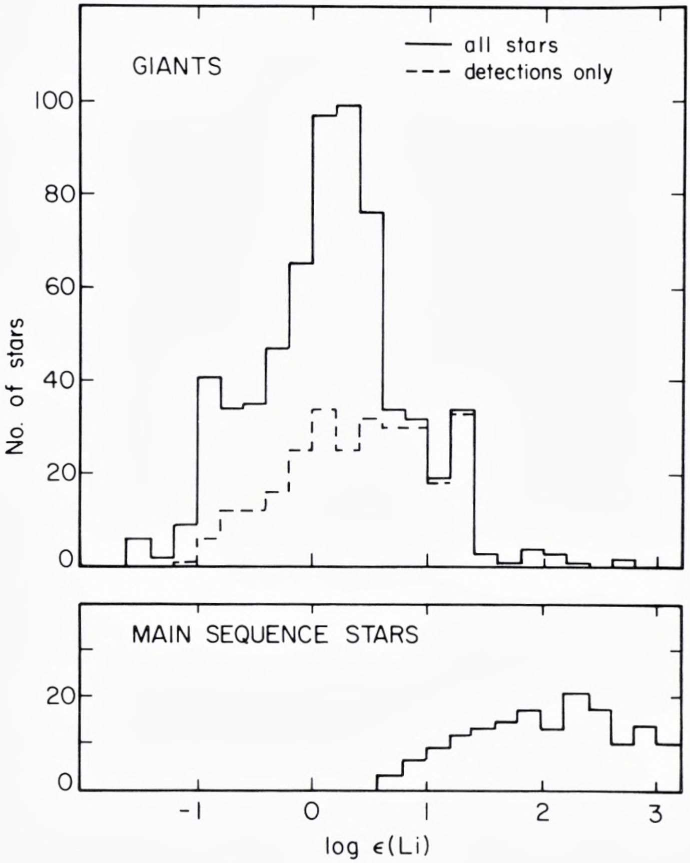

Fig. 3. Histograms of Li abundances for red giants (top panel – Brown *et al.* 1989) and main sequence stars (bottom panel – Boesgaard and Tripicco 1986 and Duncan 1981).

50 ($\triangle$ log ε(Li) $\simeq$ 1.7) to lower Li abundances. This factor represents the predicted dilution introduced by a giant's convective envelope. (Note: both histograms are partly shaped by selection effects.)

Ten of the 644 giants have a Li abundance greater than is predicted for a red giant. The ten stars are listed in Table 1 and plotted in an HR diagram in Figure 4. One star, HD 9746, resembles the prototype HD 112127 in having a near-cosmic Li abundance. An additional Li-rich (log ε(Li) = 2.8) giant HD 39583 is described by Gratton and D'Antona (1989). In searching for explanations for these peculiar stars, we dismiss temporarily the supergiant HD 205349 (No. 10 in Table 1) and the subgiant HD 126868 (No. 7). These latter stars may not yet have developed the

Table 1
Properties of the Strong Li Stars

Star	HD	log ε(Li)	[Fe/H]	log T_{eff}	M_{bol}
1	787	1.8	+0.07	3.63	−1.3
2	9746	2.7	−0.13	3.65	0.0
3	30834	1.8	−0.17	3.62	−1.4
4	108471	2.0	−0.02	3.70	−0.2
5	112127	2.7	+0.31	3.64	−0.2
6	120602	1.9	−0.07	3.70	−0.1
7	126868	2.3	−0.25	3.74	+1.8
8	148293	2.0	+0.23	3.67	+0.6
9	183492	2.0	+0.08	3.67	−0.2
10	205349	1.9	...	3.65	−5.2

convective envelope that dilutes the surface lithium. The supergiant is reminiscent of HR 8626 (Baird *et al.* 1975) and a few other stars.

The $^{12}C/^{13}C$ ratio is taken to be a monitor of a convective envelope. Our observations of CN red system lines show that both HD 9746 (No. 2) and HD 108471 (No. 4) have a $^{12}C/^{13}C$ ratio that is representative of normal giants possessing a convective envelope. This conclusion was reached earlier for HD 112127 (No. 5). Other stars on the list of ten have yet to be analysed for their $^{12}C/^{13}C$ ratio. It is conceivable that some of the remainder will prove to have retained their main-sequence ^{13}C abundance and, hence, be identifiable as giants at the base of the first giant branch with an incompletely developed convective envelope. The approximate locations for such giants with Li depleted by factors of 1.5 and 12 are shown on Figure 4. HD 120602 (No. 6), HD 148293 (No. 8) and HD 183492 (No. 9) are possibly normal giants with, as yet, a very shallow convective envelope. The more evolved stars HD 787 (No. 1) and HD 30834 (No. 3) appear to have an anomalously high Li abundance. Determinations of the $^{12}C/^{13}C$ ratios and C, N, and O abundances for the full set of 10 Li-rich giants will clarify their status. For the present, we reject only HD 126868 and 205349 and retain 8 of the 10 stars in Table 1 as peculiar Li-rich giants.

Convincing explanations for the preservation or production of Li do not exist. Several speculations may be worth noting for the observational tests they may stimulate:

(i) *Production at the He-core flash?* Six of the 8 peculiar stars are located near the clump containing He-core burning giants at the base of the AGB. The remaining 2 stars are plausibly identifiable as either evolved clump (i.e., early AGB) stars or younger giants on the first giant branch. Can Li be synthesized at the time of the He-

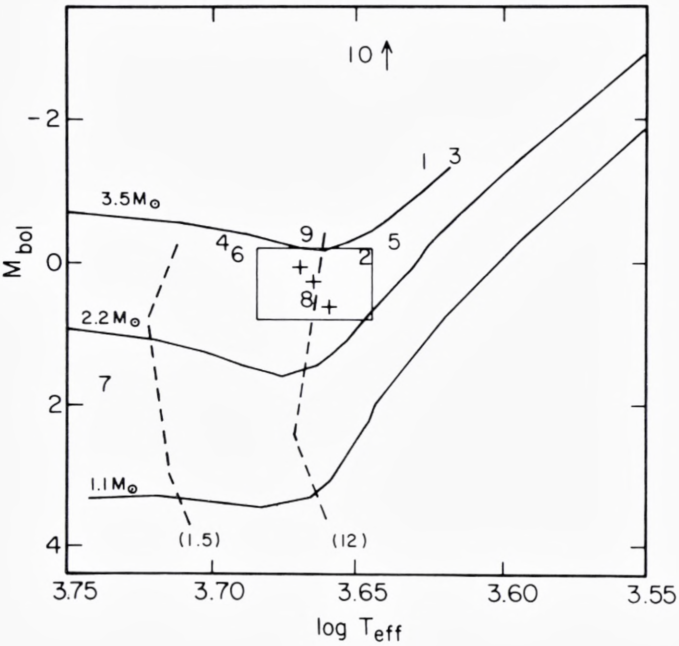

Fig. 4. A H-R diagram for the Li-rich red giants. The numbers identify the stars listed in Table 1. The box indicates the position of the He-core burning giants ('clump' giants). Crosses show the positions of the clump for 3 Galactic clusters, and the dashed lines are loci of constant Li depletions with the values of the depletion given in parenthesis.

core flash that initiates the He-core burning phase? The ^{7}Be-transport mechanism invoked for the AGB stars may be here working under different conditions.

(ii) *Preservation of Li through diffusion?* If much of a star's initial Li were to diffuse outwards, it may escape destruction by warm protons. Then, the giant's convective envelope would redistribute the Li to provide a Li-rich (relative to normal giants) envelope with an abundance in the range $1.5 \lesssim \log \varepsilon(\mathrm{Li}) \lesssim 3$. This is the process sketched by Lambert and Sawyer (1984) who noted that this diffusive process provided a natural explanation for the fact that the maximum Li abundance reported for weak G-band giants is a star's presumed initial or cosmic abundance. The same maximum applies apparently to the Li-rich G and K giants.

(iii) *Replenishment of Li by ingestion of major planets or brown dwarfs?* Alexander (1967) suggested that a giant could replenish its Li by ingesting surrounding planetary material. It is readily shown (Brown *et al.* 1989) that ingestion of terrestrial-like planets (i.e. no H or He) formed from a mass (initially including H and He) about equal to that of a red giant will restore the Li abundance to about the initial/cosmic value. Ingestion of a brown dwarf that has retained H and He has a smaller effect on the giant's Li abundance; Livio and Soker (1983, 1984) suggest that, if the mass of the brown dwarf (or terrestrial planet) exceeds about 1 percent of the giant's mass, the brown dwarf accretes a large fraction of the giant's envelope and becomes a low mass stellar companion to the giant's core.

(iv) *Li-rich giants have an active chromosphere?* There is a tantalising hint that some of these giants may possess an active chromosphere. The causal connection between Li and an active chromosphere is unclear. It could be simply that these stars possess large cool plages whose presence is ignored by standard model atmospheres. A careful examination of the abundances of elements having neutral atoms with low ionization potentials (Li, Na, K, Al, Rb) should uncover the existence of plages and result in a revision downwards of the Li abundance.

One goal of our survey was accomplished. HD 112127 is a rare but not a unique example of a G-K giant with a near cosmic Li abundance as its sole abundance anomaly. About 1 in a 100 G-K giants has an anomalously high Li abundance. A second goal proved elusive: the evolutionary origin of these Li-rich giants was left to speculation but some of the speculations are open to observational tests. For an observer, this is not an entirely unsatisfactory end – unemployment is postponed!

2.2.2 *The s-process in G and K Giants*

Barium stars were identified as a class of peculiar G-K giants by Bidelman and Keenan (1951) who noted the stars' enhanced atomic lines of heavy elements (e.g. Sr, Ba) and molecular lines of the C-containing molecules CH, CN and C_2. Overabundances of the heavy elements are now attributed to their synthesis by neutrons in the s-process in a He-burning layer that is also the site of the C enrichment. Thanks to the discovery by McClure and colleagues (McClure, Fletcher, and Nemec 1980; McClure 1985) that all Barium stars are spectroscopic binaries, the search for the origin of the stars shifted to scenarios involving binary rather than single stars. In particular, Barium stars appear to be created when an AGB S or C star transfers mass via the stellar wind or a Roche-lobe overflow to a companion that is converted to a Barium star with the core of the former AGB star remaining as a white dwarf. This hypothesis predicts that the compositions of AGB S and C stars and the Barium stars should be similar. This prediction is confirmed observationally (Lambert 1985, 1988).

Classical Barium stars for which the s-process elements are overabundant by a factor of 3 to 10 are readily identified on classification spectra. Mild Barium stars are not so easily identified and secure identification may require inspection of higher dispersion spectra. What is the frequency distribution for Barium stars of differing degrees of s-process enrichment? Can a single nucleosynthetic history account for all species of Barium stars? Before the mass-transfer hypothesis was identified, we suggested that the mild Barium stars might be quite normal giants whose parental clouds happened to be slightly more polluted with s-process elements than more typical clouds (Sneden, Lambert, and Pilachowski 1981). (This suggestion arose in part because the C abundances of mild Barium stars were very nearly normal but this is predicted on the mass-transfer hypothesis.) Is mass transfer across a binary the sole method for production of a Barium star? Perhaps, the He-core flash can trigger the running of the s-process. This flash was a leading suspect before McClure's discovery that Barium stars were spectroscopic binaries.

To investigate these and other questions, McWilliam (1988) undertook a survey of s-process elements in 570 G-K giants. Three 100 Å intervals were observed to provide a selection of s-process and iron-group lines that yielded abundance ratios s/Fe that are minimally dependent on the adopted effective temperature and surface gravity. In fact, the dominant error was, in general, provided by the uncertainties of the measured equivalent widths. Effects of systematic errors and particularly their variation across the HR diagram were minimized by examining stellar samples drawn from restricted regions of the diagram. In Figure 5, I show a series of labelled areas (A through G) whose combined area contains 70 % of the observed stars. Of the

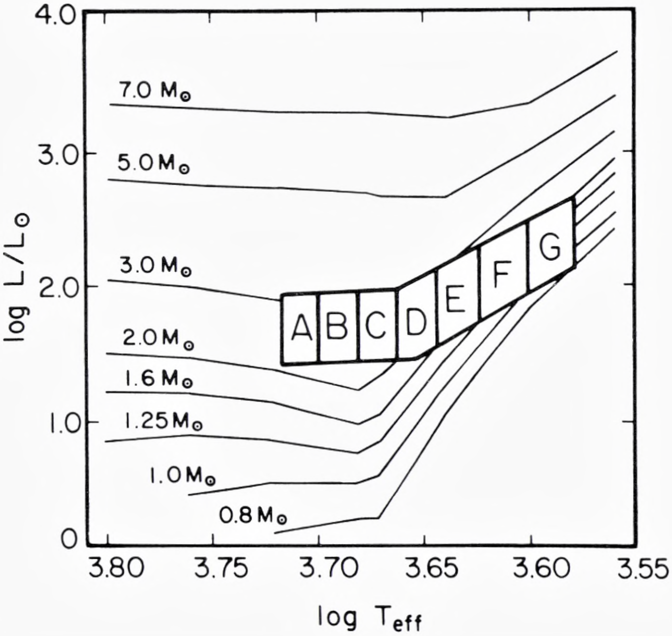

Fig. 5. A H-R diagram showing the subgroups A through G defined by McWilliam (1988).

other 30 %, approximately 60 % lie in the HR diagram at luminosities above that of the strip. My brief discussion is restricted to the Y/Ti abundance ratio of stars in the areas A-G.

Table 2
Abundance and other data for the groups A-G

Group	No. Stars	T_{eff}(K) Range	[Fe/H]	ε(Y)/ε(Ti)	Ba[b] Limit
A	35	5000-5200	-0.14 ± 0.14^a	-2.73 ± 0.12^a	-2.50
B	67	4800-5000	-0.16 ± 0.15	-2.73 ± 0.17	-2.50
C	74	4600-4800	-0.15 ± 0.14	-2.83 ± 0.13	-2.61
D	63	4400-4600	-0.09 ± 0.14	-2.86 ± 0.13	-2.65
E	55	4200-4400	-0.14 ± 0.16	-2.81 ± 0.19	-2.60
F	49	4000-4200	-0.14 ± 0.15	-2.85 ± 0.09	-2.65
G	52	3800-4000	-0.14 ± 0.12	-2.77 ± 0.11	-2.56

[a] 3σ estimate from the frequency distribution of abundances.

[b] See text.

Derived abundance ratios and other information for the 7 groups are summarized in Table 2. The frequency distributions for groups A+B, F, and G are shown in Figure 6. It is clear that the Y/Ti abundance ratios are similar across the groups. There is a hint that the groups A+B containing the hottest giants have a slightly higher mean Y/Ti ratio and a smaller dispersion. These differences are about equivalent to a 3 σ event. One may speculate that these differences are linked to the identification of the A+B stars as clump or He-core burning giants; i.e., the He-core flash that initiates He-core burning mixed s-process products into the giant's convective envelope. In offering this speculation as a hypothesis to be tested by additional observations, McWilliam (1988) notes several confirmatory hints.

First, the frequency distribution of the A+B group is slightly narrower than that of the cooler groups. Since the former is probably dominated by He-core giants and the latter groups are a mix of pre- and post-He core flash giants, the larger dispersion for the cooler stars could be the result of a superposition of two displaced distributions with the He-core flash inducing a s-process enrichment in post-He core flash giants.

Second, the Y/Ti abundance ratio of the subgiants is similar to that for the cooler groups that may contain a high proportion of pre-He core flash giants. For 41 stars with $4800\ K < T_{eff} < 5200\ K$ and $\log L/L_{\odot} < 1.30$ (this is about 0.3 dex below the minimum luminosity of a He-core burning giant), the mean $\log (\varepsilon(Y)/\varepsilon(Ti)) = -2.86$ which differs at about the 3σ level from the value (−2.73) for the A+B group.

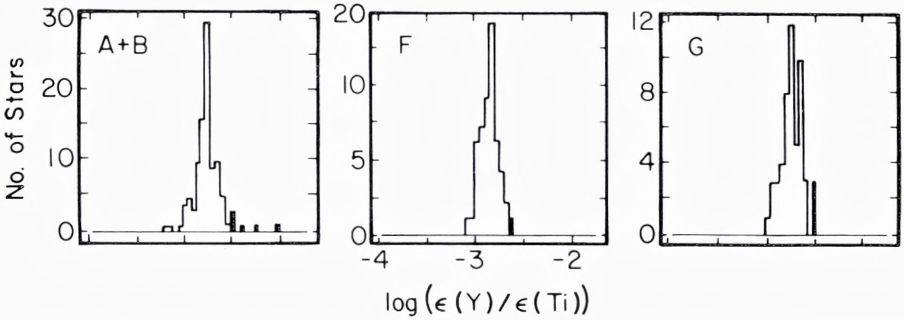

Fig. 6. Histograms of the Y/Ti abundance ratio for subgroups A+B, F, and G. The shaded portion of each histogram denotes the Barium stars that satisfy McWilliam's definition (see text).

Third, the frequency of Barium stars is higher in the A+B groups (see Figure 6). McWilliam defines a Barium star by applying a form of Chauvenet's criterion to the frequency distributions. A star is deemed a Barium star if the probability of the measurement of the Y/Ti ratio is greater than half the observed frequency of that measurement occurring by chance. The latter is calculated on the assumption that the frequency distribution is Gaussian with a dispersion derived from the distribution's width (FWHM); the lower limit to the abundance ratio for a star to be termed a Barium star is given in the far right-hand column of Table 2. These Barium stars are identified as the shaded portions in Figure 6. These Barium stars are predominantly mild Barium stars but the few classical Barium stars in the sample were extracted successfully. It is clear from the H-R diagram (Figure 7) that the Barium stars are concentrated to the area populated by the He-core burning or clump giants. Among the more luminous stars is the classical Barium supergiant ζ Cap. The frequency of Barium stars in McWilliam's sample of 568 giants and with his definition of a Barium star is 4.2 %.

As noted earlier, the mass-transfer hypothesis accounts satisfactorily for the classical and most probably a majority of the mild Barium stars. It is not yet clear whether all of the mildest of Barium stars uncovered by McWilliam's survey can yet be ascribed to mass transfer. McWilliam noted that a majority of his stars are reported to have a variable radial velocity by the *Bright Star Catalogue* and several are known as spectroscopic binaries. If, on close scrutiny, the vast majority are revealed to be spectroscopic binaries, they may be identified as products of mass-transfer across a binary system. If, however, a significant minority show no radial velocity variations to within a narrow limit, alternative hypotheses will need to be invoked; e.g. (i) contamination of the giant's envelope by s-process products at the time of the He-core flash; (ii) a 'cosmic' dispersion of the Y/Ti (equivalently, s/Fe) ratios in interstellar clouds as a result of their pollution by ejecta from evolved stars. A survey of elemental

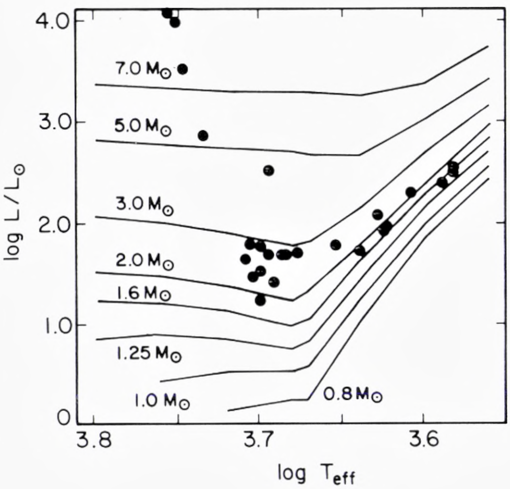

Fig. 7. A H-R diagram showing the locations of the Barium stars in McWilliam (1988).

abundances in a large sample of *single* main sequence stars would provide an estimate of the cosmic dispersion. Subgiant and even main sequence Barium stars are known (Bond 1974; Tomkin *et al.* 1989) and the majority are spectroscopic binaries (McClure 1985). An examination of a larger sample of subgiants (log L/L$_\odot$ $\lesssim$ 1.3) would also be instructive. If the He-core flash is the culprit creating mild Barium stars, the frequency of Barium stars among subgiants should be lower than is observed for group A+B.

2.3 *High-resolution Stellar Spectra*

Perhaps, the principal motivation for acquiring and analysing high-resolution stellar spectra is to detect elusive elements and isotopes whose lines, often weak, fall in crowded spectral regions or are blended with lines with more abundant isotopes. Other motivations exist and are certainly important: e.g., the measurement of intrinsic line profiles in order to characterize the atmospheric velocity field (microturbulence, macroturbulence, granular velocities, radial and non-radial pulsations).

2.3.1. *Thorium and the Age of the Disk*

Thorium is certainly an elusive element for the stellar spectroscopist. The Th II resonance line at 4019.1 Å is a weak line in the solar spectrum and blended with a Co I line. The solar Th abundance derived from the 4019 Å line is within 0.04 dex of the meteoritic value (Anders and Grevesse 1989). This agreement between solar and meteoritic Th abundances is expected and shows that the Th II contribution to the

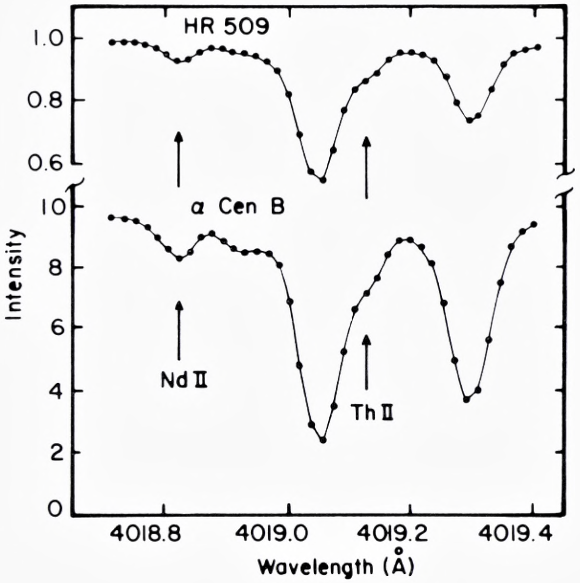

Fig. 8. High-resolution ($\lambda/\Delta\lambda \simeq 100{,}000$) spectra of two dwarfs in the region of the Th II 4019 Å resonance line (after Butcher 1987, 1988). The neighbouring Nd II line is identified.

solar line has been correctly assessed. (If the Co I line's contribution to the solar line is overlooked, the solar Th abundance is 0.10 dex larger than the meteoritic value).

Thorium is of a special interest because it represents a 'nuclear cosmochronometer'. The only isotope expected to be present in any but the most peculiar of stars is ^{232}Th with a half-life of 14 Gyr. Since Th is the only known nuclear cosmochronometer for material outside the solar system, accurate determinations of the Th abundance in stars are of great interest because they may lead to an estimate of the Galactic age that, unlike the fitting of colour-magnitude diagrams, is independent of stellar evolution theory.

Recently, Butcher (1987, 1988) obtained high-resolution ($\lambda/\Delta\lambda \simeq 100{,}000$) spectra near 4019 Å with ESO's fine Coudé Auxiliary Telescope and associated Coudé Echelle Spectrometer. Lower main-sequence disk stars of differing (stellar evolutionary) ages were observed. The blended Th II line is shown in Figure 8 for two dwarfs. It is clear that, without high resolution ($\lambda/\Delta\lambda \gtrsim 100{,}000$), the Th II (+ Co I) line would be irretrievably blended with neighbouring lines. Butcher's simple but probably adequate method of abundance analysis gave the Th/Nd abundance ratio. He chose Nd as the reference element because a low excitation Nd II line of comparable strength to the Th II line occurs only 0.3 Å to the blue (see Figure 8). The Th II and Nd II lines fall between the same "two excellent continuum windows". Conversion of the equivalent widths of these lines to a Th/Nd ratio should be insensitive to the continuum placement and to the adopted effective temperature and surface gravity of the stars. The striking result of this pioneering survey is that the Th/Nd ratios are independent of the stellar evolutionary age except perhaps for a slight increase beyond 15 Gyr.

If the Th cosmochronometer is to be exploited, a model of the rates of nucleosynthesis within the Galaxy must be adopted and its predictions fitted to the observed Th/Nd ratios. Thorium is synthesized by neutron capture in the r-process. In solar system material, the r-process is responsible for about half the Nd with the s-process providing the other half. On the assumption that Th and Nd have been synthesized at a constant rate, Butcher (1987) gave an upper limit to the Galactic (nucleosynthetic) age of about 10 Gyr. Clearly, this age is in conflict with the stellar evolutionary ages, but is consistent with the age for the disk, $T_0 = 9.3 \pm 2.0$ yr, derived from the observed luminosity function for white dwarfs (Winget *et al.* 1987). Clayton (1987, 1988) attempted to recognize that the yields of the r- and s-processes might vary differently with age (i.e., metallicity). For example, he considered a model in which the r-process abundances are primary and the s-process abundances are secondary with their relative yields adjusted to provide solar s/r ratio for Nd. This model fits the observed Th/Nd ratios using the stellar evolutionary ages. In a related approach, Mathews and Schramm (1988) conclude that "a model dependent (3σ) best upper limit of $T_0 \simeq 18$ Gyr to the age of the galaxy is derived". Butcher's (1988) riposte to these alternative models of the chemical evolution of heavy elements is direct: such models do not reproduce the observed constant ratio of Eu/Ba over the range in [Fe/H] spanned by disk stars. Eu is an almost pure r-process and Ba an almost pure s-process element.

Malaney and Fowler (1989) concoct a recipe for primary s-process production by AGB stars such that the r/s ratio of disk stars is constant. Their model of chemical evolution combines early spikes in the production of the r- and s-process elements with a subsequent period of nucleosynthesis in which the r/s ratio is maintained fixed. This model leads to "a relatively young age of $\lesssim$ 12 Gyr for the galaxy".

Two points about Malaney and Fowler's approach deserve comment: (i) this empirical approach to the observed r/s ratio yields a fair fit to the Eu/Ba observations. The galactic age is obtained by fitting predicted Th/Nd vs age relations to the observations after a simple scaling of the stellar evolutionary ages: $t = t_{ev}\, T_o/20$ where T_0 (in Gyr) is the galactic age and t_{ev} is the evolutionary age quoted by Butcher. However, if the evolutionary ages are indeed in error, it is not clear that this simple scaling will be an adequate correction. A slight stretching of the correction with age or metallicity could lead to a quite different T_0 in light of the fact that the predicted Eu/Ba and Th/Nd ratios vary little in the range 5 to 20 Gyr. (ii) Although both Eu and Th are assigned to the r-process, there is no unique prescription or even well established series of recipes for the r-process, and, hence, the relative yields of Eu and Th could vary from site to site and with galactic age. Without tighter observational constraints on the r-process yields, an even larger uncertainty must be attached to applications of the Th cosmochronometer.

(Butcher notes that his observation of a uniform Th/Nd ratio independent of a stellar age is consistent with the synthesis of all heavy elements in a 'spike' before the onset of star formation. This conclusion overlooks the fact that the abundances of the r- and s-process along with those of the lighter elements have increased by an order of magnitude since the formation of the disk. Continuing synthesis is required to account for this increase. If early synthesis of Th and Nd (and related heavy elements) is ascribed entirely to an initial "spike", the abundance ratio Th/Nd would be held constant, but their abundances relative to lighter elements (e.g., Fe) would decline in contrast to the observations).

Observers should be encouraged to pursue this unique cosmochronometer by extending the measurement of the Th II line to more metal-poor stars. Butcher's sample contained no stars with $[Fe/H] < -0.8$. Examination of Th in samples of old disk and halo stars would be informative because studies show that the r-process is the dominant source of heavy elements for $[Fe/H] \lesssim -2$ (Gilroy *et al.* 1988). An exhaustive search might reveal lines attributable to other very heavy elements whose abundance could constrain the r-process yield of Th. Finally, the prescriptions of chemical evolution must be refined by observations in order that Th may be a more accurate cosmochronometer. Thorium deserves a place on the list of the contributions from high-resolution spectroscopy to "Recent Progress on Future Possibilities" in stellar and galactic nucleosynthesis.

2.4 *Selection of Spectral Interval*

Of the several expanded opportunities now available to the observer, the ability to select the wavelength interval appropriate to a particular problem is of especial importance. In 1958, the stellar spectroscopist was constrained by the available photographic emulsions to the blue and red. Today, exploration beyond the red is made routinely with solid-state detectors: the near-infrared is accessible with CCDs and Reticons and a variety of detectors are in use for infrared (1-10μm) spectroscopy. Ultraviolet spectroscopy is now possible with the IUE satellite. Launch of the Hubble Space Telescope will greatly enhance the opportunities of ultraviolet stellar spectroscopy. In the area of 'future possibilities' for ground-based stellar spectroscopy, I would note the appearance of cryogenic echelle spectrometers with infrared array detectors as perhaps the most significant of the spectrometers now in development. One could devote an entire review to a discussion of how access to the entire (almost!) electromagnetic spectrum permits observational solutions to challenging problems in stellar physics. Here, I must confine my remarks to two topics: a search for meridional mixing in rapidly-rotating early-type stars, and detection of H- and He-burning products in the atmospheres of red giants. This pair of topics has one common feature: neither can be addressed through photographic spectra of the blue and red.

2.4.1 *Meridional mixing in rapidly-rotating early-type stars*

Do meridional currents within a rapidly rotating star mix the envelope and hot interior and, hence, change the chemical composition of the stellar atmosphere? Paczyński (1973) predicted that the surfaces of 3-10 $M_\odot$ stars rotating at typical velocities should be significantly deficient in ^{12}C and enriched in ^{14}N as a result of CN-cycling at the deepest points reached by the mixing currents. Oxygen was predicted not to decrease because the meridional currents did not extend to the deeper interior when ON-cycling operates.

In subsequent theoretical explorations, penetration of the currents was suggested to be so restricted by the gradient in mean molecular weight (μ) introduced by nuclear burning of hydrogen, that surface changes in ^{12}C and ^{14}N could be much less than suggested by Paczyński, who did not explicitly account for the inhibiting effects of the μ-gradient. Tassoul and Tassoul (1984) show that the partial penetration of the μ-gradient is possible and ought to lead to observable changes in the surface C and N abundances. Noting that predictions of the abundance changes are sensitive to "too many unknown parameters" (e.g. how does the interior rotate? Is the core rotating rapidly?), Tassoul and Tassoul concluded with a prophecy "one may thus look forward to the time when the surface abundances of C, N, and O will be used to probe the star's inner rotation and concomitant turbulent eddies."

This prophecy stands as a challenge to the observer. Until very recently, the only observational search for the predicted C deficiency appears to have been by Preston and Paczyński (1974) who measured the equivalent width of the C II 4267 Å doublet in B3 to B5 stars and found it and, hence, the carbon abundance to be independent of the projected rotational velocity (v sin i) over the range 20-300 km s^{-1}. Two recent searches for meridional mixing have exploited the enhanced opportunities listed in the Introduction. 'Selection of wavelength interval' is the key to these searches. In the rapidly rotating late-B and early-A stars, a search for a C-deficiency must exploit strong carbon lines falling either in the near-infrared (C I lines at 9000-11000 Å) or the ultraviolet (C II lines at 1335 Å, C I lines at 1657 Å).

Since the near-infrared C I lines become very shallow features in the most rapidly rotating stars, access to the near-infrared must be combined with high S/N in order to determine the C abundance in these stars. In our search (Lambert, McKinley, and Roby 1986), we obtained Reticon spectra of C I 9100 Å lines in 22 early-A stars main sequence stars with projected rotational velocities of up to 180 km s^{-1}. Although several C-deficient stars were found, the C abundance did not show the decline with increasing v sin i that might be expected from meridional mixing. Note that we selected early A stars because their longer main-sequence lifetime may enable the slow meridional currents to produce compositional changes more severe than those expected in the shorter-lived B stars.

Hardorp *et al.* (1986) and Cugier and Hardorp (1988) used IUE high-resolution spectra to derive C abundances for a sample of B3 to A0 main sequence stars with projected rotational velocities of up to about 300 km s^{-1}. The primary lines were the C II 1335 Å multiplet and the more recent results are based on a non-LTE analysis of carbon line formation. A majority of the stars have a near-solar C abundance with an interesting minority showing as severe a C deficiency as other examples reported by Lambert, McKinley and Roby (1986); e.g. ψ^2 Aqr (B5V, v sin i = 280 km s^{-1}) has log $\varepsilon(C) = 7.1 \pm 0.2$ or $[C/H] = -1.5$ relative to the Sun (Cugier and Hardorp 1988). It must be noted that the minority of the C-deficient stars are found over the entire range of projected rotational velocities. Most rapidly rotating (i.e. high v sin i) stars have a normal C abundance.

Two possible origins for the C-poor stars may be suggested as the basis for additional spectroscopic tests:

(i) *Meridional Mixing.* A naive view is that the efficiency of the meridional mixing currents in mixing CN-cycled material to the surface is fully determined by the star's mass, age, and rotational velocity. Then, the C deficiency is expected to increase with increasing projected rotational velocity: the upper envelope to the $\varepsilon(C)$ –vsin i distribution should be well defined with lowest $\varepsilon(C)$ at highest vsin i. Rapidly rotating stars seen pole-on will show a low vsin i and a low C abundance. This simple picture is not supported by the observations. It could be that the "too many unknown parameters" sketched by Tassoul and Tassoul (1984) are effective in controlling the meridional mixing and, hence, the lower surface C abundances may not show a simple correlation with the observed vsin i. One helpful test would be to measure the N abundance in the C-poor (and other) stars. If deep mixing has led to the C-deficiency, the surface must now be enriched in N. Of course, the deep mixing need not necessarily be the exclusive consequence of meridional mixing. Hardorp *et al.* (1986) intimate that at least some of the C-poor stars are not N-rich relative to normal stars of the same type; the ultraviolet N I lines are not strengthened in these stars.

(ii) *Chemically Peculiar Rapidly-rotating Stars.* Chemically peculiar (CP) stars are known to include stars having substantial C-deficiencies (Roby 1987; Roby and Lambert 1990). Since the distinctive lines by which CP stars are classified are very shallow in spectra of stars having a large vsin i, one may suspect that some CP broad-lined stars have gone undetected; e.g. the Hg II and Mn II lines that define the Ap (HgMn) class may escape detection at classification dispersions when vsin i $\gtrsim$ 100 km s^{-1} (Preston 1974). If the C-poor stars identified in the recent surveys are CP stars, high S/N spectra should now be capable of detecting the various trademarks of Bp, Ap and Am stars. Indeed, a survey of rapidly rotating A and B stars for evidence of chemical peculiarities could provide a valuable database for testing theories on the origins of CP stars.

2.4.2 *Red Giants and Dredge-Up*

To the spectroscopist fascinated by the coolest red giants, the infrared is of critical interest because

(i) these giants emit most of their flux in the infrared, and

(ii) the infrared contains the molecular transitions (Table 3) that provide the C, N, and O elemental and isotopic abundances that are key monitors of the dredge-up from H and He burning shells.

Table 3
Indicators of CNO Abundances in Red Giants

Spectral Type	Primary Lines[a]	Secondary Lines[a]	Refs.[b]
G and K	*C_2 Swan $\Delta v=0,-1$	*CH A-X $\Delta v=0,-1$	LR,K,G
	*Cn Red $\Delta v=4$ to 2	CN Red $\Delta v=-1,-2$	
	*[OI] 6300 and 6363 Å	*CN Violet $\Delta v=0,-1$	
		CO V-R $\Delta v=3$	
		OH V-R $\Delta v=2$	
M,MS,S	CO V-R $\Delta v=3,2$	H_2O V-R	SL
	OH V-R $\Delta v=2,1$		
	NH V-R $\Delta v=1$		
	CN Red $\Delta v=-2$		
SC,C	CO V-R $\Delta v=3,2$	C_2 Ballik-Ramsay	DWS
	*C_2 Phillips $\Delta v=3,2,1$	*CN Red $\Delta v\geqslant 0$	
	C_2 Phillips $\Delta v=-2$	CH V-R $\Delta v=1$	LGEH
	CN Red $\Delta v=-2$	NH V-R $\Delta v=1$	
		HCN V-R $\Delta v=1$	

[a] Unless marked by an asterisk the indicated lines are in the infrared ($\lambda \gtrsim$ 1.3 μm).

[b] DWS = Dominy, Wallerstein, and Suntzeff (1986)
LGEH = Lambert *et al.* (1986)
SL = Smith and Lambert (1985, 1986, 1990)
G = Gratton (1985)
K = Kjærgaard *et al.* (1982)
LR = Lambert and Ries (1981)

In the determination of C, N, O abundances in the warmer (G and K) red giants, a few atomic transitions provide useful data and the visible and near-infrared provides an adequate set of molecular transitions – see the references given with Table 3. For the cooler red giants, the atomic lines are unuseable because molecular formation depletes the partial pressure of the atoms and the weakened atomic lines fall in regions of intense molecular absorption. Since the useful lines of the various molecules containing C, N, and O are in the infrared, spectra in that region are an essential prerequisite for a C, N, and O analysis. Recent papers on the oxygen and carbon rich cool red giants (see Table 3) show how high resolution infrared spectra, model atmospheres, and a suite of basic molecular data are combined to yield the C, N, and O elemental and isotopic abundances.

Here, I comment briefly on how analysis of infrared spectra led to the resolution of a puzzle of long-standing: What is the ^{12}C/^{13}C ratio in cool carbon stars? These carbon stars and their C_2 Swan system bands provided the first detection of ^{13}C in extraterrestrial objects, but the same characteristic that underlay this early discovery – namely, the great strength of C_2 Swan bands – bedevils attempts to obtain an accurate estimate of the ^{12}C/^{13}C ratio. The same comments apply to the CN Red system lines in the visible and near-infrared which have proven a popular source of a ^{12}C/^{13}C ratio. A compilation of published ratios would bewilder the reader unfamiliar with the spectra (see the summary in Lambert 1980): estimates for a single star may range from $^{12}\mathrm{C}/^{13}\mathrm{C} = 3$ to 100! The root cause of the general lack of agreement is not that the ^{13}C ^{12}C or ^{13}CN lines are extremely weak but that they and their $^{12}C_2$ and ^{12}CN counterparts are strong.

It is important to obtain accurate estimates of the ^{12}C/^{13}C ratio because it is a valuable monitor of the material dredge-up into the giant's convective envelope and, hence, the atmosphere. Two limiting cases may be identified;

(i) A ratio $^{12}\mathrm{C}/^{13}\mathrm{C} \sim 50$ or so would suggest that pure ^{12}C, a product of He-burning, has been added to the atmosphere to convert the O-rich star to a C-rich star without appreciable conversion of the freshly synthesized ^{12}C to ^{14}N by the CN cycle.

(ii) A ratio $^{12}\mathrm{C}/^{13}\mathrm{C} \sim 3$ would suggest exposure to the CN cycle. Quite a weak exposure may suffice to give $^{12}\mathrm{C}/^{13}\mathrm{C} \sim 3$ but if the CN cycle operates for an extended period at a sufficently high temperature, this cycle can also reduce the O abundance to create a C-rich envelope. Extended operation at lower temperatures will convert the C-rich envelope back to an O-rich envelope.

Visible and near-infrared spectra of carbon stars are so crowded with strong lines that the location of the continuum level is uncertain and weak lines are rare. These spectroscopic facts of life surely account for the discrepancies between observers who may have analysed spectra of similar quality. In selected intervals of the infrared, the line density is lower and several favorable opportunities exist for a measurement of the $^{12}C/^{13}C$ ratio. We exploited the CN Red system $\Delta v = -2$ lines near 2μm and the CO V-R $\Delta v = 2$ and 3 lines (Lambert *et al.* 1986).

We described two methods of extracting the $^{12}C/^{13}C$ ratio from the CO V-R lines. The $\Delta v = 3$ bands near 1.6 μm provide weak ^{13}CO lines. A comparison of weak ^{12}CO and ^{13}CO lines within this sequence necessarily pairs high excitation ^{12}CO and lower excitation ^{13}CO lines and, hence, the $^{12}C/^{13}C$ ratio is dependent on the temperatures in the line-forming region; i.e., the effective temperature and the chemical composition which, through the line blanketing, influences the temperature profile. An alternative scheme combines the ^{13}CO lines from the stronger (i.e., larger f-value) $\Delta v = 2$ bands near 2.5 μm with the ^{12}CO lines at 1.6 μm, and then ^{12}CO and ^{13}CO lines of similar excitation potential are compared and the sensitivity of the $^{12}C/^{13}C$ ratio to the atmospheric structure is slight. These two methods yield similar results.

In the CN $\Delta v = -2$ sequence near 2 μm, weak ^{12}CN lines are identifiable; most are satellite lines and a few are high rotational members of the main (P, Q, R) branches. In the typical carbon star, weak ^{13}CN lines from the main branches are present in large numbers. The difference in f-values between the main and satellite lines is such that for a $^{12}C/^{13}C$ ratio of about 20 to 40, the satellite ^{12}C line and typical ^{13}CN line have comparable (and small) equivalent widths. Since the lines also have similar excitation potential, the derived $^{12}C/^{13}C$ ratio is insensitive to the adopted excitation or effective temperature. The advantage gained by combining satellite ^{12}CN and main ^{13}CN lines was noted first by Fujita and his colleagues in analyses of near-infrared CN ($\Delta v = +2$) lines – see, for example, Fujita and Tsuji (1977). Indeed, our results confirm the suggestions by Fujita and colleagues that carbon stars have, in general, a low ^{13}C content.

The CO and CN infrared lines yield consistent results. Our new results show that the typical cool carbon star has a higher $^{12}C/^{13}C$ ratio than the M giants from which the star evolved. If J-type stars rich in ^{13}C are excluded, the mean is $^{12}C/^{13}C = 60$. Inspection of the $^{12}C/^{13}C$ and $^{12}C/^{16}O$ ratios shows that they are consistent with the hypothesis that the carbon stars were produced from M giants by the third dredge-up on the AGB of nearly pure ^{12}C. For the J(^{13}C-rich) carbon stars, our infrared spectra confirm many earlier claims the ^{13}C-rich carbon stars exist; for example, for RY Dra, T Lyr, Y CVn, the $^{12}C/^{13}C$ ratios (3.6, 3.2, and 3.5, respectively) are not significantly different from the predicted ratio (3.4) for the CNO cycle in equilibrium. A fourth star commonly put with the above trio is WZ Cas, but its ratio, $^{12}C/^{13}C = 4.5$, is distinctly above this predicted value. These low $^{12}C/^{13}C$ ratios surely denote severe contamination of the envelopes with CN-cycled material. When and where this contamination occurs in the life of the J-type cool carbon star remains obscure even when additional clues offered by the C, N, and O elemental and $^{16}O/^{17}O/^{18}O$ ratios are provided. Prospective candidates for the progenitors of the cool J stars may be found among the early R stars which are carbon-rich giants with the effective temperature and luminosity of K giants. Evolution of such R stars into the cooler and more luminous cool J carbon stars is seemingly inevitable. The origin of the early R stars is unclear. Dominy (1984) suggested that a violent He-core flash in low mass stars led in a few rare cases to release of freshly synthesized carbon into the envelope of the He-core burning clump giant. Earlier I stressed the vital contributions of studies of the Magellanic Clouds to our understanding of stellar evolution. Future spectroscopic studies of carbon-rich stars at pre- and post-AGB phases of evolution are sure to shed light on the origins and history of the ^{13}C-rich and other types of carbon stars.

2.5 *High S/N Spectra*

Several of the preceding discussions involved a pairing of the enhanced opportunity to acquire high S/N spectra with the opportunity that was the focus of that section. The opportunity to obtain high S/N spectra is, in the pursuit of stellar chemical compositions, generally exploited in the detection of weak lines from trace species; e.g. lithium and the 6707 Å Li I resonance doublet in metal-poor dwarfs, thorium and the 4019 Å Th II resonance line. Other applications of high S/N spectra with relevance to the determination of chemical compositions include the accurate measurement of weak lines of common species in order to determine a star's effective temperature and surface gravity, and the accurate definition of line profiles in order to characterize the atmosphere's velocity field.

Of the many examples that might be discussed, I close this discussion of the opportunities that will define "future possibilities" with a commentary of the oxygen abundance in young and old stars. Data on the abundance of oxygen, the third most abundant element after H and He, are of especial interest to studies of the chemical evolution of the Galaxy and the ages of stars. Models of chemical evolution must account for the overabundance of O (relative to Fe) in metal-poor stars; the standard explanation is that massive stars, which are leading producers of oxygen, were more common in earlier generations of stars. With its high abundance, O is a leading contributor to the opacity of stellar interiors and, hence, an influence on main sequence (and other) lifetimes. Ages of stellar clusters derived from fitting theoretical isochrones to color-magnitude diagrams of the main sequence and subgiant branch are dependent on the assumed O abundance. Since a cluster's metallicity is readily derivable but its O abundance may be unknown, the assumption about the O abundance reduces to one about the O/Fe ratio. Current choices for this ratio are usually based on recent abundance analyses of O in dwarfs and giants. A cluster's derived age may be reduced by 2-4 Gyr as [O/Fe] is raised to the upper limit set by the available observations. With [O/Fe] at the upper band, the ages of the most metal-poor globular clusters are near 14 Gyr according to standard models of stellar interiors and evolution (VandenBerg 1988).

The presence of oxygen in the atmosphere of a metal-poor dwarf or giant is betrayed by few O I lines; e.g. the [O I] 6300 and 6363 Å lines for giants and the O I 7770 Å triplet for dwarfs. The need for high S/N spectra is well demonstrated by Barbuy's (1988) montage of high-resolution spectra of the [O I] 6300 Å line in halo giants. The [O I] line, the stronger of the two forbidden lines, has a central depth of about 20 % ($W_\lambda \simeq 50$ mÅ) in the most metal-rich halo stars ([Fe/H] ~ -1.2). In the most metal-poor giants observed by Barbuy, this line has a central of only about 3 % ($W_\lambda \simeq 8$ mÅ) at [Fe/H] ~ -2.5. Since one would like to extend the determinations of the O abundance to the most metal-poor giants known ([Fe/H] ~ -4), it is clear that high S/N is essential. In addition, high S/N spectra would permit the detection of the [O I] lines in subgiants and dwarfs where, of course, the predicted equivalent is much smaller than for a giant of comparable metallicity and temperature; the 6300 Å line is reduced to $W_\lambda \sim 2.5$ mÅ for main sequence ($\log g \sim 4$) stars as metal-rich as [Fe/H] ~ -0.6 (Barbuy and Erdelyi-Mendes 1989).

Oxygen in halo dwarfs and subgiants is detectable through the high excitation triplet of O I at 7770 Å and other similar lines. Observations of the 7770 Å lines provided the first real evidence of an O over abundance (relative to Fe) in halo stars (Sneden, Lambert, and Whitaker 1979). The strength of the lines is sensitive to effective temperature. In the warmer stars, these O I lines should be measureable off high S/N spectra in the most extreme halo stars; Sneden *et al.* found $W_\lambda = 19$ mÅ for the combined triplet in HD 140283 with [Fe/H] $\simeq -2.3$.

An association of the [O I] lines with giants and the O I lines with dwarfs should not be considered immutable. When possible, O I and [O I] lines should be observed and analysed in the same objects. These lines offer different advantages and disadvantages. In particular, the high excitation O I lines may be susceptible to non-LTE effects but the [O I] lines are expected to be formed close to LTE. Preliminary theoretical studies of the non-LTE effects on the 7770 Å lines in halo dwarfs were reported by Sneden *et al.* (1979). Empirical evidence for non-LTE enhancement of the 7770 Å lines in F and G dwarfs was given by Clegg, Lambert and Tomkin (1981) who noted that these lines when strong gave a systematically higher (LTE) abundance than other weaker permitted lines. Although an improved theoretical estimate of the non-LTE effects on the O I lines is now achievable, I would suggest that a thorough application of high S/N spectroscopy to the [O I] lines in metal-poor dwarfs and giants is likely to lead to the most reliable estimates of the O abundance. Finally, complete dependence on the O I spectrum may be eliminated through observations of the OH $A^2\,\Sigma^+ - X^2\Pi$ ultraviolet system (Bessell and Norris 1987).

The reader interested in the run of the O/Fe ratio with metallicity is referred to reviews by Lambert (1989) and Wheeler, Sneden, and Truran (1989) and to recent work by Barbuy (1988) and Barbuy and Erdelyi-Mendes (1989).

3. *Basic Atomic and Molecular Data*

3.1 *Introduction*

In the preceding sketches of astrophysical problems that may be addressed through stellar spectroscopy, I placed the emphasis on the expanded opportunities available to the observer. The methods of extracting the chemical composition from the spectra were not discussed. To conclude this essay, I offer a few illustrations of the spectroscopists' need for the accurate data on atoms and molecules of astrophysical interest which are essential components in the analytical techniques linking spectra and compositions. The data are used both in the construction of model stellar atmospheres and in the applications of the models to the computation of the synthetic spectra to be fitted to the observed spectrum. A contributing factor to my enthusiasm for quantitative stellar spectroscopy is the fact that accurate basic atomic and molecular data are being made available in increasing quantities. Rapid growth of our understanding of atoms and molecules is stimulating refinements of the analytical techniques applied to stellar spectra. I illustrate these refinements with commentaries on three recent studies of non-LTE line formation.

As long as the assumption of LTE is retained, the basic data needed by a spectroscopist includes the observed (and predicted) spectrum, the associated term diagram (i.e., excitation and ionisation/dissociation energies) and the transition probabilities for emission and absorption of photons in transitions between the terms, including continuum processes as well as lines. The extent of the required data varies from species to species and with the particular spectroscopic problem under consideration.

When the assumption of LTE is discarded, lists of basic data must be enlarged to include cross-sections for interactions between the atom or molecule of interest and the abundant particles in the atmosphere. These interactions include those leading to internal excitation of a species and others resulting in a change of species (e.g. ionization and dissociation). Each interaction has a direct inverse interaction. Often, the dominant interaction is collisional excitation (or ionisation) of an atom by free electrons. In the cooler stars, the free electrons are greatly outnumbered by H and He atoms and, in the coolest stars, by H_2 molecules. Collisional excitation by these atoms and molecules has been widely supposed to be negliglible with respect to excitation by the electrons. Recently, Holweger and colleagues have challenged this supposition (see below). Their challenge means that non-LTE studies of atoms and molecules in cool stars will now require accurate rate constants for excitation by H, He, and H_2 in addition to electrons. Theoretical and experimental data for excitation by electrons is available for many atoms and generally successful approximations for rate constants may be used when detailed studies have not been reported. However, rate constants for electronic excitation by H and He atoms or H_2 molecules have not been determined theoretically or experimentally at the low energies of interest except for a few specific cases. This is virgin territory for a quantum or experimental chemist. (Excitation within the vibration-rotation ladder of a molecule is primarily by H and He atoms or H_2 molecules – see Hinkle and Lambert [1975]).

3.2 *Line Lists*

Stellar atmospheres constitute a family of spectroscopic sources that cannot be simulated in detail in the laboratory. As a result, stellar spectra contain many absorption and emission lines neither recorded on laboratory spectra nor predicted from the available sets of energy levels. These unidentified lines present a variety of problems to the stellar spectroscopist.

Suppose that a trace element is being sought whose only imprint on the spectrum is a single resonance line (e.g. Th II at 4019 Å or Li I at 6707 Å). An unidentified line that is blended with the resonance line will compromise the abundance determination of the trace element. The presence of an extra line will often be revealed on high resolution spectra. In rare cases the wavelengths of the lines will be coincident and the stellar line profile may not reveal the contaminant. As a recent example, I note that an investigation of the Li abundance in cool Ap stars was compromised by blending with an unidentified line (Mathys *et al.* 1989). Although empirical methods may be found to correct for the unidentified blend, the proper and accurate separation of the Li line's contribution to the blend can only come when the blending line is identified. This identification will require further intensive laboratory spectroscopy of the ions abundant in atmospheres of cool Ap stars.

One may identify a second class of problems in which a statistical representation of lines suffices and the precise wavelength of individual lines is unimportant. Detailed laboratory spectroscopy may not be needed in these cases; *ab initio* quantum predictions of the transitions' wavelengths and strengths may suffice and be more readily provided. These problems include the representation of the atomic and molecular line blanketing required in the computation of a model stellar atmosphere, and the prediction of a stellar spectrum in which the continuum is depressed by quasi – continuous opacity contributed by overlapping molecular lines.

For an example of the former problem, I cite the interpretation of the H_2 quadrupole vibration-rotation lines in the spectra of cool carbon stars. Goorvitch, Goebel and Augason (1980) noted that the H_2 lines in the spectra of cool carbon stars were much weaker than predicted. The authors suggested that the stars were H deficient. However, this conclusion is sensitive to the molecular line blanketing. If the blanketing is increased above the levels introduced by Goorvitch *et al.*, the atmosphere is further backwarmed and association of H into H_2 is hindered so that the predicted strengths of the H_2 lines are reproduced *without* the introduction of H deficiency. In our work on the carbon stars (Lambert *et al.* 1986), we suggested that the additional opacity overlooked in the early models came from HCN and C_2H_2, and probably C_3 too. With preliminary estimates of the HCN and C_2H_2 opacity, we were able to reconcile the predicted and observed H_2 lines and retain a normal He/H ratio. We do not yet have a fully consistent interpretation of the spectra of these cool carbon stars – in part, the situation is compromised by a lack of a detailed prescription of the molecules' vibration-rotation band strengths. This prescription is being supplied – particularly for HCN – by a combination of laboratory measurements and *ab initio* quantum chemistry calculation, notably by Uffe Jørgensen here at Nordita, and his colleagues (Jørgensen *et al.* 1985; Smith, Jørgensen and Lehmann 1987).

3.3 *Collision Cross-sections and non-LTE*

Where a statistical representation of a spectrum suffices, quantum chemistry may be tapped to provide the necessary wavelengths and the transition probabilities. However, when unambiguous identification and precise wavelengths are required, high-resolution laboratory spectra must be obtained. Many challenging problems may be posed to the experimental and laboratory physical chemists by the stellar spectroscopists. The challenge is amplified when studies of non-LTE line formation are considered. Examples drawn from the recent literature must serve to illustrate the prevalence of non-LTE effects and the concomitant demands for accurate atomic data.

A series of non-LTE studies of common lines in the spectra of B stars is being undertaken in Munich: see Becker and Butler (1988 a and b) on O II, Becker and Butler (1988 c and 1989) on N II and Eber and Butler (1988) on C II. A summary of the C II study is given here. About 100 levels of C^+ ion were included in the model atom: all energy levels up to $n = 6$ for terms converging to the $2s^2\ ^1S$ ground state of C^{2+} and up to $n = 4$ for terms converging to the $2s^22p\ ^3P^0$ level of C^{2+}. Additional C^+ levels ($n = 7$ and 8, $n' = 5$ and 6) were included but with populations constrained to LTE values relative to the C^{2+} ground state. A total of 73 transitions were included in the linearization scheme providing the non-LTE populations. The calculation was primarily directed at the excitation equilibrium of C^+ but ionisation equilibrium was considered by including the above two levels of C^{2+} and the ground state of C^{3+}. Neutral C was ignored but it has a negligible abundance in the investigated atmospheres ($T_{eff} \gtrsim 15000$ K).

The equations of statistical equilibrium included radiative and collisional transitions as well as contributions from dielectronic recombination. Eber and Butler note that the radiative rates generally dominate the rates between levels and, hence, "errors in the collision constants are thus unimportant". Indeed Eber and Butler are content to adopt van Regemorter's (1962) formula or Allen's (1973) semi-empirical recipe for the rates for excitation by electron collisions and a comparable prescription (Seaton 1962) for ionization by electron collisions. Modern quantal calculations would yield more accurate results but the extensive computational effort would be hard to justify for this problem. (For C^{2+}, collisional excitation rates obtained by the R-matrix method (Dufton *et al.* 1978) were available and were adopted.) The radiative rates were computed, when possible, using the modern predictions of the oscillator strengths (e.g., Yu Yan, Taylor and Seaton 1987 for C II lines) and the photoionization cross-sections. In the absence of such predictions, the Coulomb approximation (Bates and Damgaard 1949) was used.

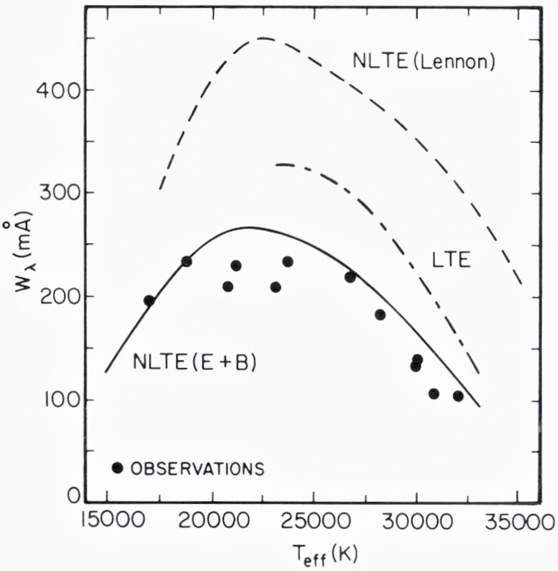

Fig. 9. Equivalent width predictions and observations for the C II 4267 Å 3d ^{2}D-4f ^{2}F multiplet. LTE as well as non-LTE predictions by Lennon (1983) and Eber and Butler (1988) are shown. The observations are from several sources – see Lennon (1983).

The non-LTE populations were used to predict the equivalent widths of a sample of 5 C II lines including the 4267 Å (3d ^{2}D-4f^{2}F) feature that is a prominent line in B-type spectra. Lennon (1983) in an earlier non-LTE study had pointed out that the observed equivalent width of the 4267 Å line was much weaker than the LTE and his non-LTE predictions. Eber and Butler point out that their non-LTE predictions for their more extensive model C^+ atom are close to the observed values (see Figure 9). (Lennon's model C^+ atom consisted of 14 doublet levels and the quartet levels were ignored. Sixteen transitions were linearized). The illustrated predictions correspond to a surface gravity $g = 10^4$ cm s^{-2}, and no microturbulence. The discrepancy between the observations and these non-LTE predictions line may be resolved through a combination of the following factors: further improvements to the non-LTE calculations including the use of improved model atmospheres, adoption of lower surface gravities and higher effective temperatures for the observed stars, and a stellar C abundance that is about 0.2 dex below the solar value. The stellar C abundance should, of course be based on a wide selection of the available lines of C II and C III. Indeed, Eber and Butler point out that the other C II lines considered by them are relatively insensitive to non-LTE effects and, hence, might be preferred for abundance studies.

These calculations by Eber and Butler resolve the discrepancy between the predicted and observed equivalent widths of 4267 Å line that was highlighted by Lennon who believed that the explanation lay in improving the model C^+ atom. Eber and Butler do not identify specific processes that control the non-LTE populations of the 3d ^2D or 4f ^2F levels but simply 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".

Since statistical equilibrium in cooler atmospheres than those considered by Eber and Butler is maintained with contributions from inelastic collisions, accurate rate constants must be known for all the important collisional processes. All investigations of the statistical equilibrium of atoms and ions include terms representing the inelastic collisions with free electrons. In cool stars, hydrogen atoms outnumber electrons by a considerable number (e.g., $n(H)/n(e) \sim 10^4$ in the upper solar photosphere) but inelastic collisions with H atoms have rarely been included in the equations of statistical equilibrium. In general, the justification for this omission is not given. There appear to be two factors whose product encourages the neglect of the H collisions. The collision rate (at unit density) is a product ($<\sigma v>$) (really an integral) of a cross-section (σ) and the relative velocity (v) of the target atom and the projectile (H atom or electron). For equal cross-sections, the rate of inelastic collisions with electrons will outnumber those with H atoms because the electrons' thermal velocities are higher by a factor of about 40. Then, there is a general argument that shows that the cross-section for excitation of optical transitions by electrons will be much larger than the cross-section for excitation by H atoms.

This argument about the cross-sections is discussed by Massey (1949). A collision occurs with a characteristic time scale $t \sim r/v$ where r is the effective range and v is the relative velocity. The transition in the perturbed molecule (or atom) corresponds to a frequency $\nu \sim \Delta E/h$. Classically and, also, quantum mechanically, the expectation is that the cross-sections for excitation and de-excitation will be small unless $1/t \sim \nu$ or $t\nu \sim 1$. It is instructive to examine this limit:

$$t\nu \approx \frac{r}{v}\,\frac{\Delta E}{h} = \frac{4r\Delta E}{\sqrt{T}} \quad \text{(electrons)}$$

$$= \frac{170r\,\Delta E}{\sqrt{T}} \quad \text{(hydrogen atoms)}$$

In these formulae, the effective range is given in Å units and the energy $\triangle E$ in eV. In the limit $tv \rightarrow o$, the cross-section will decrease from a maximum near $tv \lesssim 1$ but it will remain significantly large for small tv values. On the other hand the cross-section is expected to be very small for $tv >> 1$.

A typical optical transition, has $\triangle E \sim 3eV$ so that at $T \sim 5000$ K, $tv \sim 1/6$ for an electron collision and ~ 7 for a hydrogen atom collision. Then, the cross-section for an inelastic H atom collision is expected to be much smaller than for an inelastic electron collision. In an atom, fine-structure and some term-to-term transitions correspond to small $\triangle E$. Also, in a molecule, the rotational and vibrational transitions corresponds to small excitation energies: $\triangle E_{rot} \sim 0$ to 0.05 eV and $\triangle E_{vib} \sim$ 0.2 to 0.4 eV for typical molecules. Then, the product $tv < 1$ and excitation by hydrogen (also, helium) atoms must be included.

The total rate appearing in the equations of statistical equilibrium is the product of $<\sigma v>$ and the density of projectiles: can the small $<\sigma v>$'s expected for collisions with H atoms be offset by the large ratio $n(H)/n(e)$? Recent calculations beginning with Steenbock and Holweger (1984) suggest the answer to this question is often 'yes'. They introduced collisions with H atoms in their study for non-LTE line formation of the Li I lines in cool stars. Estimates of $<\sigma v>$ were drawn from a generalization of a 'modified classical Thomson formula' (Drawin 1968, 1969). This simple recipe is expected to yield an 'order-of-magnitude estimate of collisional excitation and ionization cross-sections'.

Here, I comment on later work on Fe I and Fe II lines. A thorough empirical LTE analysis of the iron lines in the spectrum of the K0 III giant β Gem was reported by Ruland *et al.* (1980) who noted that the high and low excitation Fe I lines gave different iron abundances. These differences are shown in the top panel of Figure 10 for lines with equivalent widths of 200 mÅ or less. The only reasonable interpretation of these differences is that they are due to non-LTE effects in the excitation of neutral iron atoms. This assertion is wonderfully supported by calculations done by Steenbock (1985 – see also Holweger 1988) whose Fe I/II/III model atoms comprise 79/20/1 levels with 52/23/0 transitions. Predicted corrections to the LTE abundances for a model atmosphere representative of β Gem are shown in the lower panel of Figure 10. Inspection shows that the NLTE calculations predict fairly well the sense of the difference between the high and low excitation lines over the entire range of equivalent widths. The illustrated predictions from Holweger (1988) were obtained with the cross-sections for the inelastic H collisions scaled by a factor $S_H = 0.2$ from the values expected on Drawin's recipe (Watanabe and Steenbock 1986). The predicted abundance spread is slightly smaller than observed. If the H collisions are neglected ($S_H = 0$), the spread in $\log\varepsilon_{LTE}/\varepsilon_{NLTE}$ is increased from 0.3 dex to 0.6 dex, a spread somewhat larger than indicated by the empirical results. As S_H is increased, the non-LTE effects are reduced. At $S_H = 1$, Holweger remarks that 'the calculated NLTE effects become too small«. Similar calculations and their fit to empirical

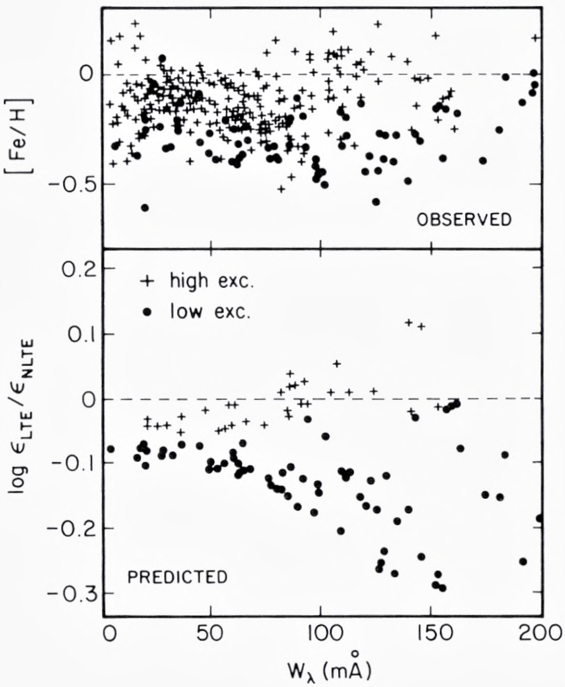

Fig. 10. Observed LTE iron abundances [Fe/H] (top panel) and the predicted corrections to LTE abundances (bottom panel) for Fe I lines in the spectrum of β Gem. The observed abundances are taken from Ruland *et al.* (1980). The predicted log $\varepsilon_{LTE}/\varepsilon_{NLTE}$ are taken from Holweger (1988).

results have been undertaken for the metal-poor K2 giant α Boo, the Sun, and main sequence stars Procyon (F5 IV-V) and Vega (A0V) – see Gigas (1986) for a discussion of Vega. (The predicted NLTE corrections for the Fe II lines are very small [Steenbock 1985]. The Fe I – Fe II abundance difference for giants cannot be readily established empirically because this and other atom-ion pairs are used to determine the surface gravity by imposing the condition that Fe I and Fe II lines yield the same Fe abundance).

This fascinating series of non-LTE calculations shows that (i) the observed departures from LTE in complex spectra such as Fe I may be understood semi-quantitatively, and (ii) firm quantitative predictions and, hence, abundances unbiased by non-LTE effects cannot be made until accurate information is available on cross-sections for excitation and ionisation by electrons *and* H atoms. While the theoretical and experimental literature on electron collisions is extensive, Drawin's crude recipe would appear to be sole extant tool for the astrophysicist needing estimates of the cross-sections for inelastic collisions with H atoms at the low thermal energies encountered in cool stellar atmospheres. Perhaps, a brave theoretician here at NORDITA will assume the challenge.

To close this discussion of non-LTE studies, I comment on one remarkable abundance anomaly that was uncovered through LTE analyses but is confirmed by a fairly exhaustive non-LTE analysis. I refer to the Na overabundance seen in F-K supergiants – see summary by Boyarchuk and Lyubimkov (1983) and also Sasselov (1986). After noting that the Na abundances were to be considered preliminary for lack of a non-LTE study of Na I line formation, Boyarchuk and Lyubimkov suggested that the Na overabundance may indicate the occurrence of deep convective mixing leading to the dredge-up of material exposed to the NeNa cycle (Marion and Fowler 1957). This suggestion was examined by Denisenkov and Ivanov (1987) who showed that the ^{22}Ne(p,γ)^{23}Na reaction can enrich the H-burning core of massive ($M \gtrsim 1.5\ M_{\odot}$) main sequence stars by factors of 5 to 6. Substantial amounts of this core material must be mixed with the envelope to account for the observed (LTE) overabundances. Such mixing is not predicted by standard models of the massive stars that evolve into the F-K supergiants. However, Denisenkov and Ivanov point to a correlation between the Na overabundance and the measured ^{12}C/^{13}C ratio as evidence for deep mixing.

The overabundance of Na has been confirmed by non-LTE calculations made by Boyarchuk *et al.* (1988a,b). The model atom consisted of 19 levels plus the ground state of the Na^+ ion. Nine transitions were linearized and many more were fixed during the iterations. Collisional exicitation and ionization by electrons but not H atoms was considered; the latter omission is most probably unimportant. The primary uncertainty in the calculations would appear to come from the representation of the ultraviolet radiation field that controls the photoionization rates. The pleasing (surprising?) result is that the Na abundances are changed only slightly by the introduction of non-LTE: $\triangle \log\varepsilon = \log\varepsilon_{NLTE} - \log\varepsilon_{LTE}$ ranges from $+0.06$ to -0.17 for four supergiants examined by Boyarchuk *et al.* (1988b).

The sceptic is left to ponder two questions: How does so much Na-rich material from the core get into the atmosphere? Are there further extensions to be made to the model atom and the atomic processes that would dramatically increase the predicted Na I equivalent widths for the non-LTE case and so lead to lower, even normal, abundances? The observer will hasten to the telescope to search for further spectroscopic evidence of extensive contamination by material from the H-burning core.

4. *Epilogue*

A majority of Bengt Strömgren's audience in 1958 would have entered the University Museum through the main door on their way to the lecture room in the far lefthand corner. A stuffed dodo bird from Mauritius would have greeted those members who took one of the possible routes to the lecture room. An hour later, attentive listeners would have recognized that Strömgren photometry would not rapidly follow the dodo into extinction. The informed listeners may even have predicted that Strömgren's scheme would become the premier photometric system.

A well-known historian in contemporary Oxford has been reported as despondent because, in his view, historians have run out of questions to answer. Professor Strömgren demonstrated in his 1958 lecture and by his energetic pursuit of problems to the end of his life that astronomy has not yet run out of questions and that the imaginative observer can forge the tools with which to extract the answers. In this essay, I have endeavoured to show how quantitative stellar spectroscopy may serve to answer a wide variety of the remaining outstanding questions. History may be an academic dodo but astronomy is far from extinction!

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