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Mixing in Stars

GEORGE WALLERSTEIN

Analysis of the chemical and isotopic composition of stellar surfaces reveals the types of nuclear reactions that have occurred in the stellar interiors as well as the timing and depths from which material once deep in the star has reached the surface. Mass loss from the stellar surface and, in some cases, mass transfer from a companion enhance the opportunity to observe material that is the product of internal nuclear reactions. Detailed studies show substantial deficiencies in current models with the timing and depth of convective and other forms of mixing.

ALMOST 35 YEARS AGO MERRILL (*1*) ANNOUNCED THE discovery of the lines of the unstable element technetium in the spectrum of the star R Andromeda (abbreviated R And). Because the half-life of the longest lived isotope of Tc is 2.6×10^6 years it was evident that the Tc seen on the surface of R And was produced by nuclear transformations within that star and mixed to the surface. For the first time a way had been found to test the theory of stellar interiors.

The basic theory of the structure of stars was worked out by Sir Arthur Eddington and others in the 1920s (*2*). Stellar structure is described by four first-order differential equations that use the conservation of mass, conservation of energy, hydrostatic equilibrium, and energy transport. In addition, the equation of state, the opacity of the material to radiation, and the rates of nuclear reactions that generate energy must be known (*3*). With reasonable boundary conditions the equations can be solved for a spherical star in a few seconds with a modern computer (although it took Eddington months with a desk-top calculator to solve them 60 years ago).

It is not so easy to verify our calculations. Since the opacity of stellar material is very high no radiation emitted except by the surface layers can reach us. Only neutrinos can travel from the center of a star to an external observer and even these may suffer a conversion that permits only a fraction of the emitted neutrinos to emerge from the stellar surface unchanged (*4*). Solar neutrinos are barely detectable with modern instrumentation and only from supernovae can we detect neutrinos from any other stellar source within our galaxy or the Local Group (*5*). Checks on the correctness of the theory of stellar structure and evolution can be made if one uses the integral properties of stars such as the radius and luminosity. These checks are not very critical, however, because the solutions of stellar structure may predict an observed radius and luminosity even though the internal structure is not unique, especially for evolved stars.

The latter have converted their internal hydrogen to helium and hence are now generating energy by helium burning. The best test of our calculations for such stars is to determine the chemical composition of the visible layers of a star and endeavor to relate the composition to events in the interior revealed by the mixing of previously deep layers to the surface. In some cases we are greatly assisted in this process by the loss of material from the stellar surface. Extensive mass loss may be driven by the absorption of radiation by the outer atmosphere of the star. For hot stars highly ionized species of light elements such as carbon, nitrogen, and oxygen are the absorbers, whereas for the coolest stars the absorbing agent is dust. In binary stars mass loss may be induced by the gravitational field of a companion. In some situations significant amounts of mass may be transferred to a companion so the star with peculiar atmospheric abundances may be the recipient, rather than the producer, of the anomalous material.

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Convection Theory

In the simplest formulation of stellar models, heat transfer is assumed to occur by radiation only. However, Schwarzschild (*6*) showed as early as 1906 that if the radiative temperature gradient becomes too steep a stellar atmosphere or interior region (just like the earth's atmosphere on a sunny day) becomes unstable to vertical perturbations and convection begins. Once a certain volume of a star becomes convective it is homogenized and any prior differences in chemical composition that may have existed will be smoothed out. Hence, if convection can penetrate to the layers in which nuclear reactions have occurred the products of those reactions are distributed throughout the convective region.

There usually are two causes for convective instability. In stars that generate energy by fusion of hydrogen into helium by way of the carbon cycle the rate of energy generation is so temperature sensitive that near the center of the star the energy generation rises too rapidly with depth for radiation to carry it all outward. This effect is important for main-sequence stars of mass greater than 1.2 solar masses ($M_\odot$). Nuclear reactions during later stages of stellar evolution such as the $3^4He \rightarrow {}^{12}C$ reaction are even more sensitive to temperature and are likely to be responsible for vigorous convective zones. The second cause of convection is important in cool stars (that is, stars with effective temperatures less than about 6000 K) and is caused by the high atmospheric opacity in zones in which hydrogen and helium are partly ionized. In order to drive the energy through the high-opacity zone the temperature gradient reaches and even exceeds the convective limit. This outer convection zone in the sun reaches down to layers with temperatures as high as 10^6 K and actually encompasses the entire star for main-sequence stars of less than about 0.5 $M_\odot$. In red giant stars the outer convection plays a critical part in mixing the products of internal nuclear reactions to the stellar surface. However, the calculation of the extent of convective mixing in a star is not easy.

In the first-order approximation formulated by Schwarzschild, the criterion for convection is given by the inequality:

$$\frac{d \log T}{d \log P} > 0.4 \qquad (1)$$

for convective instability (where T is temperature and P is pressure). Hence, all layers whose radiative temperature gradient exceeds the value given by inequality 1 are convective, whereas all layers with a smaller temperature gradient are stable. However, it is too simple to use only the stability criterion because it only tells us where the acceleration of a convective element is zero but does not tell us how far into a stable zone the convection will penetrate.

From the observational point of view, to calculate homogenization by mixing we need to know the maximum extent of the statistical fluctuations in velocities and masses of convecting elements. One is reminded of the problem of predicting the strongest wind gust that a structure must sustain during a period of 100 years on the basis of the previous 20 or 30 years of data. For astrophysics we need to predict the most penetrating convective elements in millions or perhaps a billion years! Since the theory of convection is not sufficiently sophisticated for this, we must turn to the observations to infer both the extent of mixing and the physical conditions experienced by the mixed material when it was deep within the star.

Types of Stars That Show the Effects of Mixing

For some 70 years astronomers have characterized stars by evaluating their total luminosity and effective surface temperature, and plotting these data in the color-magnitude (also called the Hertzsprung-Russell) diagram. Because of the relationship

$$L = 4\pi R^2 \sigma T_{\mathrm{eff}}^4 \qquad (2)$$

where L is luminosity, R is radius, σ is a constant measured in the laboratory, and T_{eff} is effective temperature. Knowledge of L and T_{eff} allows R to be calculated and a star to be classified as a supergiant, giant, main-sequence, or degenerate star. I show such a diagram in Fig. 1 and have labeled the region in the H-R diagram in which stars show the most interesting and revealing effects of mixing; equally interesting in some cases is the region of extreme stability. Tracks of stars of various masses are also shown as their L, T_{eff}, and R values change with evolution of the stellar interior as a result of nuclear reactions and changes in the physical state of the gas.

I will review these interesting regions in the H-R diagram briefly before discussing each one in detail. In the upper left-hand corner are the extremely hot, very luminous, and very massive stars called Wolf-Rayet stars after their discoverers. Owing to rapid mass loss they reveal the contents of their inner convection zones. In some cases the products of hydrogen burning by the CNO cycle and in more advanced cases the enhancement of carbon through helium burning are seen. Going down the main sequence of hydrogen-burning stars we see next a region of extremely stable atmospheres in which gravitational settling and radiatively driven diffusion have caused very unusual elemental abundances to appear in the stellar atmospheres. From about 8000 K to 6000 K we see a region of atmospheres of moderate stability where the easily burned lithium is

Table 1. Predicted and observed lithium depletions for main-sequence stars of various masses and effective temperatures and three ages.

$M/M_\odot$	T_{eff}	1×10^9 years		5×10^9 years		15×10^9 years	
		Predicted*	Observed	Predicted*	Observed	Predicted†	Observed
1.50	8000	1.0	1.0	1.0	—	—	—
1.35	7000	1.0	1.0	1.0	—	—	—
1.25	6600	1.0	10^{-2}	1.0	—	—	—
1.20	6300	1.0	1.0	1.0	1.0	1.0	1.0
1.10	5800	0.95	10^{-1}	0.95	10^{-2}	1.0	1.0
1.00	5500	0.90	10^{-2}	0.90	$<10^{-1}$	—	1.0
0.90	5200	—	—	—	—	0.9	—
0.90	5000	0.70	$<10^{-3}$	0.70	—	—	$<3 \times 10^{-2}$
0.875	4750	—	—	—	—	1.6×10^{-3}	—
0.75	4500	0.10	—	0.09	—	—	—
0.70	4300	2×10^{-2}	—	5×10^{-3}	—	—	

*From (*23*) using models with solar metals and standard mixing theory. †Also from (*23*) with 1/20 solar metals, but with additional mixing of 0.7 pressure scale height arbitrarily introduced during the contraction stage.

preserved except for a narrow interval near 6500 K where lithium has diffused downward to burn. From 6000 K to 4000 K the outer convection zone of stars deepens and lithium is depleted. Below 4000 K the outer convection zone penetrates very deeply and finally the stars are fully convective and fully mixed.

In the giant region of the diagram (upper right) we see stars with surface temperatures between 4500 and 3500 K that show progressively deeper mixing as evidenced by the depletion of lithium and the enhancement of ^{13}C and ^{14}N that are enhanced in CNO cycling. Standard convection theory predicts homogenization of the surface with regions that had previously burned only a little hydrogen but nevertheless resulted in repeated captures of protons by ^{12}C, ^{13}C, ^{14}N, ^{15}N, and (at sufficiently high temperatures) ^{16}O. During such a cycle the abundance of each species is inversely proportional to the capture rate. After further evolution, stars of less than about 10 $M_{\odot}$ become bright giants and the effects of sudden rapid nuclear burning of helium in a shell source combine with convective mixing to produce the carbon stars and stars with heavy element excesses, including the Tc lines whose discovery opened up the whole field of heavy element synthesis in stellar interiors.

Lastly, I mention the white dwarfs (lower left) whose equation of state follows the laws of degeneracy (rather than the perfect gas law) throughout most of the star. They show a fascinating combination of effects including gravitational settling, radiative diffusion, convection, and accretion, well worthy of a full review paper here. Since their processes are rather different from the other stars in this discussion we will not review their properties but rather refer the reader elsewhere (7).

The Determination of Stellar Chemical Compositions

Astronomers determine the chemical composition of a star by measuring the amount of light absorbed from the spectrum by atoms, ions, and molecules of various species. With the help of a model atmosphere, which mimics the depth dependence of the temperature, pressure, and other parameters, we can predict the dependence of the strength of spectral lines on the abundance of each species. Modern spectrographs with charge-coupled devices as detectors in the optical region and Fourier transform spectrometers in the infrared region provide very accurate data for comparison with the models. This procedure provides abundance data accurate to about $\pm 25\%$ if the atomic and molecular data are accurate; the uncertainties are, however, sometimes larger. For example, the uncertainty in the dissociation energy of the CN molecule introduces a systematic uncertainty in the nitrogen abundances that affects all cool stars nearly equally.

Massive stars with winds and thick convective cores. Among the hottest stars near the main sequence of hydrogen burners are the emission-line stars discovered by Wolf and Rayet (*8*). Most of them can be readily separated into those that show primarily nitrogen ions and those that show carbon ions, namely the WN stars and WC stars. Observations of WN stars (*9, 10*) show N/C ratios from 15 to 50, whereas observations of WC stars show the same ratio to be less than 1/60. These analyses have been challenged (*11*) but the evidence strongly favors the large inversion of the N/C ratio between types WN and WC.

Qualitatively, the explanation of the WN and WC types is clear but there are problems when the evolution of massive stars is investigated in detail (*12*). The WN stars show the expected composition of material that has undergone the CNO cycle in a large convective core. Such cores have been revealed by extensive mass loss, for which there is strong evidence (*8*). Similarly the WC stars have evolved further and their convective cores have been burning helium by the $3\alpha \rightarrow {}^{12}C$ reaction and depleting nitrogen by $^{14}N(\alpha,\gamma)^{18}F(\beta^{+}\nu)^{18}O(\alpha,\gamma)^{22}Ne$. By looking at the rates of each of these processes we can learn about the nature of the convection and the degree of overshooting at the core-envelope boundary.

The extent of overshooting at the edge of the convective core determines the size of the homogeneous region that is revealed by mass loss. Hence, an early appearance of the core with its high nitrogen content indicates either substantial overshooting or mass loss somewhat beyond the high end of the observed range. Most of the WN stars in young stellar associations still show some hydrogen, indicating greater homogenization than found in the models without overshooting and favors the models with overshooting rather than with very large mass loss (*13*). Similarly, models with strong overshooting predict early core revelation during He burning so that relatively low ratios of C/He (near 0.1 mass fraction) should be detectable in "young" WC stars. Standard models, on the other hand, predict that the core should not be visible until C and He are near equal abundances. The observed values range from 0.025 to 0.1 according to Smith and Willis (*9*) who analyzed seven stars and ratios of 0.3 to 0.6 according to Nugis (*10*) who analyzed three stars. If the former data are correct, large overshooting is again required whereas the latter indicate smaller, but not negligible, overshooting. The prediction of low N in WC stars is generally confirmed and a very high Ne abundance, in accord with the N-burning reaction given above, has been found in the WC star γ^2 Velorum (*14*). This Ne should be almost all ^{22}Ne and the source of most ^{22}Ne in the universe (including the NeE component in meteorites). Only mass loss rates a factor 3 to 4 times greater than indicated by observations could reveal the C-enriched cores with the relatively low levels of C enrichment.

Stars with extremely stable atmospheres. Within the mass interval of about 1.8 to 6 $M_{\odot}$ on the main sequence there exist stars with strange chemical compositions (*15*). The range of peculiarities is enormous, consisting, for example, of either enhanced or depleted helium; enhanced P, Kr, and Ga; enhanced Mn and Hg; enhanced heavy rare earths (but not light rare earths); and depleted Ca and Sc accompanied by a small excess of the iron peak elements and substantial excesses of Sr and Ba. Attempts to explain these anomalies by nuclear reactions induced by magnetically accelerated particles on the stellar surface were not successful, nor were efforts to trace the anomalies to nuclear reactions in stellar interiors followed by mixing.

The most plausible explanation lies in the stability of stellar atmospheres with effective temperatures between 8,000 and 20,000 K (*16*). The stability of their atmospheres is enhanced in many, but not all, such stars by the presence of magnetic fields of roughly 10^3 to 10^4 G (*17*). For such a field the magnetic pressure, $B^2/8\pi$, is greater than the gas pressure in the atmosphere of a 10,000 K main-sequence star even at an optical depth of 30 and, hence, will dominate the atmosphere in all layers. Rotation may upset the stability for surface velocities above about 50 km s^{-1} but does not always do so. Once the atmosphere is stabilized two effects cause changes in the surface composition. Gravitational settling causes helium and all heavier elements to sink. More important, however, is the effect of radiation pressure on trace elements that have ionization edges near the wavelength of strong radiative flux. Such elements float upward and can achieve concentration factors as great as 10^3 to 10^4 in the top few optical depths of the atmosphere. Such diffusion processes can be effective only if local gas currents are less than about ten times the diffusion velocity, which is a remarkable level of stability in a stellar atmosphere especially considering the vigor of convection in the atmospheres of only slightly cooler stars. A detailed calculation (*18*) for various elements that show excesses and

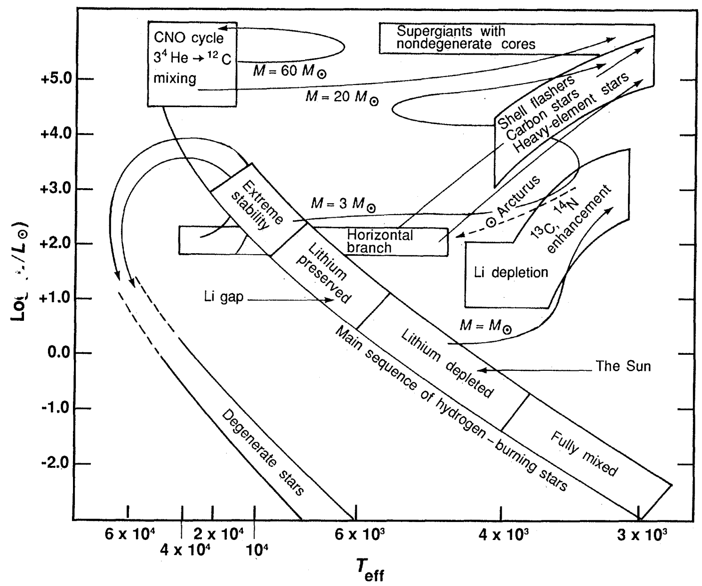

Fig. 1. The stellar types are plotted in this color-magnitude diagram whose physical coordinates are luminosity, in solar units, and effective surface temperature in kelvins. All the stars above and to the right of the main sequence are giant stars.

deficiencies in the cool metallic-line stars ($M \simeq 1.55\ M_\odot$) shows how sensitive the predictions are to the radiative diffusion and to the turbulence below the hydrogen convection zone. Only in the absence of helium that results from gravitational settling will the convection zone terminate near $T = 35{,}000$ K (*19*). Below this level large accumulations of Sc, Y, and Zr develop. Turbulent diffusion below the convection zone is essential to bring a sufficient concentration of these elements to the visible atmosphere, but the theory predicts a much larger excess of Sr and Eu than observed. This severe condition can hardly be avoided because no other theory of the elemental (and isotopic for $^3He/^4He$) anomalies in these stars comes close to the success of the diffusion theory.

Lithium as a tracer of the outer convection zone of intermediate mass stars. Starting with stars near 1.3 $M_\odot$ and increasing rapidly with smaller mass the outer convection zone that is primarily due to the high opacity caused by hydrogen photoionization deepens. To predict the actual surface abundance of a species such as lithium it is necessary to calculate the physical conditions at each depth in an evolving model including the contraction phases when the star was completely convective, even though the central temperature was not nearly as high as in stable main-sequence stars (*20*). The element that best reveals the sensitivity of the stellar model to mixing is lithium. The lithium nucleus reacts with protons at relatively low temperatures, about 3×10^6 K for ^7Li and 2×10^6 K for ^6Li, and, hence, is depleted in all except the outer layers of main-sequence stars. Hence, if we can measure the abundance of lithium in stars of known age we can see if the limits as calculated in the models are obeyed. The abundance data for the light elements were recently reviewed (*21*) and there have been significant developments since then.

I compare the observational data with the prediction of models (*20*) in Table 1. The sun provides abundances or limits on light element abundances for a star with an accurately known age, 4.5×10^9 years (*22*). We can also learn about the dependence of mixing on mass for main-sequence stars of much younger age, about 0.8×10^9 years, by studying the Hyades clusters and for stars of solar age from the cluster M67 (*23*). For the so-called subdwarfs, which are very old (15×10^9 years) metal-poor stars, the theory correctly predicts the mass at which the surface lithium drops rapidly only when some additional mixing is introduced. For stars that are 10^9 years old the data show a gradual drop between 1.2 and 0.9 $M_\odot$ (*24*). Furthermore, a startling deficiency of lithium was discovered by Boesgaard and Tripicco for stars in the Hyades cluster with a narrow range of surface temperatures near 6500 K and masses near 1.25 $M_\odot$ which is confirmed in the Coma cluster and in NGC 752 (*25*).

It is clear from the data for lithium that substantially deeper mixing occurs in normal-metal stars that are 1×10^9 to 15×10^9 years in age than is predicted by standard theory. The theory can be perturbed by introducing "extra mixing" by 0.7 scale heights during the contraction of the stars to the main sequence. D'Antona and Mazzitelli clearly introduce this as a "fudge" factor, while Endal and Sofia find it to occur as a result of differential rotation in the evolving sun (*20*).

The "lithium gap" in the Hyades, NGC 752, and Coma clusters requires a different explanation. As with abundance anomalies among hotter stars the only explanation offered to date depends upon diffusion of Li below the convection zone (*26*). For stars with effective temperatures above about 6900 K, Li is supported by radiation pressure below the convection zone. From 6900 to 6400 K radiation pressure fails to support Li. Below 6400 K the convection zone is sufficiently deep to mix the relevant layers and radiative support is not needed to counter gravitational settling. Young clusters ($\sim 7 \times 10^7$ years) do not show the lithium gap, thus limiting the time scale for settling to the interval of roughly 10^8 to 3×10^8 years.

Summarizing the data and their implications for mixing in main-sequence stars we see that the standard criterion for the depth of mixing fails to predict lithium abundances correctly and that extra mixing during contraction to the main sequence is needed. The nature and physical cause of this extra mixing is not known.

Normal giants and the appearance of CNO products on stellar surfaces. Just as the depth of convective mixing depends on effective temperature for main-sequence stars, so does it for red giants. Although the effective temperatures of main-sequence stars form a mass sequence, for giants they correlate with the star's evolution as an increasing fraction of the stellar central mass is converted to helium and forms a degenerate core for stars less than about 2.25 $M_\odot$ or a shrinking, nondegenerate core that becomes steadily hotter as it contracts in more massive stars. The fitting conditions at the core-envelope boundary strongly affect the envelope solution resulting in a steadily expanding radius as the star becomes brighter and the surface becomes cooler. For small-mass stars with degenerate cores the evolution is interrupted by the onset of helium burning, which increases unstably until the increasing temperature removes the degeneracy and allows the core to expand. This "helium flash" may seriously disrupt and, hence, thoroughly mix the star (*27, 28*), but the existence of numerous horizontal branch stars in globular clusters demonstrates that the explosion is usually well contained. The resulting structure is a quietly burning helium core of roughly half the mass living off the $3\,^4He \rightarrow {}^{12}C$ reaction occurring in its inner 10% surrounded by a hydrogen envelope. Between the hydrogen and helium zones is a shell in which hydrogen is converted to helium by the CNO cycle. The position of such a star in the log L versus T_{eff} diagram depends on the ratio of helium core to envelope mass and the ratio of helium burning to hydrogen burning. The latter depends on the abundance of the CNO catalysts. Large core-to-envelope ratios drive the star blueward and low CNO abundances do the same. The luminosity is independent of those parameters, hence, the name "horizontal branch" stars in the color-magnitude diagram. Once the helium is exhausted in the core it shrinks and once again becomes degenerate, now with a largely carbon core containing some oxygen owing to the $^{12}C + {}^4He \rightarrow {}^{16}O$ reaction. Again the fitting conditions—now more complicated because two burning shells must be considered—force the envelope to expand and the star to become a red giant again. The star advances up the "asymptotic giant branch" (AGB), so called because the coolest stars may have almost the same surface properties as stars that are red giants for the first time. During this stage the interaction of mixing and nuclear burning becomes very complicated and may result in gross changes in the surface composition of the star.

Let us now go back to trace the mixing-induced changes in chemical composition expected on the surface and compare them with observed surface compositions. As the surface temperature falls, the outer convection zone deepens and progressively more lithium-poor and CN-cycled material is convected to the surface. Stellar model calculations can track the abundances of Li, ^{12}C, ^{13}C, ^{14}N, and so forth (*29*) whereas observations of these species can be made readily with modern high-resolution spectrographs with digital detectors (*30*).

Observations of a large number of bright red giants of uncertain mass (since they are not cluster members) confirm the predicted trends of declining lithium, declining ^{12}C, increasing ^{13}C and ^{14}N as stars of solar metallicity advance up the red giant branch and then settle down into quiescent helium burning at the red end of the horizontal branch, the so-called "clump giants" typified by four such stars in the Hyades cluster.

A comparison of theory and observation is most useful if the stellar masses are known. The old cluster M67 provides a sequence of stars of near 1.3 $M_\odot$ advancing up the red giant branch. Models predict a gradually changing C/N ratio along the sequence but observations show the change to be quite sudden at the point at which the stars change their evolution from decreasing surface temperature to increasing luminosity. This is just the time when the outer convective zone rapidly deepens. This change is not as gradual as the models predict but rather is sufficiently sudden that overshooting may immediately result in mixing that the models predict to happen only gradually as the star evolves.

Although the models are able to predict evolution and mixing on the giant sequence fairly well there remain some puzzles that have been known for years and others that have recently come to light. The nearest red giant to the sun is the moderately metal-poor star Arcturus. Metal-poor stars are old and of small mass, perhaps between 0.9 and 1.2 $M_\odot$ when on the main sequence. Arcturus's CNO abundances and isotope ratios have been measured by Lambert and Ries as accurately as can be done for any star (*30*). The problem arises with its $^{12}C/^{13}C$ ratio of 7.2 indicating that half of its atmospheric material has been CNO processed. Appropriate models (*31*) with standard mixing predict ratios in the range of 28 to 60. The observed C/N ratio is 2.95, within range of the predictions, but for a $^{12}C/^{13}C$ ratio of 7 the expected C/N ratio is less than unity. Two similar stars, the binary system γ Leo A and B, show $^{12}C/^{13}C$ ratios of 6.5 and 9, respectively, with C/N ratios of 1.0 and 1.3. At least their C/N ratios are closer to the predictions of CN processing even if the degree of such processing is far above the predicted level. To make matters worse, an extension of the $^{12}C/^{13}C$ analysis to 15 red giants of 10 to 100 times lower metallicity than Arcturus shows that all stars above the subgiant branch have ratios smaller than 20 with nine stars less than 10 and four stars less than 5. The last value is within the uncertainties of observation and reaction rates to say that nearly all of the material in the atmosphere has been at temperatures at which the $^{12}C(p,\gamma)^{13}N(\beta^+\nu)^{13}C$ reaction could proceed on a time scale of 1.5×10^{10} years. A temperature near 10^7 K is required. A careful analysis shows that no such models exist unless additional meridional circulation or turbulence caused by factors other than convective instability has been mixing the envelope with the interior over a long time scale (*31, 32*).

When the star's interior becomes about 50% helium core and 50% envelope the core temperature reaches about 8×10^7 K, and the $3\alpha \rightarrow {}^{12}C$ reaction as well as the $^{14}N(\alpha,\gamma)^{18}F(\beta^+\nu)^{18}O$ reactions commence. For stellar masses less than about 2.25 $M_\odot$ the reactions start in degenerate gas and the rate increases exponentially until the degeneracy is removed and the core expands. Extremely superadiabatic temperature gradients can be set up and the mixing event must be followed by dynamical calculations rather than by standard convection (*27*). If the star were to mix completely it would return to the main sequence at a higher luminosity than it had when it was composed of the usual 75% hydrogen, 23% helium, and 2% heavy elements owing to its increase in molecular weight, μ, combined with the dependence of the luminosity of homogeneous stars on $\mu^{7.5}$. No such stars have been identified to date. However, two classes of carbon stars that are not sufficiently luminous to be in a more advanced stage of evolution have been suggested to be stars that have experienced the He core flash. They show enhanced carbon and, in some cases, enhanced ^{13}C and N indicating both that the $3\alpha \rightarrow {}^{12}C$ reaction has initiated the event and that the rising material has interacted with the hydrogen-burning shell to process some of the ^{12}C through the CN cycle (*28*). In the metal-poor subspecies called the "subgiant CH stars," there is evidence of neutron-capture reactions that are probably the result of the release of neutrons by way of the $^{13}C(\alpha,n)^{16}O$ reaction during the interaction of the carbon and helium from the core with the hydrogen-burning shell. The other subgroup, called the R stars, shows no enhancement of heavy elements.

Carbon Stars, S Stars, and Heavy-Element Production

After the post–helium flash stars have quiescently burned helium into carbon in their cores they face the same problem as main-sequence stars after core hydrogen burning is completed. Their inert carbon cores contract and a shell source develops at the carbon core–helium shell boundary. Meanwhile, an outer shell source continues to convert hydrogen to helium at the boundary between the helium region and the hydrogen envelope (*33*). As the inner carbon core increases in mass the outer envelope expands, the star becomes a red giant again (an AGB star), and a deep convective envelope develops in the hydrogen-rich material. The situation is ripe for deep mixing to bring the products of all the nuclear reactions now occurring at the two shells to the observable stellar surface.

Before describing the abundance anomalies that have resulted from nuclear processing and mixing we must emphasize that about 90% of the evolved red giants, including many that are surrounded by extensive gas and dust envelopes that they have cast off to reveal their once deeper layers, show almost no abundance anomalies. Why should the majority not exhibit anomalous compositions? We will come back to this question after describing the anomalies.

The two most easily recognized anomalies in cool stars are a C/O ratio greater than unity and an excess of heavy elements. The former results in strong molecular bands attributable to C_2, CN, and CH rather than oxide bands in the stellar atmospheres. This anomaly is so evident that it was recognized a century ago by the visual spectroscopic observer Secchi (*34*). The excess heavy element anomaly is most easily recognized by the prevalence of ZrO bands instead of the usual TiO and at high resolution by the enhancement of atomic lines from Sr through the light rare earths, including Tc.

Carbon stars. If the C/O ratio is only a few percent above unity, chemical equilibrium in a stellar atmosphere cooler than about 4500 K dictates that all the oxygen will be tied up in CO and the excess carbon will be free to form carbon compounds. In addition, the ^{13}C isotope is readily visible in all the compounds whereas ^{17}O and ^{18}O

are seen in the CO molecule in both oxygen and carbon stars. The observable composition parameters with high signal-to-noise data of 50,000 to 100,000 resolving power are then ^{7}Li, ^{12}C, ^{13}C, ^{14}N, ^{16}O, ^{17}O, and ^{18}O as well as other species ranging from sodium to europium. We will discuss these in order of increasing temperature of the nuclear reactions in which they are involved.

The two lithium isotopes are the most susceptible of all nuclear species to proton capture except for deuterium. As discussed above, ^{7}Li has a lifetime of about 10^6 years at $T = 4 \times 10^6$ K and $\rho = 1$ g cm^{-3} so it is impossible for lithium to survive quiescent H burning, not to mention the temperatures near 10^8 K that are required for the $3\alpha \rightarrow {}^{12}$C reaction. The reaction most likely to produce Li in carbon stars is ^{3}He$(\alpha,\gamma)^7$Be$(\beta^+\nu)^7$Li, which requires a temperature of at least 15×10^6 K and rapid convection to bring the ^{7}Be to a low enough temperature before decaying to ^{7}Li. Otherwise the ^{7}Li atoms immediately react with protons (*35*). Despite this restriction some carbon stars have lithium contents about 100 times that in young stars and meteorites. The range of Li abundances in carbon stars is from 10^4 solar to below one-tenth of the solar value (*36*). This shows the wide variety of mixing conditions throughout the envelopes of carbon stars all the way from below the 15×10^6 K level to the surface. There is no correlation of Li abundances with other abundances in carbon stars except that it is not present in stars with high space velocities and hence low masses. The ^{6}Li isotope is destroyed by proton capture at lower temperatures than is ^{7}Li and there is no thermal reaction in stellar interiors that produces it.

Like ^{7}Li, ^{12}C is produced at far higher temperatures than when it reacts with protons. The $3\alpha \rightarrow {}^{12}$C reaction is active at near 10^8 K whereas the CN cycle which largely converts ^{12}C to ^{14}N operates efficiently at 2×10^7 K. Hence, any mixing through a H-burning shell must be rapid to preserve the ^{12}C and convert a normal atmosphere into a carbon-rich one. Furthermore, He burning at sufficiently high temperatures can further process the ^{12}C by way of the ^{12}C$(\alpha,\gamma)^{16}$O reaction whose rate remains uncertain but is apparently larger than thought 5 years ago (*37*). Perhaps the large number of normal advanced AGB stars is due to ^{16}O rather than ^{12}C production during shell flashing. Carbon abundances in 30 carbon stars have been obtained from high-resolution spectra in the near-infrared region (*38*). The ratio of (^{12}C + ^{13}C)/O ranges from 1.01 to 1.76, but only two stars show a ratio over 1.34. This uniformity is rather startling in view of the instability of He shell flashing that produces the excess ^{12}C, and contrasts to the wide range of the ^{12}C/^{13}C ratio.

The ^{12}C/^{13}C ratio in carbon stars varies from near the CN-cycle equilibrium value of 3.5 to values near 90, the ratio in the sun and meteorites. There is a peak in the distribution near 55 with 57% of the stars having ^{12}C/^{13}C between 40 and 70. Only four stars out of 30 surveyed lie very close to 3.5 (*38*). The wide spread in the ^{12}C/^{13}C ratio shows either a range in CN cycling subsequent to helium burning or a range in mixing ratios between ^{12}C- and ^{13}C-rich material.

Like ^{13}C and in contrast to ^{7}Li and ^{12}C, ^{14}N is produced at a lower temperature than it is destroyed. If the CN and especially the CNO cycle goes to equilibrium much of the initial material with masses from 12 to 17 units is converted into ^{14}N. It is destroyed by ^{14}N$(\alpha,\gamma)^{18}$F$(\beta^+\nu)^{18}$O. For 30 carbon stars (*38*) the N/H ratios range from 0.1 solar to only 1.4 solar. Contrary to the predictions of CN-cycle equilibrium, nitrogen is not greatly enhanced, even in stars with ^{12}C/^{13}C $\simeq$ 3.5. One suspects substantial N depletion by α capture before ^{12}C and ^{13}C came into equilibrium (or else the ^{13}C would also be depleted by α capture) or possibly there was such a shortage of protons that most were used up in converting ^{12}C to ^{13}C. The paucity of stars with ^{12}C/^{13}C $\simeq$ 3.5 would agree with the latter. For most stars the excess ^{12}C has reached the surface without encountering protons at temperatures about 20×10^6 K for an appreciable length of time.

Oxygen is depleted by CNO cycling for temperatures above 25×10^6 K and is enhanced by high-temperature helium burning. In the carbon stars small oxygen depletions, reaching a factor 5 in the most extreme case and averaging a factor 1.8, are common. Hence, some CNO-cycle depletion has occurred. The high ^{13}C stars tend to be the low oxygen stars but this would only work if the full CNO equilibrium is reached because ^{16}O is depleted by ^{16}O$(p,\gamma)^{17}$F$(\beta^+\nu)^{17}$O$(p,\alpha)^{14}$N and a very high nitrogen would result. Oxygen depletion must have occurred earlier than nitrogen depletion by α capture. Since the sample in (*38*) consisted only of stars with ^{12}C + ^{13}C > O, stars in which helium burning had produced more ^{16}O than ^{12}C were excluded. However, no such stars are known, but they would be difficult to recognize. Possibly the cool stars surrounded by OH and H_2O masers have enhanced oxygen from this process.

The carbon stars show a wide range of oxygen isotope ratios. For ^{16}O/^{17}O the range is from 350 to 2000 with two stars showing larger, though very uncertain, ratios. The ^{16}O/^{18}O ratio is more difficult to obtain, but values from 700 to 2400 are found. In the interstellar medium of which these stars formed, the ratios of ^{16}O/^{17}O and ^{16}O/^{18}O are 1750 and 500, respectively (*39*). Hence, the ^{17}O [from earlier processing by way of ^{16}O$(p,\gamma)^{17}$F$(\beta^+\nu)^{17}$O] abundance has been substantially enhanced in most carbon stars and the ^{18}O abundance has probably been lowered in many. Most likely the increase of ^{17}O occurred during the first dredge-up as the star evolved up the giant branch the first time. Ratios from 170 to 1500 are seen in K and M giants (*40*) confirming this suggestion. For ^{16}O/^{18}O the K and M giants show no changes from the expected original value, whereas in some carbon stars the ^{18}O is depleted. For the ratio to be raised by a factor of 3 from its original value, at least

Table 2. Isotope ratios and nitrogen abundances as described by the range and median values of various classes of evolved stars.

Type of star	Sample size	^{12}C/^{13}C		^{16}O/^{17}O		^{16}O/^{18}O		[^{14}N/H]¶		s-Process
		Range	Med.	Range	Med.	Range	Med.	Range	Med.	
K giant	28	6.5–44	16	240– 550*	410	400– 600*	490	−0.2–+0.6	+0.4	No
M giant	8	7 –17	12	170–1050	425	425– 875	500	+0.2–+0.6	+0.4	No
MS + S	8	18 –71	26	550–3000	860	875–4600	1325	+0.4–+0.8	+0.5	Yes
SC	7	17 –53	30	75–1200	430	—	> 300†	−1.3–+0.9	+0.7	Yes
C, low ^{13}C	25	19 –97	59	550–4100	1275	700–2400	1200‡	−1.1–+0.2	−0.4	Yes
C, high ^{13}C	6	3.2–13	3.5	350– 850	400	—	—§	−0.8–+0.0	−0.5	No
R	9	4 –15	6	—	—	—	—	+0.4–+0.8	+0.6	No
Ba	4	8 –15	12	100– 500	300	60– 550	500‖	+0.2–+0.5	+0.3	Yes

*Only seven stars have been analyzed for oxygen isotopes. Arcturus has been omitted from the ^{16}O/^{17}O statistics because its ratio is 1500. Its ^{12}C/^{13}C ratio is surprisingly low, namely 7. †Rough estimates, no quantitative evaluation was attempted. ‡For four stars only lower limits from 240 to 700 could be estimated. §One star shows 1600; four others yielded lower limits ranging from 150 to 1000. ‖One additional star shows a lower limit of 500. ¶For the nitrogen abundance we show the logarithm of the N/H ratio minus the same quantity in the sun.

two-thirds of the material in the present photosphere must have suffered from gross depletion of ^{18}O. Present models cannot account for this (*41*). Since the nuclear reaction rates involving ^{18}O are quite well known now (*42*) the problem must lie with the stellar models, especially the depth and timing of the mixing events.

Many of the carbon stars show excess line strengths for heavy elements produced by neutron capture. The neutrons must be liberated by either $^{13}C(\alpha,n)^{16}O$ or $^{22}Ne(\alpha,n)^{25}Mg$ which requires temperatures near 10^8 or 2.5×10^8 K, respectively. Quantitive analyses of heavy elements in carbon stars have not been made with sufficient accuracy to warrant their description in detail at this time, but the excess of heavy elements, including Tc, in most (but not all) carbon stars, is beyond doubt (*43*).

In summary, the carbon stars show all the effects of helium burning with little effect of subsequent CN cycling (except for the stars with $^{12}C/^{13}C \simeq 3.5$). Somehow they have mixed material subjected to at least 10^8 K (to produce ^{12}C) and probably 2.5×10^8 K (to deplete ^{14}N and release neutrons) to the surface. Furthermore, they have done this without subjecting it to substantial CN or CNO cycling at the main H-He boundary that must lie between the helium-burning region and the surface. This calls for a complex sequence of mixing and shell burning rather than a single event that combines the two (*44*).

The S-type stars. In a small percentage of stars with oxide bands the ZrO bands are much stronger than those of TiO. This subclass of cool stars is easily distinguishable and was called type S (*45*). Stars that show both TiO and ZrO bands are called type MS. A small group of stars called type SC has carbon and oxygen abundances equal to within about 1%. Both elements are exhausted in CO formation so almost no other molecular bands are present. All the SC stars show heavy element enhancements. I will discuss all these subgroups together. Recent high dispersion analysis of these stars provides good data for the light elements (*41, 46*).

I summarize a comparison of the most important abundance parameters for all the major classes of peculiar cool stars in Table 2. The first two rows, K giants and M giants, are considered to be "normal" stars even though they show lower $^{12}C/^{13}C$ ratios than do unevolved stars and a spread in their oxygen isotope ratios. Clearly their $^{16}O/^{17}O$ ratios have been altered, probably by dredge-up of material enhanced in ^{17}O by proton capture since the $^{16}O/^{17}O$ ratio in the solar system is 2750 and in the interstellar medium is 1750. The barium stars, all of which show an excess of heavy elements and seem to be binaries, are included and will be discussed later. The low luminosity carbon stars, called type R, are also included.

The game that one plays in stellar modeling is to find a logical sequence of evolution starting with type M employing reasonable stellar mixing events, rather than "pipes and valves" (to move material at will rather than by the convection that is part of the stellar model), to produce the observed abundance ratios in the sequence. The standard sequence is M → MS → S → SC → C with no immediate subclassification of carbon stars into the high and low ^{13}C groups. The logic of this is a gradually increasing C/O ratio crossing unity at type SC. The median ratio of $^{12}C/^{13}C$ increases steadily along that sequence. The $^{16}O/^{17}O$ ratio does not fit because it goes down and then up (*47*). The $^{16}O/^{18}O$ ratio behaves similarly unless the analyses of the SC stars are systematically low as compared to the analyses of the MS stars and the C stars. All three groups show heavy element enhancement, though the degree of enhancement is known in only a few stars. Two SC stars, CY Cyg and UY Cen, have been analyzed in detail. They show enhancements of elements from Sr to the light rare earths by factors of 8 and 20, respectively (*48*).

I can momentarily raise $^{16}O/^{17}O$ and $^{16}O/^{18}O$ ratios in the SC star model to see if the morphological sequence might make sense for stars suffering helium shell flashes. Either the ^{12}C must increase by a factor of 5 or the ^{13}C must decrease by a similar factor to explain the change in $^{12}C/^{13}C$ ratio. The former does not agree with analyses of carbon stars (*38*), hence, depletion of ^{13}C by the $^{13}C(\alpha,n)^{16}O$ reaction must be invoked. It depletes ^{13}C and produces the neutrons to enhance the heavy elements by neutron capture. Qualitatively this works but the ratio of $^{13}C/^{56}Fe$ in an M star with $^{12}C/^{13}C = 12$ is near unity, whereas roughly 40 neutrons need to be captured by iron to produce the observed overabundances of the heavy elements including barium and the light rare earths. This preliminary morphological scheme is much too simple.

A gradual increase in $^{16}O/^{17}O$ is possible if some ^{16}O was produced along with ^{12}C. The depletion of ^{18}O between types M and MS without further change due to either $^{14}N(\alpha,\gamma)^{18}F(\beta^+,\nu)^{18}O$ or $^{18}O(\alpha,\gamma)^{22}Ne$ (even though the temperature—as implied by the enhancement of ^{12}C through the 3α reaction or the depletion of ^{13}C discussed above—is right for these reactions) seems strange. We are pushed toward the much more complicated sequence of flashes and mixing events described earlier (*44*).

The carbon stars with high ^{13}C present a special problem. Since they show little, if any, evidence for heavy element production by neutron capture they cannot be part of the hypothetical sequence. They must have produced ^{12}C and ^{13}C without altering their $^{16}O/^{17}O$ ratios. The ^{13}C-rich stars may be evolved R stars that we discussed under the helium flash (*28*). However, the ^{13}C-rich stars do not show the substantial—up to a factor of 5—enhancement of ^{14}N. If the ^{14}N had been depleted by α capture so would the ^{13}C, thus the sequence does not really work no matter what mixing scheme is invoked.

It appears that a careful analysis of the composition of the cool stars reveals no simple evolutionary sequence. Most likely a dispersion of initial masses results in a diversity of evolutionary sequences with the added possibility that the inherently unstable events involved with helium burning in a shell could also cause some sort of branching of the evolutionary sequence as a result of either a flash that is much more active than modeled or a mixing event that exceeds expectations and, hence, influences the subsequent evolution significantly.

There are two classes of very cool stars with little or no evidence of post–shell flash mixing. There are the M supergiants and longest period variables also of type M. Stars with masses greater than about 8 $M_{\odot}$ never develop a degenerate C-O core and, hence, do not suffer helium shell flashes. Thus, their interiors do not feel the sudden rise in the temperature gradient that can induce mixing. Envelope mixing due to the development of a superadiabatic gradient in the low-density hydrogen ionization region causes much mixing in the outer layers. Aside from homogenizing layers that included some CNO burning, as occurs during all first giant branch evolution, the M stars show no evidence of deep mixing that might bring fresh ^{12}C, and so forth, to the surface. None of these stars show Tc on their surfaces (*43*). The longest period variables, discovered by their OH molecular masers and detectable only in the infrared (hence, they are called OH/IR stars) probably belong to this class, that is, they had masses greater than about 8 $M_{\odot}$ before their present activity, which involves extensive mass loss. Since their envelopes show OH they have not convected much carbon to their surface layers. This may be the result of helium burning at sufficiently high temperature to produce more oxygen than carbon. This would enhance the OH and H_2O content of their atmospheres, thus enhancing maser activity.

Somewhat more difficult to understand are the coolest of the classical long period variables of type M. Their periods are comparable to the periods of carbon and S-type long period variables yet they do not show much evidence of mixing. Their periods lie mostly between 300 and 400 days with a few stars showing periods up to

500 days. Most M stars in this period range do show Tc but no other anomaly except possibly a deficiency of Nb, both of which may be the result of a very small degree of s-processing (*49*). Such stars must have suffered from only a minor shell flash, yet one that was able to induce deep mixing. It would appear that shell flashing without mixing is extremely rare.

Returning briefly to the question raised earlier: why do we see so many more stars of normal abundance than stars of types C and S? Although the total time spent on the AGB is several million years, the interval between shell flashes gradually decreases as the core mass increases (*33*). If the first few flashes fail to produce sufficient mixing to convert the star into a carbon or S-type star then the remaining lifetime after mixing may be quite short. Of course the time and depth of mixing may depend on secondary parameters such as rotation of the core and internal magnetic field in addition to mass.

The barium stars. The barium stars were recognized many years ago as giants with temperatures in the 4000 to 5000 K range and anomalously strong lines of a variety of elements from Sr through Ba and the light rare earths as well as the diatomic carbon compounds (*50*). The analysis of the composition of one Ba star played an important part in the development of the theory of neutron capture in stellar interiors (*51*). Recent measurements show that they are probably all spectroscopic binaries with degenerate companions (*52*).

I have compared the composition of the barium stars with other cool evolved stars in Table 2. Their enhanced heavy elements and oxygen isotope ratios make them appear to be similar to the SC stars. Their $^{12}C/^{13}C$ ratios are not terribly different from those in the SC stars though the spread is smaller. In fact, the coolest barium star, HD 121447, has also been classified as the hottest SC star (*53*).

The binary nature of the Ba stars has led to the natural hypothesis that their anomalous atmospheres have been transferred from their companions either by overflow of the Roche lobe or by a stellar wind (*54*). The data in Table 2 indicate that the carbon and oxygen isotopes of the Ba stars restrict their hypothesized red giant companions to SC stars. Why such mass transfer should occur only for such a rare and special type of star is extremely mysterious. Possibly the companion served more to strip down a larger giant by mass transfer to itself or to enhanced mass loss without recapture. Even then we still must ask why the stripping stopped precisely when they look like the SC stars. The $^{12}C/^{13}C$ ratios and luminosities of the barium stars are similar to those of the R stars (low-luminosity carbon stars) but it is difficult to relate them to the helium flash, and the latter show no excess of heavy elements.

Summary

I have shown how the chemical composition of stellar atmospheres may be profoundly affected by mixing processes. All three types of mixing, convective cores in massive main sequence stars, convective envelopes that scoop up previously processed material, and convective regions that interact with shell flashes, seem to cause greater mixing than predicted by current theories. Although progress along theoretical lines is extremely difficult—though far from impossible with modern computers—new insights on stellar mixing are being obtained by detailed analysis of the chemical and isotopic composition of stellar atmospheres (*55*).

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