# Abundance Variations within Globular Clusters 

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#### Abstract

■ Abstract Abundance variations within globular clusters (GCs), and of GC stars with respect to field stars, are important diagnostics of a variety of physical phenomena, related to the evolution of individual stars, mass transfer in binary systems, and chemical evolution in high density environments. The broad astrophysical implications of GCs as building blocks of our knowledge of the Universe make a full understanding of their history and evolution basic in a variety of astrophysical fields. We review the current status of the research in this field, comparing the abundances in GCs with those obtained for field stars, discussing in depth the evidence for H-burning at high temperatures in GC stars, describing the process of self-enrichment in GCs with particular reference to the case of the most massive Galactic GC ( $\omega$ Cen) , and discussing various classes of cluster stars with abundance anomalies. Whereas the overall pattern might appear very complex at first sight, exciting new scenarios are opening where the interplay between GC dynamical and chemical properties are closely linked with each other.


## 1. INTRODUCTION

Globular clusters (GCs) are vast and dense aggregates of stars, including up to millions of stars. They are among the most beautiful objects in the sky. However, their importance for astronomy goes far beyond their magnificent appearances: For several reasons GCs are among the building blocks of our knowledge of the Universe. They are intrinsically bright objects that can be observed at large distances. They may be almost as old as the known Universe, so that they can sample very early phases of the formation of galaxies and test the age of the Universe. Because GCs are made up of such a large population of stars, all located at virtually the same distance from us, and possibly of the same age and chemical composition, they
are the best examples of simple stellar populations, and thus natural laboratories to study stellar evolution. For these reasons, GCs have been subject to intensive investigations in the past decades, leading to large progress in our understanding of stellar and Galactic evolution, as well as to precious information for cosmology. This intensive scrutiny has led to the discovery of a number of peculiarities in the properties of GCs, showing that they are not as simple as initially imagined. Clusters evolve dynamically; there are significant and peculiar star-to-star chemical composition variations in them; and they host a wide variety of interesting and unusual objects (millisecond pulsars, blue stragglers, O- and B-subdwarfs, cataclysmic variables, etc.). A full understanding of these features requires an adequate modeling for the formation and evolution of stellar populations in GCs. We have begun to make only the first few exploratory steps in this direction: A comprehensive, robust model is still to be found.

This review is devoted to the presentation of the current status of observations and models about the chemical composition of GCs. Among others, previous reviews on this topic were presented by Smith (1987), Kraft (1994), and Sneden (1999, 2000). We concentrate mainly on the most recent developments in the field. However, it should be clear to the reader that chemical composition is only one aspect of the problem: It is now becoming increasingly evident that dynamics play a fundamental role not only in the evolution of a cluster as a whole, but also in the evolution of the individual stars in the clusters, and that a full understanding of the relevant mechanisms should take into consideration both of these issues. Recent comprehensive reviews concerning the dynamics of and the interplay with stellar evolution in GCs are by Bailyn (1995), Meylan \& Heggie (1997), and Hut et al. (2003).

This review is organized as follows: In Section 2 we compare abundances in GCs with those obtained for field stars; in Section 3 we discuss in detail the abundances of those elements involved in H-burning at high temperature; in Section 4 we present the case of $\omega$ Cen, the best case identified thus far for a well-developed chemical evolution history among GCs. In Section 5 we review a number of stars with abundance anomalies present in GCs: These may result from the evolution of single stars, as well as from the evolution of wide or close binary systems. Finally, brief conclusions are drawn in Section 6.

## 2. CLUSTER AND FIELD STAR ABUNDANCES OF HEAVY ELEMENTS

In previous reviews on GC chemistry and in Section 3 of this paper, most attention is focused on the light elements, including observationally accessible Li , $\mathrm{C}, \mathrm{N}, \mathrm{O}, \mathrm{Na}, \mathrm{Mg}$, and Al , which exhibit very large inter- and intracluster abundance variations. The abundances of these elements can be significantly altered by proton-capture fusion reactions that occur during quiescent hydrogen and helium burning of low-to-intermediate mass stars. In this section we consider heavier elements whose abundances should be immune to such processes. This discussion
generally follows the outline of a more abbreviated review by Sneden (2003). We consider in turn members of the Fe-peak, $\alpha$, and neutron-capture element groups.

First, we briefly comment on possible intracluster $[\mathrm{Fe} / \mathrm{H}]$ metallicity variations. Evolutionary models of GCs often predict that various generations of stars within clusters will experience significant Fe (and other element) enrichment from the ejecta of the earliest, massive core collapse SNe (Cayrel 1986; Brown, Burkert \& Truran 1991b, 1995; Murray \& Lin 1993; Parmentier et al. 1999). But apart from the case of $\omega$ Centauri, to be discussed in depth in Section 4, observational evidence for such star-to-star variations is sparse and not universally accepted. A case has been made for significant Fe abundance variations in M22 (LloydEvans 1975; Hesser, Hartwick \& McClure 1977; Lehnert, Bell \& Cohen 1991), but recently there have been suggestions that the observational data might be better explained by variations in interstellar reddening (Richter, Hilker \& Richtler 1999; Ivans et al. 2003b). More intriguing is the case of M92, which has a very low reddening value. Langer et al. (1998) found variations in $[\mathrm{Fe} / \mathrm{H}]$ values at the level of $\sim 0.1$ dex from their differential analysis of three giants. However, the modest range of these variations coupled with the small sample size suggests caution here, and the Langer et al. study should be confirmed and extended in future studies. On the other hand, low upper limits in the spread of the abundances of Fe (of the order of 0.04 dex, r.m.s.) have been found for several clusters from both spectroscopy and from the widths of main sequence (MS) and red giant branch (RGB) stars in the color magnitude diagrams CMDs (for summary and discussion, see Suntzeff 1993). At present the verdict on Fe metallicity variations in CGs except $\omega$ Cen must remain, "not proven."

The question addressed in the remainder of this section is whether GC abundance ratios are consistent with the more well-documented ratios in halo field stars. To this end the literature has been searched for high resolution ( $\mathrm{R} \equiv \lambda / \Delta \lambda \geq$ 30,000 ), high signal-to-noise (typically $\mathrm{S} / \mathrm{N} \geq 50$ ) cluster abundance studies. The R and $\mathrm{S} / \mathrm{N}$ restrictions generally limited the search to post-1990 CCD echelle spectrograph studies; the earliest paper referenced here is that of Gratton (1987). In Table 1 we list the clusters whose abundances will be considered in this section, the literature references from which the abundance ratios were taken, and four different estimates of the cluster metallicities. The $[\mathrm{Fe} / \mathrm{H}]_{\text {ZW84 }}$ values are those of Zinn \& West (1984), who derived their metallicity scale from a combination of low-resolution spectra and photometric Ca II K-line strength indices. The $[\mathrm{Fe} / \mathrm{H}]_{\mathrm{CG} 97}$ scale was developed by Carretta \& Gratton (1997) from their homogeneous analyses and reanalyses of high-resolution spectra of giant stars in 24 GCs. The $[\mathrm{Fe} / \mathrm{H}]_{\mathrm{KI} 03}$ estimates are from Kraft \& Ivans (2003), who also base their new cluster metallicity scale on high-dispersion spectra, but anchor it to just the [ $\mathrm{Fe} / \mathrm{H}]$ estimates from Fe II lines, which they argue are less affected by possible departures from local thermodynamic equilibrium (LTE) than are metallicities based on Fe I lines or on the mean of Fe I and Fe II. Finally, the $[\mathrm{Fe} / \mathrm{H}]_{\text {paper }}$ values are the average cluster values of the Fe I and Fe II means; this choice was made

TABLE 1 Open clusters data and references

| $[$ Fe/H] |  | \# Stars | Reference |
| :--- | :---: | :---: | :--- |
| NGC 1435 or M45 | +0.06 | 2 | King et al. 2000 |
| NGC 2112 | -0.09 | 2 | Brown et al. 1996 |
| NGC 2243 | -0.48 | 2 | Gratton \& Contarini 1994 |
| NGC 2264 | -0.23 | 4 | King et al. 2000 |
| NGC 6705 or M11 | +0.10 | 10 | Gonzalez \& Wallerstein 2000 |
| NGC 6819 | +0.09 | 3 | Bragaglia et al. 2001 |
| Mel 66 | -0.38 | 2 | Gratton \& Contarini 1994 |
| Mel 71 | -0.30 | 2 | Brown et al. 1996 |

because of the heterogeneity in the literature of metallicity estimates in individual studies.

These four cluster metallicity scales generally agree to at best $\pm 0.1$ dex, and we echo the conclusion of Kraft \& Ivans (2003) that "there exists no definitive set of cluster metallicities that are systematically reliable on the 0.02-0.05 dex level. Any discussion using cluster abundances needs to state clearly the underlying assumptions concerning models used, whether Fe I or Fe II or a mean thereof is what is meant by 'metallicity,' which effective temperature ( $\mathrm{T}_{\text {eff }}$ ) scale has been adopted, etc." Fortunately, the overall metallicity scales adopted do not seriously impact most of the discussion here, which will focus on trends in abundance ratios $[\mathrm{X} / \mathrm{Fe}]$ over the nearly three-decade range in $\mathrm{GC}[\mathrm{Fe} / \mathrm{H}]$ values. Abundance ratios $[\mathrm{X} / \mathrm{Fe}]$ typically can be determined more accurately than $[\mathrm{Fe} / \mathrm{H}]$ metallicites because abundance uncertainties induced by errors in $\mathrm{T}_{\text {eff, }}$, gravity $(\log g)$, and microturbulent velocity $\left(v_{t}\right)$ partially, or nearly completely, cancel in many comparisons of elements X and Fe . This is especially true if care is taken to form abundance ratios of species formed in similar ways in cool stellar atmospheres, e.g., $[\mathrm{Ni} / \mathrm{Fe}]$ determined from Ni I and Fe I lines, or $[\mathrm{Sc} / \mathrm{Fe}]$ determined from Sc II and Fe II lines. We concentrate on abundance ratios for which the formal errors in standard analyses are considered small, and argue that uncertainties at the 0.1 dex level in overall cluster metallicities $[\mathrm{Fe} / \mathrm{H}]$ do not perturb any of the major conclusions.

A more limited, noncomprehensive survey of the sparser literature on open clusters was conducted. In the discussions below, we show results when possible for the following clusters, which we list in Table 1 with their metallicities and number of stars employed in the paper cited in the form $([\mathrm{Fe} / \mathrm{H}]$, \# stars, reference):

Chemical compositions have been reported for far more field stars than cluster members, and large-sample ( $\sim 50-200$ ) abundance surveys covering large metallicity ranges have been published in recent years (see Table 2). Whenever possible we have employed the following surveys that include many metal-rich stars: Woolf,

TABLE 2 Cluster metallicities and abundance references

| NGC (Other) | $[\mathbf{F e} / \mathbf{H}]_{\text {ZW84 }}^{\text {a }}$ | $[\mathrm{Fe} / \mathbf{H}]_{\mathrm{CG} 97}^{\mathrm{b}}$ | $[\mathrm{Fe} / \mathrm{H}]_{\mathrm{KI} 103}^{\mathrm{c}}$ | $[\mathrm{Fe} / \mathbf{H}]_{\text {paper }}^{\mathrm{d}}$ | \# | Reference |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 104 (47 Tuc) | -0.71 | -0.73 | -0.70 | $\begin{aligned} & -0.64 \\ & -0.67 \end{aligned}$ | $\begin{aligned} & 4 \\ & 12 \end{aligned}$ | Brown \& Wallerstein (1992) <br> Carretta et al. (2004) |
| 288 | -1.40 | -1.17 | -1.41 | -1.39 | 13 | Shetrone \& Keane (2000) |
| 362 | -1.27 | -1.06 | -1.34 | -1.33 | 12 | Shetrone \& Keane (2000) |
| 1904 | -1.69 | -1.46 | -1.64 | -1.42 | 2 | Gratton \& Ortolani (1989) |
| 2298 | -1.85 | -1.64 | -1.97 | -1.90 | 3 | McWilliam, Geisler, \& Rich (1992) |
| 3201 | -1.61 | -1.37 | $-1.56$ | $\begin{aligned} & -1.48 \\ & -1.20 \end{aligned}$ | $\begin{aligned} & 18 \\ & 6 \end{aligned}$ | Gonzalez \& Wallerstein (1998) Covey et al. (2003) |
| 4590 (M68) | -2.09 | -1.95 | -2.43 | -1.92 | 2 | Gratton \& Ortolani (1989) |
| 4833 | -1.86 | -1.66 | -2.06 | -1.74 | 2 | Gratton \& Ortolani (1989) |
| 5272 (M3) | -1.66 | -1.43 | $-1.50$ | -1.51 | 23 | Sneden et al. (2004) |
| 5897 | -1.68 | -1.45 | -2.09 | -1.84 | 2 | Gratton (1987) |
| 5904 (M5) | -1.40 | -1.17 | -1.26 | $\begin{aligned} & -1.28 \\ & -1.29 \end{aligned}$ | $\begin{aligned} & 36 \\ & 25 \end{aligned}$ | Ivans et al. (2001) <br> Ramírez \& Cohen (2003) |
| 6121 (M4) | -1.33 | -1.11 | -1.15 | -1.18 | 36 | Ivans et al. (1999) |
| 6205 (M13) | -1.65 | -1.42 | -1.60 | -1.58 | 17 | Kraft et al. (1997), Sneden et al. (2004) |
| 6254 (M10) | $-1.60$ | $-1.36$ | $-1.51$ | $-1.53$ | 14 | Kraft et al. (1995) |
| 6287 | -2.05 | -1.90 | -2.20 | -2.08 | 3 | Lee \& Carney (2002) |
| 6293 | -1.92 | -1.73 | -2.00 | -2.09 | 2 | Lee \& Carney (2002) |
| 6341 (M92) | -2.24 | -2.17 | -2.38 | -2.34 | $\begin{aligned} & 3 \\ & 29 \end{aligned}$ | Shetrone (1996a) <br> Sneden et al. (2000b) |
| 6352 | $-0.51$ | -0.66 | -0.78 | -0.79 | 2 | Gratton (1987) |
| 6362 | -1.08 | -0.92 | -1.15 | -1.04 | 2 | Gratton (1987) |
| 6397 | -1.93 | -1.74 | -2.02 | -2.00 | 16 | Castilho et al. (2000) |
| 6528 | +0.12 | -0.63 |  | $+0.07$ | 4 | Carretta et al. (2001) |
| 6541 | -1.83 | -1.62 | $-1.83$ | -1.81 | 2 | Lee \& Carney (2002) |
| 6553 | -0.29 | -0.62 |  | $\begin{aligned} & -0.16 \\ & -0.55 \end{aligned}$ | $\begin{aligned} & 2 \\ & 5 \end{aligned}$ | Cohen et al. (1999) <br> Barbuy et al. (1999) |
| 6656 (M22) | -1.75 | $-1.53$ | $-1.71$ | -1.48 | 7 | Brown \& Wallerstein (1992) |
| 6715 (M54) | -1.42 | -1.19 | -1.47 | -1.55 | 5 | Brown et al. (1999) |
| 6752 | -1.54 | -1.30 | -1.57 | -1.40 | 38 | D. Yong et al. (2003) |
| 6838 (M71) | -0.58 | -0.68 | -0.81 | -0.78 | 25 | Ramírez \& Cohen (2002) |
| 7006 | -1.59 | -1.35 | -1.48 | -1.55 | 6 | Kraft et al. (1998) |
| 7078 (M15) | -2.15 | -2.04 | -2.42 | -2.40 | 18 | Sneden et al. (1997, 2000b) |
| -(Pal 5) | -1.47 | -1.24 | -1.28 | -1.31 | 4 | Smith, Sneden \& Kraft (2002) |
| -(Pal 12) | -1.14 | -0.96 | -0.95 | -0.98 | 2 | Brown, Wallerstein, \& Zucker (1997) |
| -(Rup 106) |  | -1.18 |  | -1.36 | 2 | Brown, Wallerstein, \& Zucker (1997) |
| -(Liller 1) | -0.21 | -0.61 |  | $-0.30$ | 2 | Origlia et al. (2002) |

${ }^{\text {a }}$ Zinn \& West (1984).
${ }^{\mathrm{b}}$ Carretta \& Gratton (1997).
${ }^{\mathrm{c}} \mathrm{Kraft}$ \& Ivans (2003a,b) except as noted in the text.
${ }^{\mathrm{d}}\left\langle[\mathrm{Fe} / \mathrm{H}]_{\mathrm{Fel}},[\mathrm{Fe} / \mathrm{H}]_{\mathrm{FeI}}\right\rangle$ from named references.

Tomkin \& Lambert (1995) ( $+0.3 \geq[\mathrm{Fe} / \mathrm{H}] \geq-0.9$ ); Feltzing \& Gustafsson (1998) $(+0.5 \geq[\mathrm{Fe} / \mathrm{H}] \geq-0.1)$; Fulbright (2000) $(0.0 \geq[\mathrm{Fe} / \mathrm{H}] \geq-3.0)$; Reddy et al. (2003) $(+0.1 \geq[\mathrm{Fe} / \mathrm{H}] \geq-0.7)$; Gratton et al. (2003) $(+0.1 \geq[\mathrm{Fe} / \mathrm{H}] \geq-2.6)$; and Simmerer et al. (2003) and J.A. Simmerer, T.C. Beers, C. Sneden \& B.W. Carney (unpublished manuscript) $(+0.1 \geq[\mathrm{Fe} / \mathrm{H}] \geq-0.7)$. In the metal-poor domain, we chiefly employed the studies of McWilliam et al. (1995) ( $-2.0 \geq[\mathrm{Fe} / \mathrm{H}] \geq-4.0$ ); Ryan, Norris \& Beers (1996) ( $-2.6 \geq[\mathrm{Fe} / \mathrm{H}] \geq-3.6$ ); Burris et al. (2000) ( $-0.9 \geq$ $[\mathrm{Fe} / \mathrm{H}] \geq-2.7)$; Johnson \& Bolte (2001) $(-1.7 \geq[\mathrm{Fe} / \mathrm{H}] \geq-3.2)$; Carretta et al. (2002) $(-2.0 \geq[\mathrm{Fe} / \mathrm{H}] \geq-3.6)$; Johnson (2002) $(-1.7 \geq[\mathrm{Fe} / \mathrm{H}] \geq-3.2)$; and Cayrel et al. (2003) $(-2.0 \geq[\mathrm{Fe} / \mathrm{H}] \geq-4.2)$. No attempt was made to normalize results of different surveys using stars in common among them. However, the recent work of Cayrel et al. includes many stars studied earlier by McWilliam et al. and Ryan et al., but with spectra that have better R and $\mathrm{S} / \mathrm{N}$ values. The Cayrel results have been adopted wherever possible. We note results from other more limited studies in discussions of individual elements.

### 2.1. Fe-Peak Elements

First, we consider abundance trends with respect to Fe for the Fe-peak elements $\mathrm{Mn}, \mathrm{Ni}$, and Cu . Several other elements were considered, but they were rejected for this exercise. For example, Ti can be claimed both by Fe-peak and $\alpha$-element groups; V abundances (determined from V I lines) are extremely sensitive to $\mathrm{T}_{\text {eff }}$ choices in cool GC giants; and $\mathrm{Cr}, \mathrm{Co}, \mathrm{Zn}$ have few accessible spectral features in the yellow-red spectral region where most cluster data are obtained. The most obvious choice for discussion is Ni : Lines of Ni I occur throughout the entire visible spectral domain, uncertainties in $[\mathrm{Ni} / \mathrm{Fe}]$ ratios in the literature are in the $0.05-0.10$ dex range, and Ni may be the most commonly reported abundance after Fe for field and cluster stars.

In the top panel of Figure 1 we plot $[\mathrm{Ni} / \mathrm{Fe}]$ ratios versus $[\mathrm{Fe} / \mathrm{H}]$ metallicities for disk and halo field stars, using data from the surveys cited above. The abundances shown here clearly indicate that $\langle[\mathrm{Ni} / \mathrm{Fe}]\rangle \sim 0^{1}$ over the entire Galactic metallicity range, although a small trend with Galactocentric distance may be present (R. Gratton, unpublished manuscript). There are no significant differences between the results of different investigations. The star-to-star scatter in $[\mathrm{Ni} / \mathrm{Fe}]$ increases with decreasing $[\mathrm{Fe} / \mathrm{H}]$, but it is not clear whether the larger scatter at low metallicity is astrophysical in origin or simply a product of observational/analytical uncertainties. At lower metallicities, for example, line absorption weakens considerably, yielding fewer spectral features available for abundance analysis. Additionally, the most metal-poor stars often are distant and thus faint. Both of these effects can limit the number and accuracy of line measurements in lower metallicity stars, which may explain their larger star-to-star scatter in $[\mathrm{Ni} / \mathrm{Fe}]$.

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Figure 1 Correlation of $[\mathrm{Ni} / \mathrm{Fe}]$ abundance ratios with $[\mathrm{Fe} / \mathrm{H}]$ values over nearly the full metallicity range of the Galactic halo and disk. In the top panel, only field stars are plotted, with different symbols representing data from the surveys named in the panel legend. In the bottom panel, all field stars are plotted as small filled circles, and abundances for GCs (large filled circles) and open clusters (open circles) have been added.

In the bottom panel of Figure 1 we re-plot the field stars, this time not distinguishing between different studies, and add $[\mathrm{Ni} / \mathrm{Fe}]$ data for GCs and open clusters. This panel illustrates the well-known truncation of the GC metallicity domain at $[\mathrm{Fe} / \mathrm{H}] \sim-2.5$. There are no GCs in the Galactic ultra-metal-poor domain; substantial chemical enrichment apparently occurred prior to the formation of the clusters that exist today.


Figure 2 Correlation of $[\mathrm{Ni} / \mathrm{Fe}]$ with $[\mathrm{Fe} / \mathrm{H}]$, with the metallicity range limited to that populated by open and GCs. Error bars representing the larger between 0.03 dex and the star-to-star $[\mathrm{Ni} / \mathrm{Fe}]$ abundance standard deviations $\sigma$ have been added to the cluster points.

To see field and cluster star Ni abundances more clearly in their region of metallicity overlap, in Figure 2 we re-plot the bottom panel of Figure 1 but only for $[\mathrm{Fe} / \mathrm{H}]<-2.6$. Error bars have been added to the cluster points that represent the single-star standard deviations $\sigma$, and several possibly anomalous individual clusters have been noted by name. With few exceptions, we find $\langle[\mathrm{Ni} / \mathrm{Fe}]\rangle \simeq 0.0$ in all stellar groups. No significant differences are found between $[\mathrm{Ni} / \mathrm{Fe}]$ in field stars, GCs and open clusters. This is not extremely surprising, as predictions of outputs from Type I and Type II supernovae (SNe; see Woosley, Langer \& Weaver 1995; Iwamoto et al. 1999) suggest that Ni production approximately tracks that of Fe .

Of the apparently discordant clusters named in Figure 2, NGC 5897 and NGC 6362 probably can be ignored since their abundances have been taken from Gratton (1987), the earliest study included here, and only two stars were analyzed in each of these clusters. New abundance studies certainly are desirable for NGC 5897 and NGC 6362. Of more immediate interest are the apparent 0.3-0.4 dex deficiencies of $[\mathrm{Ni} / \mathrm{Fe}]$ in Rup 106 and Pal 12 (Brown, Wallerstein \& Zucker 1997). These
two clusters are relatively young, outer-halo clusters (Harris 1996) ${ }^{2}$ that might not share a common origin with the majority of Galactic GCs. Rup 106 and Pal 12 are more notably underabundant in $\alpha$ elements (Brown et al. 1997), so we defer further discussion of them to Section 2.2. Finally, the open cluster M11 (Gonzalez \& Wallerstein 2000) appears to have significant Ni deficiencies. There is no easy nucleosynthetic explanation for this phenomenon, especially because other open clusters have no obvious Ni anomalies. This open cluster deserves renewed spectroscopic investigation.

Cu and Mn are two odd-Z elements of the Fe-peak that exhibit significant departures from solar abundance ratios among metal-poor stars: Both elements have subsolar abundance ratios with respect to Fe . The literature on these two elements is not as extensive as it is for Ni because there are fewer convenient Cu I and Mn I transitions and because hyperfine structure must be taken into careful account in their abundance computations. In the top panel of Figure 3 we show the $[\mathrm{Cu} / \mathrm{Fe}]$ trend with metallicity. The field-star results are only from Reddy et al. (2003) and Mishenina et al. (2002); these data reproduce the familiar severe drop in $[\mathrm{Cu} / \mathrm{Fe}]$ discovered by Sneden, Gratton \& Crocker (1991a). A new systematic Cu abundance survey by Simmerer et al. (2003) of GCs studied earlier by the Lick-Texas group provides all of the cluster points in this panel, from which one concludes that clusters and field stars share the same Cu deficiencies.

The bottom panel of Figure 3 demonstrates that the situation may be the same for Mn , although the cluster data are quite sparse. There are Mn abundances for only five GCs and one open cluster. With these few points it is difficult to make too much of the single anomaly, NGC 6528 (Carretta et al. 2001), but this question can be easily addressed with more data on Mn in GCs (like Cu , there exist Mn I lines in extant high-resolution cluster spectra that simply have yet to be analyzed).

## 2.2. $\alpha$ Elements

The $\alpha$ elements are those light elements ( $\mathrm{Z} \leq 22$ ) whose most abundant isotopes are multiples of ${ }^{4} \mathrm{He}$ nuclei: $\mathrm{C}, \mathrm{O}, \mathrm{Ne}, \mathrm{Mg}, \mathrm{Si}, \mathrm{S}, \mathrm{Ar}, \mathrm{Ca}$, and Ti. However, the noble gas elements Ne and Ar cannot be detected in cool stars; S has only very weak spectral lines in the near-IR; and Ti can be synthesized in several different nucleosynthesis events. Additionally, observation and theory agree that the abundances of $\mathrm{C}, \mathrm{O}$, and, to a lesser extent, Mg can be altered during the quiescent evolutions of low-to-intermediate mass stars in proton fusion reactions (see Section 3). Therefore the easily observed "pure $\alpha$ " representatives for GCs are reduced to just Si and Ca.

The general abundance trend of Si and Ca elements with metallicity in both field and cluster stars has been known for some time: Both $[\mathrm{Ca} / \mathrm{Fe}]$ and $[\mathrm{Si} / \mathrm{Fe}]$ increase as $[\mathrm{Fe} / \mathrm{H}]$ declines from 0 to -1 , attaining values of +0.2 to +0.5 and retaining them at all lower metallicities. These overabundances in halo field stars are interpreted in terms of a decrease in the contributions of Type Ia SNe to Fe

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Figure 3 Correlation of $[\mathrm{Cu} / \mathrm{Fe}]$ (top panel) and $[\mathrm{Mn} / \mathrm{Fe}]$ (bottom panel) with $[\mathrm{Fe} / \mathrm{H}]$. The symbols are identified in the panel legends.
production at the low metallicities characteristic of stars that formed very early in the Galaxy's history. Abundances of Ca are generally more reliable than are those of Si , probably because Ca I has more accessible transitions than does Si I, with more reliable transition probabilities. Smaller star-to-star scatter is usually more often found in $[\mathrm{Ca} / \mathrm{Fe}]$ than $[\mathrm{Si} / \mathrm{Fe}]$ in individual GCs . In Figure 4 we show the run of $[\mathrm{Ca} / \mathrm{Fe}]$ ratios with $[\mathrm{Fe} / \mathrm{H}]$, which suggests that the majority of GCs and open clusters have the same Ca abundances as do field stars of similar metallicities. The cluster-to-cluster scatter is small, especially considering that no attempt has been


Figure 4 Correlation of $[\mathrm{Ca} / \mathrm{Fe}]$ with $[\mathrm{Fe} / \mathrm{H}]$ in field and cluster stars. The lines, symbols, and data sources are as in Figure 2.
made to normalize different investigations to a common system; for low-metallicity $([\mathrm{Fe} / \mathrm{H}]<-1) \mathrm{GCs},\langle[\mathrm{Ca} / \mathrm{Fe}]\rangle=+0.25 \pm 0.02(\sigma=0.11,28$ clusters $)$.

The most obvious exceptions to the cluster/field agreement are labeled in Figure 4. The large [ $\mathrm{Ca} / \mathrm{Fe}]$ for NGC 4833 was reported in a relatively early paper by Gratton \& Ortolani (1989) from a sample of only two stars; this value should be viewed with caution. As noted above, the younger outer-halo clusters Rup 106 and Pal 12 have deficiencies of all $\alpha$ elements (Brown et al. 1997). A handful of halo field stars also have $\alpha$-element underabundances (Ivans et al. 2003a, and references therein). These anomalous abundance ratios (not seen in any other GCs studied to date) may suggest that Rup 106 and Pal 12 are not native to our Galaxy, but have been captured from close encounters by the Galaxy and local-group dwarf galaxies. More simply, the heavy-element material of these two clusters probably was generated in regions with larger Type I to Type II SN nucleosynthesis output than is typical in the metal-poor interstellar medium (ISM). Perhaps the early initial-mass functions (IMFs) of those regions were unusually deficient in high-mass stars, or star formation proceeded at a slower rate that allowed lower-mass Type I events
to contribute to the element mix. Equally interesting are the high $[\mathrm{Ca} / \mathrm{Fe}]$ ratios of the most metal-rich GCs (Liller 1, NGC 6553, and NGC 6528); these values are about a factor of two larger than those of open clusters or field (disk) stars at comparable metallicities. In fact, with the exceptions of Rup 106 and Pal 12, the entire GC population appears to exhibit a single $[\mathrm{Ca} / \mathrm{Fe}]$ ratio, regardless of metallicity, indicating continuing dominance of Type II supernovae in generating their element mix even at very high $[\mathrm{Fe} / \mathrm{H}]$ values. However, this conclusion is based on just three metal-rich GCs only, and certainly Ca abundances in other metal-rich clusters should be obtained.

Silicon is also overabundant in low-metallicity field and cluster stars. Lee \& Carney (2002) suggested that [ $\mathrm{Si} / \mathrm{Fe}]$ ratios are inversely correlated with GC galactocentric distance, and $[\mathrm{Ti} / \mathrm{Fe}]$ ratios are directly correlated, creating a sharply decreasing [ $\mathrm{Si} / \mathrm{Ti}$ ] with increasing distance from the Galactic center. Fulbright (2000) and Stephens \& Boesgaard (2002) found that field stars exhibit the same galactocentric distance trend in [Si/Fe]. Following Fulbright (2003), in Figure 5 we plot $[\mathrm{Si} / \mathrm{Fe}]$ ratios for GCs as functions of apogalactic distance R (apo), using orbit solutions of Dinescu, Girard \& van Altena (1999) when available, otherwise using present galactocentric distance $\mathrm{R}(\mathrm{GC})$ from Harris (1996). A mean [Si/Fe] trend with $R$ (apo) for field stars is reproduced from Fulbright's (2003) figure 1.5. Neglecting the anomalous clusters Rup 106 and Pal 12 , the $[\mathrm{Si} / \mathrm{Fe}]$ variation with R is similar in field and cluster stars. However, adding cluster Ca abundances to this same figure yields a different story, as $[\mathrm{Ca} / \mathrm{Fe}]$ does not appear to vary at all with R, as argued by, for example, Lee \& Carney (2002). Those authors suggest that Type II SNe of different mass ranges contributed more to element generation in the inner and outer halos, as a way of understanding the variation in $[\mathrm{Si} / \mathrm{Fe}]$. The lack of related $[\mathrm{Ca} / \mathrm{Fe}]$ variations would fit with this idea, as the production of Si in Type II SNe is a much more sensitive function of progenitor mass than is that of Ca (Woosley et al. 1995; see figure 6 of McWilliam 1997). The reason for this suggested differentiation in SNe mass ranges is not as yet obvious. But for $\alpha$-elements Si and Ca , abundances in halo field stars and GCs agree to first approximation, just as they do for the Fe-peak elements. This accord might break down with further discussion and exploration of kinematic correlations of $\alpha$ elements for the field stars (R. Gratton, unpublished manuscript) and Galactic orbital data to augment the results of Dinescu et al. (1999) would be welcome.

### 2.3. Neutron-Capture Elements

All abundant isotopes of elements with $\mathrm{Z}>30$ are synthesized in neutron bombardment reactions. The neutron-capture ( $n$-capture) reaction sequence can occur either in the $s$-process, in which the neutron ingestion rates by target-seed nuclei are small compared with $\beta$-decay rates, or in the $r$-process, with these relative rates reversed. The $s$-process can occur during quiescent helium-burning in low-to-intermediate-mass stars, and is chiefly responsible for Solar System abundances of elements such as $\mathrm{Sr}, \mathrm{Zr}, \mathrm{Ba}$, and La . The $r$-process arises in events surrounding


Figure $5[\mathrm{Ca} / \mathrm{Fe}]$ and $[\mathrm{Si} / \mathrm{Fe}]$ ratios as functions of distance of the globular clusters from the Galactic center. When possible, the apogalacticon distance R(apo) from Dinescu et al. (1999) is used; otherwise, the present galactocentric distance R(GC) from Harris (1996) is adopted. Filled circles and $\times$ symbols represent Ca and Si abundances, with different symbol sizes indicating whether R (apo) or $\mathrm{R}(\mathrm{GC})$, respectively, is being plotted. A dashed line represents the mean $[\mathrm{Ca} / \mathrm{Fe}]$ value in GCs, neglecting Rup 106 and Pal 12 . The dotted line represents the average $[\mathrm{Si} / \mathrm{Fe}]$ trend with R (apo) found by Fulbright (2000) for halo field stars.
the deaths of high-mass stars and is mainly responsible for the Solar System abundances of, for example, Rh, Ag, Eu, and Pt.

Most GC abundance studies have been conducted with yellow-red region spectra because the brightest cluster members are cool giants that have much lower fluxes in the blue-violet than at longer wavelengths. Unfortunately, most strong transitions of $n$-capture elements (always arising from their ionized species) occur at wavelengths below $5000 \AA$. This has severely limited the number $n$-capture abundances derived for GCs. Most often, studies will report Ba and Eu abundances, sometimes La, and to a lesser extent $\mathrm{Y}, \mathrm{Zr}$, and Nd abundances. For this reason our comments will be limited to just $\mathrm{Ba}, \mathrm{La}$, and Eu . The surrogate for $r$-process nucleosynthesis is Eu , and those for the $s$-process are Ba and La .

At the very lowest metallicities $([\mathrm{Fe} / \mathrm{H}]<-2.5)$, two prominent variations are seen in field-star $n$-capture element abundances. First, their bulk amounts vary from star to star by more than two orders of magnitude, roughly $-0.5 \geq[n$-capture $/ \mathrm{Fe}] \geq$ +2.0 (e.g., McWilliam et al. 1995, Burris et al. 2000, Truran et al. 2002). Second, the abundance distribution among the $n$-capture elements ranges from $r$-process dominance (characterized by $[\mathrm{Eu} / \mathrm{Ba}] \sim+1$; e.g., Cowan et al. 2002, Hill et al. 2002, Sneden et al. 2003) to $s$-process dominance ([Eu/Ba] $\sim-1$; e.g., Aoki et al. 2002, Lucatello et al. 2003, Van Eck et al. 2003).

Among halo field stars of less extreme metal deficiency $([\mathrm{Fe} / \mathrm{H}]>-2.5)$ the star-to-star variations are less extreme, but on average $[\mathrm{Eu} / \mathrm{Fe}] \geq 0$ and $[\mathrm{Eu} / \mathrm{Ba}] \geq 0$. Abundances in GCs are generally similar. In Figure 6 we illustrate these trends. Consider first the data in the top panel just on the $r$-process element Eu. We emphasize that Figure 6's metallicity lower limit of $[\mathrm{Fe} / \mathrm{H}]=-2.6$ eliminates the most extreme examples of extremely metal-poor but $r$-process-rich stars $([\mathrm{Fe} / \mathrm{H}] \sim-3.0,[\mathrm{Eu} / \mathrm{Fe}] \simeq+1.6)$ such as CS 22892-052 (Sneden et al. 2003) and CS 31082-001 (Hill et al. 2002). Among clusters, Eu exhibits little variation: For 20 GCs with $[\mathrm{Fe} / \mathrm{H}]<-1$, including the obviously anomalous Rup 106, $\langle[\mathrm{Eu} / \mathrm{Fe}]\rangle=+0.40 \pm 0.03(\sigma=0.13)$. Excluding Rup 106, the mean Eu abundance is changed only slightly: $\langle[\mathrm{Eu} / \mathrm{Fe}]\rangle=+0.42 \pm 0.02(\sigma=0.09)$. Thus, the cluster-to-cluster scatter in the $r$-process element $[\mathrm{Eu} / \mathrm{Fe}]$ appears generally to be no larger than it is in $[\mathrm{Ni} / \mathrm{Fe}]$ or $[\mathrm{Ca} / \mathrm{Fe}]$.

In the bottom panel of Figure 6 we show the run with $[\mathrm{Fe} / \mathrm{H}]$ of the quantity $[\mathrm{Eu} / \mathrm{Ba}, \mathrm{La}]$, where " $\mathrm{Ba}, \mathrm{La}$ " is defined as the mean of Ba and La abundances when both are available, or as just the Ba or La abundance for the remaining stars. Because both elements are $s$-process-dominated and different observational uncertainties attend the abundances of Ba II and La II lines observed in field and cluster stars, probably their abundance means are more reliable than either $[\mathrm{Ba} / \mathrm{Fe}]$ or $[\mathrm{La} / \mathrm{Fe}]$ alone. Inspection of the bottom panel of Figure 6 suggests that field star and cluster values of $[\mathrm{Eu} / \mathrm{Ba}, \mathrm{La}]$ are in rough accord, but the scatter in $[\mathrm{Eu} / \mathrm{Ba}, \mathrm{La}]$ is much higher than it is for $[\mathrm{Eu} / \mathrm{Fe}]$. Again, computing averages for clusters with $[\mathrm{Fe} / \mathrm{H}]<-1$, we get $\langle[\mathrm{Eu} / \mathrm{Ba}, \mathrm{La}]\rangle=+0.23 \pm 0.04$ ( $\sigma=0.21$, 28 clusters $)$. These values would not be significantly different for either $\langle[\mathrm{Eu} / \mathrm{Ba}]\rangle$ or $\langle[\mathrm{Eu} / \mathrm{La}]\rangle$ alone. Thus, on average, GCs, like halo field stars, are modestly $r$-process-rich compared with Solar System material. This is consistent with the greater influence of massive-star nucleosynthesis in the $n$-capture-element domain, just as it is for $\alpha$ elements.

Some anomalous clusters called out by name in Figure 6 deserve extended comment here. First, note that Rup 106 exhibits by far the lowest [ $\mathrm{Eu} / \mathrm{Fe}$ ] value of any GC: The mean is $[\mathrm{Eu} / \mathrm{Fe}]_{\text {Rup } 106}=+0.02$, $(\sigma=0.07$, two stars; Brown et al. 1997). But for the "companion" young outer-halo GC Pal 12, that same study derived $[\mathrm{Eu} / \mathrm{Fe}]_{\text {Pal12 }}=+0.55(\sigma=0.20$, two stars $)$. Moreover, with nearly identical $[\mathrm{Eu} / \mathrm{Ba}, \mathrm{La}]_{\mathrm{Rup} 106} \sim[\mathrm{Eu} / \mathrm{Ba}, \mathrm{La}]_{\text {Pal12 }} \sim+0.4$, it is clear that the $r-/ s$ process ratios of these two unusual clusters are little different than in most other GCs; Ba, La, and Eu do not provide much information with which to distinguish


Figure 6 Correlations of $n$-capture element abundance ratios with $[\mathrm{Fe} / \mathrm{H}]$. Symbols and lines are as in Figure 2. In the top panel, $[\mathrm{Eu} / \mathrm{Fe}]$ ratios are shown to illustrate the trend in $r$ abundances with metallicity. In the bottom panel, $[\mathrm{Eu} / \mathrm{Ba}, \mathrm{La}]$ are shown to illustrate the relative strengths of the $r$ - and $s$-processes as functions of metallicity. When possible, the abundances of Ba and La have been averaged; otherwise, either Ba or La abundances are shown.
formation scenarios of Rup 106 and Pal 12 from those of the rest of the cluster population.

In the top panel of Figure 6 the point for M15 is labeled, not because of an aberrant Eu abundance, but to call attention to the large star-to-star scatter: $[\mathrm{Eu} / \mathrm{Fe}]_{\mathrm{M} 15}=+0.49 \pm 0.05(\sigma=0.20,18$ stars $)$. This scatter in $[\mathrm{Eu} / \mathrm{Fe}]$ is the
largest yet discovered in any well-observed cluster, and it is astrophysical in nature, not a result of observational/analytical errors. Sneden et al. (1997) found that M15 has a star-to-star spread of $\sim 0.4$ dex in $[\mathrm{Eu} / \mathrm{Fe}]$, and (with the exception of one star) the Ba abundances vary from star to star in concert with the Eu abundances. The point for M15 in the bottom panel of Figure 6 indicates consistency of its $r$ - $/ s$ process ratio with most other clusters: $[\mathrm{Eu} / \mathrm{Ba}, \mathrm{La}]_{\mathrm{M} 15}=+0.39 \pm 0.03(\sigma=0.14$, 18 stars). Sneden et al. (2000b) extended this result by acquiring blue spectra of three M15 giants, determining abundances of eight elements with $56 \leq \mathrm{Z} \leq 66$, and demonstrating that these abundances were consistent with $r$-process dominance in their production. The star-to-star bulk $n$-capture scatter in M15 giants constitutes essentially the only reported indication of "local" massive-star nucleosynthesis in normal GCs.

Finally, consider the $n$-capture elements of $\mathrm{M} 4([\mathrm{Fe} / \mathrm{H}]=-1.15)$ and M 5 $([\mathrm{Fe} / \mathrm{H}]=-1.26)$. These two clusters have nearly identical and unremarkable Eu abundances: $[\mathrm{Eu} / \mathrm{Fe}] \simeq+0.4$ (Figure 6, top panel). However, the $[\mathrm{Eu} / \mathrm{Ba}, \mathrm{La}]$ values differ by $\sim 0.6$ dex (Figure 6, bottom panel), far greater than analytical errors. This is clear evidence for an $s$-process difference between these two clusters. The material of M4 that formed the stars observed today was infused with substantial amounts of ejecta of former asymptotic giant branch (AGB) intermediate-mass (probably) stars, whereas the material of M5 was not. The Galactic orbits of these two similar metallicity clusters are very different, as indicated by their values of apogalactic distances (Dinescu et al. 1999): R (apo) $=35.4$ for M5, and 5.8 for M4. Is this an indication of a halo-cluster versus disk-cluster population effect? The statistics currently are insufficient to address this question.

## 3. H-BURNING AT HIGH TEMPERATURES IN GLOBULAR CLUSTERS

### 3.1. The Beginning: Globular Clusters Are Not So Simple

A quarter of a century ago, Cohen (1978) was the first to notice that in RGB stars of M13 and M3 a scatter in Na abundances existed that exceeded the observational errors. Two years later, Peterson (1980) found star-to-star variations of an order of magnitude in the Na abundances of stars of M13. Norris et al. (1981) discovered differences of a similar magnitude in the Al I resonance line strengths in NGC 6752. Additionally, a few reports of non-constant O abundances in clusters began to appear in the literature (e.g., Pilachowski, Sneden \& Wallerstein 1983; Leep, Wallerstein \& Oke 1986; Hatzes 1986).

The discoveries of $\mathrm{O}, \mathrm{Na}$, and Al variations were further pieces of evidence added to an already complex GC light element phenomenology. A lot of work already had been done on C and N abundances using photometric or low-dispersion indices for large samples of cluster stars in different evolutionary phases. Several studies, starting from Osborn (1971), showed that GCs are very heterogeneous in C and N. Reviews on this subject can be found in, for instance, Smith (1987)
and Kraft (1994). Here we summarize the main points of these studies, with a few recent updates.

- Molecular band-strengths of CN and CH are generally found to be anticorrelated among stars with similar temperature and gravity (i.e., at the same evolutionary phase) in most GCs: CN-strong stars have weak CH bands and vice versa, the strong CN bands being produced by the high N content in the atmospheres of these stars.
- The detailed pattern of CN and CH differs from cluster to cluster. Most of the GCs surveyed present a bimodal distribution of CN strength on the RGB; some clusters have predominantly CN -strong stars (e.g., M13), whereas in other similar metallicity clusters the stars are mostly CN -weak (e.g., M3, Suntzeff 1981). Moreover, some clusters show a CN-bimodality on the RGB, but one of the two components (weak or strong) is missing in later evolutionary stages (e.g., M5, Smith \& Norris 1993); other clusters have a bimodal distribution also on the HB and AGB (Smith \& Norris 1993).
- Anticorrelated variations in CN and CH are seen all the way down to MS turn-off (TO) stars in all clusters where data are available: 47 Tuc (see Cannon et al. 1998, and Harbeck, Smith \& Grebel 2003, for references to the many studies of this cluster), in NGC 6752 (Suntzeff \& Smith 1991); and in M71 (Cohen 1999, Ramírez \& Cohen 2002).
- An anticorrelation between [C/Fe] ratios and the stellar luminosities is seen in several low- and intermediate-metallicity clusters (M92, Carbon et al. 1982, Langer et al. 1986, and recently Bellman et al. 2001; M15, Trefzger et al. 1983; NGC 6397, Briley et al. 1990; M3 and M13, Suntzeff 1981; NGC 6752, Suntzeff \& Smith 1991).
- In some clusters (see recent results of Cohen, Briley \& Stetson 2002 for M5) the sum $\mathrm{C}+\mathrm{N}$ increases as C decreases; this also suggests that the products of incomplete ON -cycle processing are involved, because $\mathrm{C}, \mathrm{N}$, and O are catalysts and their sum has to remain constant.
- The C and N abundances in GCs are strikingly different than in field giants (Carbon et al. 1982; Langer, Suntzeff \& Kraft 1992), which commonly show very weak CN bands and strong CH bands. This is an indication that GC environments play an important rôle.
- The isotopic ratio ${ }^{12} \mathrm{C} /{ }^{13} \mathrm{C}$ in the more luminous GC giants is very low, typically in the range 3.5 (the equilibrium value of the CNO cycle) to 10 (Brown \& Wallerstein 1989; Smith \& Suntzeff 1989; Bell, Briley \& Smith 1990; Brown, Wallerstein \& Oke 1991a; Briley et al. 1997; Pavlenko, Jones \& Longmore 2003). Shetrone (2003) has shown that in NGC 6528 and M4 this ratio declines steeply with increasing luminosity along the RGB.
- Finally, the C and N abundance anomalies are related to those of the light elements: $\mathrm{Na}, \mathrm{Al}$, and Mg are correlated with the CN -strength in metal-poor clusters, only with Na and Al in clusters of intermediate metallicity, whereas
only Na is found correlated to the CN in metal-rich clusters such as 47 Tuc (Smith \& Wirth 1991), suggesting metallicity-dependent variations (Cottrell \& Da Costa 1981).

The C and N data by themselves do not demand that GC stars are initially formed with different chemical signatures because these two elements can be synthesized and destroyed by nuclear burning in the cores of low-mass stars. It is only necessary to show that a mixing mechanism exists that is able to bring to the surface these fusion products. However, standard stellar evolutionary models fail to explain the observed pattern. In these models, the so-called first dredge-up is the only predicted substantial mixing episode in low-mass stars. As such stars start to climb up the RGB, the convective envelope deepens until it reaches the regions where nuclearprocessed (by the CNO cycle) matter is found. Theoretical predictions (Iben \& Renzini 1984) suggest that for stars of solar mass and metallicity, the first dredgeup episode will decrease the atmospheric abundance of ${ }^{12} \mathrm{C}$ by a factor $<2$, increase the abundance of ${ }^{14} \mathrm{~N}$ by a corresponding amount, and lower the ${ }^{12} \mathrm{C} /{ }^{13} \mathrm{C}$ ratio from the initial value (assumed to be solar at $\sim 90$ ) down to about 20 to 30 . At the end of MS evolution, the surface Li abundance suffers a sudden decrease owing to the expansion of the convective envelope and consequent Li dilution.

The first dredge-up depends only on mass and initial chemical composition and therefore it cannot explain features such as the CN bimodal distributions seen in GC RGB stars. The discrepancy becomes worse as metallicity decreases, because in this case standard metal-poor low-mass stellar models predict that the convective envelope will never dig deep enough to come in contact with the H-burning shell along the entire RGB evolution. This has been a long-standing problem for even moderately metal-poor field stars, which often possess much lower C abundances and ${ }^{12} \mathrm{C} /{ }^{13} \mathrm{C}$ ratios than predicted by standard models (e.g., Day, Lambert \& Sneden 1973; Cottrell \& Sneden 1986; Sneden, Pilachowski \& VandenBerg 1986; Gilroy \& Brown 1991). Thus, homogenization of inner and outer regions via an additional mixing episode must be a basic feature of evolving Pop. II red giants.

A "bridge" must be postulated to connect the nuclearly processed inner regions with the deepening convective envelope. Sweigart \& Mengel (1979) showed that meridional currents, likely induced by slow core rotation, could be activated between the H-burning shell and the base of the convective envelope, after the molecular weight barrier left behind by the retreating envelope is erased by the advancing H -shell, hence, not before the luminosity of the RGB-bump (Thomas 1967, Iben 1968). The ensuing mixing could explain several variations found among the lighter elements in GC and field giants, its observed effects being lower in higher metallicity giants, where the molecular weight barrier is more difficult to overcome (Sweigart \& Mengel 1979, Charbonnel 1995).

### 3.2. High-Resolution Spectroscopic Surveys:

## A New Feature Stands Out

The advent of improved and more efficient echelle spectrographs at the beginning of the 1990s allowed study of the previously neglected element O in GCs.

Starting in 1989, a collaboration between The Lick Observatory and McDonald Observatory (Texas) led by R.P. Kraft began a systematic spectroscopic survey of GCs spanning almost their entire metallicity range. This survey produced abundances of light elements ( $\mathrm{O}, \mathrm{Na}, \mathrm{Mg}$, and Al , in particular), $\alpha$ - and Fe-peak elements in stars typically within a magnitude from the RGB tip. Keying on smaller studies that suggested that O and Na abundances were anticorrelated in some clusters (M13, Pilachowski 1989; M4, Drake, Smith \& Suntzeff 1992), the LickTexas survey concentrated on homogeneous abundances for statistically significant ( $n \geq 10$ ) samples of stars in many clusters (Sneden et al. 1991b, 1992, 1994, 1997, 2000a, 2004; Kraft et al. 1992, 1993, 1995, 1997; Ivans et al. 1999, 2001; Pilachowski et al. 1996a; Smith, Sneden \& Kraft 2002a). Important large-sample studies have also been undertaken by other groups: NGC 3201 (Gonzalez \& Wallerstein 1998); NGC 288 and NGC 362 (Shetrone \& Keane 2000); M71 (Ramírez \& Cohen 2002); M5 (Ramírez \& Cohen 2003); NGC 6752 (Gratton et al. 2001, Grundahl et al. 2002, Yong et al. 2003); NGC 6397 (Gratton et al. 2001); NGC 2808 (E. Carretta, A. Bragaglia, C. Cacciari, G. Mulas, unpublished manuscript); and 47 Tuc (Carretta et al. 2004). Here we discuss the major results from these surveys.
3.2.1. THE Na-O ANTICORRELATION IN GC STARS An anticorrelation between O and Na abundances exists among evolved RGB stars in all GCs studied to date. ${ }^{3}$ A recent summary of some Lick-Texas results is shown in Figure 7, taken from Ivans et al. (2001). Whenever C and N abundances are available, N is found to be anticorrelated with O , which itself positively correlates with C abundances. This strongly suggests that we are seeing the outcome of a redistribution of $\mathrm{C}, \mathrm{N}$, and O in CNO-cycle H-burning. Variations in Al and Mg (anticorrelated with each other) have also been discovered.

When the Na-O anticorrelation was first discovered, it was thought to support a mixed scenario, where both primordial and evolutionary components were required. In this way variable amounts of Na could be synthesized in the only nucleosynthesis site known at the time, massive stars. But this proved to be unsatisfactory because it was unlikely that variations of O and Na could be produced by $n$-captures without accompanying large scatter in heavy elements $\mathrm{Y}, \mathrm{Zr}, \mathrm{Ba}, \mathrm{La}$, etc. Armosky et al. (1994) demonstrated that such large $n$-capture element scatter usually does not exist in GCs.

Fortunately, Na can be synthesized in other ways. Langer, Hoffman \& Sneden (1993) expanded on the original idea by Denissenkov \& Denissenkova (1990) that in advanced $p$-capture chains ${ }^{23} \mathrm{Na}$ could be produced at the expense of ${ }^{22} \mathrm{Ne}$ in the

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Figure $7[\mathrm{Na} / \mathrm{Fe}]$ vs $[\mathrm{O} / \mathrm{Fe}]$ ratios for intermediate metallicity clusters studied by the Lick-Texas group (from Ivans et al. 2001).
same regions where O begins to deplete in the ON cycle. At deeper, hotter layers ( $\mathrm{T} \geq 40 \times 10^{6} \mathrm{~K}$ ) in regions of O depletion, ${ }^{20} \mathrm{Ne}$ could generate ${ }^{23} \mathrm{Na}$. In even hotter conditions ( $\mathrm{T} \geq 70 \times 10^{6} \mathrm{~K}$ ), ${ }^{27} \mathrm{Al}$ could be produced by $p$-captures first on ${ }^{25} \mathrm{Mg}$ and ${ }^{26} \mathrm{Mg}$, then on ${ }^{24} \mathrm{Mg}$ (see also Denissenkov \& Weiss 1996; Cavallo, Sweigart \& Bell 1998; Salaris, Cassisi \& Weiss 2002, and references therein). The origin of essentially all of the correlations among the light elements via $p$-capture reactions within or near H -burning shells in cluster giants is now widely accepted. What is still debated is the true site where $\mathrm{CNO}, \mathrm{NeNa}$, and MgAl cycles occur. The p-capture chains can exist in the H -burning shells of low mass ( $<1 M_{\odot}$ ), first-ascent RGB stars, and in the so-called Hot Bottom Burning (HBB) regions (Blöcker \& Schönberner 1991, Boothroyd \& Sackmann 1992) of the outer convective envelope of intermediate mass ( $3-8 M_{\odot}$ ) AGB stars. The first (evolutionary) scenario
requires a nonstandard dredge-up of nuclearly processed material to the surface from very hot interior layers. Accretion and recycling of matter ejected from the AGB stars is assumed in the second (primordial) scenario. Cannon et al. (1998) summarize causes of the observed star-to-star light element abundance variations in GCs. With the recent large number of theoretical and observational studies in this area, here we summarize the main assets and liabilities of primordial and evolutionary scenarios.
3.2.2. EVOLUTIONARY MIXING Evidence for internal mixing contributions to C and N abundances in GC stars include: (a) the steady decline of [C/Fe] to very low values toward the RGB tip in several clusters, (b) the decrease of the ${ }^{12} \mathrm{C} /{ }^{13} \mathrm{C}$ isotopic ratios in bright RGB stars well below the level predicted by standard models, and (c) the (rough) constancy of the sum $\mathrm{C}+\mathrm{N}+\mathrm{O}$ and $\mathrm{Al}+\mathrm{Mg}$ (Brown et al. 1991a, Briley et al. 1996). Additionally, in order to understand the O, Na, and Al variations, several groups (Smith \& Tout 1992; Charbonnel 1994, 1995; Denissenkov \& Weiss 1996; Charbonnel, Brown \& Wallerstein 1998; Cavallo et al. 1998; Boothroyd \& Sackmann 1999; Weiss, Denissenkov \& Charbonnel 2000; Denissenkov \& Tout 2000; Denissenkov \& VandenBerg 2003) have tried to reproduce the effect of additional mixing taking place between the H-burning shell and the base of the convective envelope in the RGB evolution. Following Sweigart \& Mengel (1979), models including extra mixing start to differentiate drastically from standard models at the RGB bump luminosity.
3.2.2.1 The lesson from field stars Models by Charbonnel $(1994,1995)$ with rotation-induced mixing fit well the ${ }^{12} \mathrm{C} /{ }^{13} \mathrm{C}$ ratios of some metal-poor field halo giants and RGB stars of M4, and reproduce the run of Li abundances in evolved halo stars (Pilachowski, Sneden \& Booth 1993). Moreover, Pilachowski et al. (1996a) and Charbonnel \& Do Nascimiento (1998), using much more extended samples of field and cluster giants, showed that the majority of stars on the upper part of the RGB presented ${ }^{12} \mathrm{C} /{ }^{13} \mathrm{C}$ ratios in clear disagreement with standard models and thus are likely experiencing extra mixing.

A homogeneous sample of more than 60 field stars of a restricted metallicity range $(-2<[\mathrm{Fe} / \mathrm{H}]<-1)$ in different evolutionary phases was observed by Gratton et al. (2000) to study the behavior of evolving low-mass field stars. They derived $\mathrm{Li}, \mathrm{C}, \mathrm{N}, \mathrm{O}$, and Na abundances and ${ }^{12} \mathrm{C} /{ }^{13} \mathrm{C}$ ratios, and correlated these with stellar luminosities. They showed (Figure 8) that stars on the lower RGB (at luminosities fainter than the RGB-bump, at $\log \left(L / L_{\odot}\right) \sim 1.8$ ) have light element abundances in good agreement with first dredge-up predictions of standard models. Upper RGB stars, however, clearly show the existence of a second mixing episode (see also Smith \& Martell 2003). This event depletes the surface abundance of ${ }^{12} \mathrm{C}$ and increases the N abundance. The ${ }^{12} \mathrm{C} /{ }^{13} \mathrm{C}$ ratios are also lowered, but not exactly down to their equilibrium value. All remaining Li disappears, as seen in Figure 8, upper panel. However, in none of the field stars are O and Na affected by this mixing.

Denissenkov \& VandenBerg (2003) have used a parametrical diffusion model of the extra mixing episode to quantitatively reproduce the field-star abundances observed by Gratton et al. (2000). This mixing event, called canonical extra-mixing in the terminology of Denissenkov \& VandenBerg (2003), does not depend strongly on metallicity, and has a rate and depth not very different from star to star. Thus, using metal-poor field stars as a benchmark of mixing processes, we conclude that (a) a further mixing episode besides the standard first dredge-up is required; (b) this extra mixing explains well the changing abundances of $\mathrm{Li}, \mathrm{C}, \mathrm{N}$, and the ratios ${ }^{12} \mathrm{C} /{ }^{13} \mathrm{C}$; but (c) it leaves untouched the O and Na abundances. Hence, this mixing is not deep enough to reach inner regions where $p$-capture reactions might produce N and Na from O and Ne .
3.2.2.2. Digging deeper: the lesson from Mg and Al If the $\mathrm{Na}-\mathrm{O}$ and $\mathrm{Mg}-\mathrm{Al}$ anticorrelations observed in GCs stars result from H-burning at high temperatures in the low-mass stars presently under scrutiny, then this mixing should be deeper than the one explaining the abundance pattern of field stars, because such anticorrelations are not found in them. The heaviest affected elements ( Mg and Al ) are more useful probes of inner regions because higher temperatures are required to overcome their higher Coulomb barriers. Observational data on the various correlations among these elements are not as simple as one might hope. A clear $\mathrm{Na}-\mathrm{Al}$ correlation is observed in several clusters (see Shetrone 1996a, Ivans et al. 2001, and references therein). However, the Al abundance range is, on average, smaller than the range spanned by Na abundances, and differences among clusters of similar metallicity have been interpreted as owing to a different "floor" of primordial enrichment of Na and Al (Ivans et al. 1999). The $\mathrm{Mg}-\mathrm{Al}$ anticorrelation is most easily seen in intermediate-metallicity clusters such as M13 (Shetrone 1996b, Kraft et al. 1997); less obvious patterns appear to exist in the most metal-poor clusters like M92 and M15 (in the last cluster, however, the sum of $\mathrm{Al}+\mathrm{Mg}$ is not constant for all stars, and a clear anticorrelation is hard to detect in M92 giants, which include some Mg-poor/Al-rich objects, Sneden et al. 1997). In more metal-rich clusters the situation is less well understood. For example, in M71, Ramírez \& Cohen (2002) found a $\mathrm{Na}-\mathrm{Al}$ correlation that is significant at the $2 \sigma$ level, but the data of their figure 13 suggest that the correlation rests mainly on only one star. Recently, Carretta et al. (2004) analyzed a sample of slightly evolved stars (SGB and turn-off stars) in 47 Tuc, a cluster with about the same metallicity of M71. They found clear evidence for the $\mathrm{Na}-\mathrm{O}$ anticorrelation, but no significant correlation between Na and Al.

Detailed computations show that the presence of Al enhancements should be accompanied by corresponding enhancements in He abundances, with consequences affecting the subsequent evolution of the stars (see Sweigart \& Catelan 1998). The extent of the $\mathrm{Na}-\mathrm{O}$ anticorrelation itself can be used as a probe of the depth involved in any deep mixing (Weiss et al. 2000). In fact, approaching the H-burning shell, the Na abundance profile shows two distinct rises, as shown in Figure 9 (adapted from Weiss et al. 2000). The first rise is due to production of Na from ${ }^{22} \mathrm{Ne}$, whereas
the second one derives from Na production by partial consumption of ${ }^{20} \mathrm{Ne}$, which is much more abundant than ${ }^{22} \mathrm{Ne}$ and ${ }^{23} \mathrm{Na}$. Therefore, if the additional mixing would reach deep inside the H shell, where Al is produced (and where H starts to decrease and He to increase), it could also penetrate into the region of the second Na rise. We should expect then very large amounts of $[\mathrm{Na} / \mathrm{Fe}]$ dredged-up to the surface, which is actually not observed. This also implies that appreciable amounts of He-enrichment could not be achieved.

Hence, although several authors like Denissenkov \& VandenBerg (2003) proposed that an enhanced extra mixing, deeper and faster than their canonical extra mixing, could contribute to explaining the $\mathrm{Na}-\mathrm{O}$ and $\mathrm{Mg}-\mathrm{Al}$ relationship seen in GC red giants, this mechanism has difficulties in fully explaining observations.
3.2.2.3. Unevolved stars Abundances of elements produced in H burning at high temperatures in scarcely evolved stars (and, in particular, MS stars) provide strong constraints on the mechanism responsible for the O-Na anticorrelation. These lowmass stars have negligible convective envelopes, they burn H primarily in the p-p chain (not in the CNO cycle), and certainly their core temperatures are too low for p-capture reactions to produce Na and Al (Langer et al. 1993, Weiss et al. 2000, Cavallo et al. 1998).

Generally speaking, all variations observed below the luminosity of RGB bump near $\log \left(L / L_{\odot}\right) \sim 1.8$ are at odds with the constraint that deep-mixing may take place only in the absence of a noticeable molecular-weight barrier (Charbonnel 1994, 1995; Sweigart \& Mengel 1979). In Section 3.1 we described some evidence for CH and CN variations in GC stars on or near the main sequence. For instance, note the decrease of C abundances in M92 starts well below the RGB-bump level (Bellmann et al. 2001). The spread in [C/Fe] deduced from CH band strengths in MS and SGB stars of several clusters similarly indicates that part of the dispersion must have an external origin.

Recently, Gratton et al. (2001) have provided further strong evidence against mixing as the only explanation for the $\mathrm{Na}-\mathrm{O}$ anticorrelation. Their UVES/VLT high-resolution spectra yielded the first reliable O abundances in dwarfs in a GC. They found a clear anticorrelation between Na and O among TO and early subgiant stars, very similar to that seen among giants. Also, an anticorrelation was observed between Mg and Al , most clearly among subgiants, but it likely exists also among TO stars. Even accounting for the higher central densities of TO stars, the $\sim 2 \times$ $10^{7} \mathrm{~K}$ are insufficient for advanced $p$-capture cycles. Hence, deep mixing alone cannot explain observations. ${ }^{4}$

Some other less direct evidence also favors the primordial scenario. First, Smith (2002), collecting a large sample of CN band strengths of giants in M3, found that

[^3]both CN -weak and CN -strong stars have C abundances anticorrelated with luminosity along the RGB, a sign of mixing occurring during RGB evolution. However, N abundances in CN -weak giants increase with luminosity. He argued that an interpretation might be that CN -weak giants are not totally unmixed but either they have suffered less mixing or began their lives with lower [ $\mathrm{N} / \mathrm{Fe}$ ] abundances than CN-strong stars.

Second, the absence of a luminosity dependence in the abundances of $\mathrm{O}, \mathrm{Na}$, Mg , and Al in NGC 6752 (Yong et al. 2003), and the similar extent of variations in MS, the subgiant branch SGB, and the RGB stars in this cluster (Gratton et al. 2001, Yong et al. 2003) are not easily reconciled with a mixing scenario.

Finally, Ivans et al. (1999) noted that differences in the Na-O and Al-Na planes found for M4, M5, and NGC 7006 can be best explained if a slightly different primordial floor is taken into account and modified by mixing processes.
3.2.3. PRIMORDIAL VARIATIONS Which kind of star is responsible for the primordial floor of abundance variations over which the effects of internal mixing (likely, the canonical extra-mixing in the terminology of Denissenkov \& VandenBerg) may successively operate? Cottrell \& Da Costa (1981), several years before the acknowledgment of the relevance of $p$-capture reactions in H -burning shells, devised a scenario to explain the observed $\mathrm{CN}-\mathrm{Na}$ and $\mathrm{CN}-\mathrm{Al}$ correlations, in which an early generation of AGB stars polluted the intracluster matter with the release of Na and Al produced in a neutron-rich environment in the intershell region, during the thermal pulses (Iben 1976). Intermediate-mass AGB stars (IM-AGB) are still commonly considered to be the best candidates for polluting the early protoclusters, not via $n$-capture reactions, but rather Hot Bottom Burning (HBB) p-captures. For stars of $\mathrm{M}>4-5 M_{\odot}$ (a lower limit decreasing with decreasing metal abundances), the bottom of the convective envelope sinks into the top of the H -burning shell; this brings fresh fuel into the burning region, and the HBB takes place. Because the HBB temperature can be as high as $10^{8} \mathrm{~K}$, the $\mathrm{CNO}, \mathrm{NeNa}$, and MgAl cycles are all active, and when the products of these reactions are mixed to the surface, chemical variations of surface abundances can be seen.

Yong et al. (2003) argued that candidate polluters cannot be first Galactic generation (i.e., metal-free) AGB stars, because in this case the large enhancement (and depletion) factors in $\mathrm{O}, \mathrm{Na}, \mathrm{Mg}$, and Al could not be reconciled with the uniform overall metallicity of the cluster. Several recent theoretical studies have modeled metal-poor IM-AGB yields (e.g., Forestini \& Charbonnel 1997; Marigo, Bressan \& Chiosi 1998; Ventura, D’Antona \& Mazzitelli 2002; Karabas \& Lattanzio 2003). To briefly summarize, first note that $4-5 M_{\odot}$ AGB stars may eventually eject almost $80 \%$ of their mass (Marigo et al. 1998), which ends up as potential polluting matter. Such IM-AGB stars experiencing HBB will have envelopes where C is reduced by up to a factor of 10 owing to processing in N , and the ratio ${ }^{12} \mathrm{C} /{ }^{13} \mathrm{C}$ is close to the CN equilibrium value. Because O is very efficiently cycled to N at low metallicity (Denissenkov, Weiss \& Wagenhuber 1997; Ventura et al. 2002), metal-poor AGB stars are important producers of N. Acting on seeds of Ne and
$\mathrm{Mg}, \mathrm{Na}$ and Al can be synthesized in $p$-capture reactions, because temperatures at the base of the convective envelope $\geq 10^{8} \mathrm{~K}$ are achieved.

Isotopic Mg ratios can now be derived from GC stellar spectra, yielding new constraints on IM-AGB yields. Yong et al. (2003) derived very high abundances for ${ }^{25} \mathrm{Mg}$ and ${ }^{26} \mathrm{Mg}$ (relative to the more abundant ${ }^{24} \mathrm{Mg}$ ) in giants of NGC 6752. These minor isotopes are found to be much more abundant than in the Solar System (Lodders 2003) and than predicted for ejecta of SN II (Timmes, Woosley \& Weaver 1995). This agrees with model nucleosynthesis of low-metallicity IM-AGB stars by Siess, Livio \& Lattanzio (2002) and Karabas \& Lattanzio (2003) that overproduce ${ }^{25} \mathrm{Mg}$ and ${ }^{26} \mathrm{Mg}$, enhance ${ }^{27} \mathrm{Al}$, and lead to depletion of O and ${ }^{24} \mathrm{Mg}$ and to excesses of N and Na .

While the overall pattern of nucleosynthesis in IM-AGB stars is reasonably established, some authors warn that the yields depend on two of the most uncertain physical inputs: the treatment of mass loss and the efficiency of the convective transport. Denissenkov \& Weiss (2001) and Denissenkov \& Herwig (2003) pointed out that if the temperature at the HBB is high enough to efficiently deplete O , then ${ }^{23} \mathrm{Na}$ is first produced, but then depleted in the interpulse phase. The overall final budget of the O and Na abundances, as well as Mg isotopes, depends critically on the interplay between dredge-up, HBB, and mass loss. Simultaneous O-depletion and Na-enhancement is still possible, but this would require some ad hoc fine tuning. Moreover, the results of Yong et al. (2003) in NGC 6752 seem to show that ${ }^{24} \mathrm{Mg}$ is the dominating Mg isotope even in stars with strong O-depletion. Following models by Ventura et al. (2002), ${ }^{16} \mathrm{O}$ is depleted in the envelope of AGB stars if the HBB temperature is higher than $10^{8} \mathrm{~K}$. However, Denissenkov \& Herwig (2003) showed that ${ }^{24} \mathrm{Mg}$ is consumed even faster than O at such high temperature. Polluting material processed in AGB stars should then result in a sum of ${ }^{25} \mathrm{Mg}$ and ${ }^{26} \mathrm{Mg}$ abundances much larger than observed in NGC 6752.

There are additional reasons to consider IM-AGB good candidates for the proposed mechanism. (a) These stars do not synthetize $\alpha$ or Fe-peak elements, thus their contribution does not give star-to-star variations for these elements, as demanded by the evidence presented in Section 2. (b) They lose mass to the intracluster medium only after the massive stars ended their life as core-collapse SNe , dispersing the primeval cluster interstellar medium. (c) The UV energy produced during their very fast planetary nebula phase is not enough to expel the gas away from the cluster (Ventura et al. 2002). (d) The low-speed winds from IM-AGB may be retained in the cluster, with a trend to be concentrated toward the center. Supporting circumstantial evidence is the radial trend in CN distribution in a few clusters. The most clear evidence comes from 47 Tuc (Norris \& Freeman 1979, Briley 1997, and references therein), where the dominance of CN-strong stars in the central regions can be explained as indirect evidence of material retained by this high-density and concentrated GC at its center.

The nuclearly processed matter from IM-AGB stars either may have been mixed into an intracluster medium, from which a second generation of stars may have
formed within the cluster (the Cottrell \& Da Costa scenario), or may have been accreted in appreciable fraction by existing stars with a well-developed radiative core (the accretion scenario: D'Antona, Gratton \& Chieffi 1983; Cannon et al. 1998; Ventura et al. 2001; Thoul et al. 2002).

Neither of these two hypotheses is free of problems. If only the surface layers are contaminated, abundances in the photospheres of MS stars may be easily modified noticeably because they do not possess large convective envelopes and small amounts of contaminating material are enough to cause significant changes. On the contrary, such changes would be erased again by the deepening of the convective envelope during the RGB phase, and no longer detected, which is at odds with observations. In M13 (Briley, Cohen \& Stetson 2002) the large spread in CH strengths at all luminosities argues against a simple contamination of stellar surface. Note that (large) ranges in abundance variations are found to be similar in passing from MS to RGB in extensively surveyed clusters (47 Tuc: Cannon et al. 1998; NGC 6752: Gratton et al. 2001; Yong et al. 2003). The immediate implications are then that (a) we are probably seeing the effects of the same phenomenon and (b) the primordial variations cannot be confined to a thin outer layer, but they likely affect a large fraction of the star.

Finally, it is interesting to note that the theoretical background for modifications of the composition in GC stars owing to a possible second generation of stars born from the low-velocity wind of the intermediate mass stars (IMS) is already available in the literature (Cayrel 1986, Parmentier et al. 1999, Parmentier \& Gilmore 2001, Thoul et al. 2002).

### 3.3. The State of the Art: Latest Results and Perspectives

Ample statistics are required to properly address the importance of deep mixing and primordial variations. This is well exemplified by the case of M13. This is the cluster with the largest ( $>100$ ) sample of stars analyzed along the RGB, and the one showing the most severe abundance variations. Using this large sample, Pilachowski, Sneden \& Kraft (1996b) and Kraft et al. (1997) made a case for evolutionary effects being strongly at work in M13 because they found that the $[\mathrm{Na} / \mathrm{Fe}]$ ratios are larger and less dispersed for higher luminosity stars.

However, this result is not confirmed by observations of other clusters. Recently, Carretta et al. (2003) analyzed a sample of 81 RGB stars in NGC 2808. Although they do not have any O indicator, they found the usual large variations in Na abundances at all luminosity levels along the RGB. However, when compared with the Na distribution in M13, clearly skewed to higher [ $\mathrm{Na} / \mathrm{Fe}$ ] values ascending toward the RGB tip, the NGC 2808 distribution showed an opposite trend, with the RGB-tip stars being, on average, Na-poorer. Ivans et al. (2001) noted in their study of M5 that this cluster does not behave like M13, and the same result was found by Carretta et al. (2003) in examining the Na distributions found by Sneden et al. (2000a) for M15 and M92. In all these three last cases the $[\mathrm{Na} / \mathrm{Fe}]$ distribution does not change significantly along the RGB.

Combining the results for all clusters, the evidence for evolutionary effects is much less clear. Therefore, M13 is then unique among GCs? Perhaps not, and the solution of this conundrum might be offered by a very recent paper by Sneden et al. (2004). They reconsidered the case of the extreme anomalies seen in M13, as compared with M3. One of their results is that the same anticorrelation between O abundances and the excess of minor Mg isotopes $\left({ }^{25} \mathrm{Mg}+{ }^{26} \mathrm{Mg}\right) /{ }^{24} \mathrm{Mg}$ holds for both M13 (using isotopic ratios from Shetrone 1996b) and NGC 6752 (Yong et al. 2003). Because the last authors convincingly demonstrated that the abundance pattern of NGC 6752 was mostly shaped by primordial variations, Sneden et al. (2004) concluded that the abundance ratios of NGC 6752 and M13 come from the same process that enriched the protoclusters in AGB ejecta. This process seems to have advanced to a much greater degree in M13 (see figure 15 in Sneden et al. 2004). Hence, the very low O abundances seen in stars near the RGB tip in M13 are probably not the result of deep mixing but of HBB processing of $\mathrm{C}, \mathrm{N}$, and O in the same IM-AGB stars responsible for the origin of the Mg isotopes’ overabundance (but see also Smith \& Martell 2003 for a different view).
3.3.1. IS THERE A LINK BETWEEN CHEMICAL VARIATIONS AND GENERAL CLUSTER PROPERTIES? Searches of possible links between abundance variations and cluster HB morphology date back to Norris et al. (1981) and Norris (1981), who noted that some GCs showing a bimodal distribution of stars on the HB also had a bimodal distribution of CN band strength among RGB stars. However, Norris \& Smith (1983b) found no evidence of a CN bimodality predicted on the basis of HB morphology in NGC 2808.

Starting from the theoretical working hypothesis that O depletion and Na enhancement might be the results of an overall cluster-driven angular-momentum signature (Sweigart \& Mengel 1979) and prompted by the studies of rotation in HB stars by Peterson (1983) and Peterson, Rood \& Crocker (1995), Kraft et al. (1995) explored for M10, M3, and M13 whether the blueness of a cluster's HB was correlated with the degree of O depletion among its giants. The connection between O depletion and rotation of BHB stars seems now less promising than originally thought because Behr (2003b) has shown that there are fast rotators also among field BHB stars. However, even if rotation may perhaps not play an important role, a connection between the $\mathrm{O}-\mathrm{Na}$ anticorrelation and the color of the HB may still exist, as suggested by Carretta \& Gratton (1996), who noticed a correlation between the HB morphology and the amount of O depletion in RGB stars. This result hinted that whatever is responsible for the O depletion might also be causing the blueward shift in the HB morphology. The Carretta \& Gratton analysis should be repeated using larger data sets.

Cavallo \& Nagar (2000) tried to account for the HB Blue Tail in M13 on the hypothesis that deep mixing enhanced the He content in the envelope when the inner region of H -burning is reached, causing a star to lie on the blue side of the HB during its following evolution. However, further studies showed that whereas deep
mixing driven by rotation in an RGB star could indeed result in slower RGB evolution, enhanced mass loss and eventually in a bluer HB (Sweigart 1997), this hypothesis faces the same shortcomings as mixing scenarios do (see Section 3.2).

Obviously, these objections are ruled out in the alternative scenario where ab initio differences in He abundances exist among cluster stars as a consequence of He-enriched ejecta of IM-AGB stars (D'Antona et al. 2002). In this scenario, He-enriched stars naturally evolve into BHB stars simply because their TO-mass is smaller. This opens the possibility of a correlation between some of the properties of the HB and the $\mathrm{O}-\mathrm{Na}$ anticorrelation. As usual, more extensive data sets are needed to further explore this possibility.

### 3.4. Puzzling Issues

There are a few observations that do not fit well into the paradigms of primordial variations caused by AGB-IM stars plus canonical extra-mixing. We will briefly consider a couple of them.
3.4.1. Al Abundances in m13 A large-sample survey of Al abundances (Cavallo \& Nagar 2000) in M3 and M13 finds that in M13 there is a large spread in [ $\mathrm{Al} / \mathrm{Fe}$ ] along the RGB, and that Al correlates with Na ; both these effects were confirmed by the recent high-resolution study of Sneden et al. (2004). Moreover, Cavallo \& Nagar found that the distribution of Al abundances is bimodal at all luminosities along the RGB in M13, and that the amount of enhancements for both Al and Na increases toward the tip of the RGB. This result is difficult to confirm from the small samples ( $\sim 30$ stars in each cluster) involved in the Sneden et al. study. This observation led Cavallo \& Nagar to conclude that deep mixing might be at work in M13 but not in M3. This poses a problem, acknowledged in several nucleosynthesis studies (e.g., Langer, Hoffman \& Zaidins 1997; Cavallo et al. 1998; Powell et al. 1999): Na and especially Al require very high temperatures in order to be synthesized via p-captures, but the H shell in a low-mass, low-metallicity RGB star is not believed to be hot enough to produce significant amounts of these elements.
3.4.2. Li abundances in unevolved stars Whereas observations of the Na-O anticorrelation show that the surface of these stars sometimes consists of material that was exposed to temperatures as high as $10^{8} \mathrm{~K}$, causing depletion of primordial O, these stars still show a significant Li content. In the case of NGC6397 (Castilho et al. 2000, Bonifacio et al. 2002) and M92 (Bonifacio 2002), the average Li abundance in TO stars is not much different from that observed for stars on the Spite's plateau, with a scatter around this value consistent with observational errors alone (see, however, Boesgaard et al. 1998, for a different point of view). On the other hand, Li appears to be depleted, but not completely absent, in stars with very low O abundances in NGC6752 and 47 Tuc (P. Bonifacio, L. Pasquini, P. Molaro, E. Carretta, M. Centurion et al., unpublished manuscript). Li can be produced
in IM-AGB stars (Ventura et al. 2001) and then dispersed to the ISM through the Cameron-Fowler mechanism (Cameron \& Fowler 1971): However, a puzzling fine tuning is required in order to reproduce roughly as much Li as is destroyed in the previous evolution of the stars.

## 4. $\omega$ CENTAURI

The lack of star-to-star variations in the abundances of elements having large Coulomb barriers, and then not affected by nuclear burning at the temperatures typical of H-burning, has implications for the mechanism of cluster formation. Regardless, the case of $\omega$ Cen is special, worth an entire conference devoted to this single cluster (van Leeuwen, Hughes \& Piotto 2002). $\omega$ Cen is the only Galactic GC for which evidences for star-to-star abundance variations for all elements are clear; it is also the brightest and likely most massive cluster in our Galaxy, with a mass of $5 \times 10^{6} M_{\odot}$ (Meylan et al. 1995). This is probably related to its unique spread in metal abundance: Similar spreads have recently been proposed for the most massive clusters in M31 (Meylan et al. 2001), and may indeed be a general property of very massive GCs. However, other possible explanations for the abundance variations have been proposed (merging of two clusters: Norris et al. 1997; Icke \& Alcaino 1988; peculiar dynamical conditions of formation: Tsujimoto \& Shigeyama 2003), and it is also possible that $\omega$ Cen was the nucleus of a now-dissolved small galaxy (see Section 4.5).

### 4.1. Metallicity Distribution

The anomalous width of the giant branch in the CMD of $\omega$ Cen was first discovered by Geyer (1967), and then confirmed by Cannon \& Stobie (1973). These early studies attributed this width to a variable interstellar reddening; however, this soon appeared not compatible with the observed distribution of stars in the two-color diagram (Newell, Rodgers \& Searle 1969). It was then suggested that the width of the RGB may be due to an abundance spread. Such a spread (from $[\mathrm{Ca} / \mathrm{H}]=-1.6$ up to $[\mathrm{Ca} / \mathrm{H}]=-0.6$ ) was indeed found by Freeman \& Rodgers (1975) using the strength of the Ca II K line in 25 RR Lyraes (these abundances were slightly revised downward by 0.3 dex by a more quantitative analysis by Manduca \& Bell 1978). This spread was confirmed using a larger sample of RR Lyrae (50 objects) by Butler, Dickens \& Epps (1978), and more recently by Rey et al. (2000) from intermediate- and narrow-band Caby photometry of 131 variables.

RR Lyrae stars represent a biased sample of the abundance distribution in $\omega$ Cen because only a fraction of the stars crosses the instability strip. Several authors tried to obtain unbiased metal abundance distributions using stars along the RGB of the cluster. Whereas all low-mass stars pass through this evolutionary phase, appropriate corrections should be considered to take into account the time spent by stars of different metallicities at various luminosities. First, exploratory studies were done by Norris \& Bessel (1975, 1977), Mallia (1976), Dickens \& Bell


Figure 10 (Lower panel) Metallicity distribution function for $\omega$ Cen from Suntzeff \& Kraft (1996) (filled squares) and Norris et al. (1996) (open squares). (Upper panel) The metallicity distribution obtained from photometric data by Pancino et al. (2000). All data are reduced to a metallicity scale consistent with that of Suntzeff \& Kraft.
(1976), Rodgers et al. (1979), Bell et al. (1981), and Hesser et al. (1985). However, extensive spectroscopic surveys of cluster red giants, including some 500 objects each, were presented only a few years later by Suntzeff \& Kraft (1996) and Norris, Freeman \& Mighell (1996). The metal abundance distributions obtained by these two studies are very similar once the different calibrations are taken into account (see Figure 10). The distributions are characterized by the absence of very metalpoor stars (stars with $[\mathrm{Fe} / \mathrm{H}]<-1.8$ ), by a sharp peak at low metallicities $([\mathrm{Fe} / \mathrm{H}]$ $\sim-1.7$ ), with a width not significantly larger than the observational errors, and by a wide tail extending up to high metallicities.

A quite different distribution was obtained by Hilker \& Richtler (2000) using Strömgren photometry of about 1500 stars. However, as noted by the same authors, the abundance index used is heavily affected by the strength of the CN-band. Their results cannot be then directly compared with those of other investigations.

Trends for increasing concentration of stars toward the cluster center with increasing metallicity were found by Norris et al. (1996). The spectroscopic studies were based on the Woolley (1966) star selection, which is largely incomplete in the central regions ( $<4 \mathrm{arcmin}$ ) of the cluster, where only the brightest, metal-poor red giants could be detected on the photographic plates. Because the metal-rich population is centrally concentrated (Norris et al. 1996), a bias against it arises. New extensive, high-quality CCD CMDs were obtained in very good seeing conditions by Lee et al. (1999) and Pancino et al. (2000). These diagrams are complete for the whole upper part of the RGB even at the cluster center, providing a much better sampling of the metal-rich population. Whereas previous studies essentially showed the presence of a sparse scatter of metal-rich stars, these new investigations based on photometric data evidenced the presence of at least four distinct sequences (Pancino et al. 2000: see Figure 10 here) characterized by different metal abundances. In particular, a completely new, much more metal-rich red giant sequence at $[\mathrm{Ca} / \mathrm{H}] \sim-0.05([\mathrm{Fe} / \mathrm{H}] \sim-0.5)$, including about $5 \%$ of the whole cluster mass, was found to exist. This sequence was later confirmed with highresolution spectroscopic data by Pancino et al. (2002), although with a slightly reduced metallicity value.

### 4.2. The Age-Metallicity Relation

The history of metal-enrichment of $\omega$ Cen could be directly derived if ages could be obtained for the sequences having different metallicity. Whereas this is relatively easy for the metal-poor sequence based on the main sequence turn-off, which can be traced very well in the outer regions (where deep CMD can be obtained), the play becomes increasingly difficult for the more concentrated metal-rich populations. Hughes \& Wallerstein (2000) and Hilker \& Richtler (2000), using Strömgren photometry of turn-off stars, found that the metal-rich stars ( $[\mathrm{Fe} / \mathrm{H}] \sim-1$ ) are $2-4$ Gyrs younger than the metal-poor ones $([\mathrm{Fe} / \mathrm{H}] \sim-2)$, with the intermediatemetallicity stars having also an intermediate age. Note, however, that the very metal-rich population of Pancino et al. $(2000,2002)$ was not adequately sampled because observations were obtained for a region far from the cluster center: However, Hilker \& Richtler suggested that these stars can be up to 6 Gyr younger than the oldest population.

Very recently, Stanford et al. (2003) obtained abundances and ages for more than 400 stars close to the TO. The region sampled is an annulus between 15 and 25 arcmin from the cluster center (then under-sampling the metal-rich population). They found a clear relation between ages and metal abundances, with a spread as large as $\sim 5$ Gyrs (see Figure 11).

### 4.3. Metallicity and Kinematics

At variance with most other GCs, the relaxation time for $\omega$ Cen is very long due to its low central concentration (the concentration parameter, that is the logarithm of the ratio between the tidal and core radii, is $c=1.23$ ): according to Meylan


Figure 11 Age-metallicity relation for $\omega$ Cen from Stanford et al. (2003): all stars (upper panel) and only unevolved stars (lower panel) (courtesy of L. Stanford).
et al. (1995), the relaxation time of $\omega$ Cen is as long as $\sim 1 \mathrm{Gyr}$ in the cluster core ( 3 arcmin), and exceeds twice a Hubble time at half-light radius ( 13 arcmin ). For comparison, the relaxation time in the center of 47 Tuc with a concentration of $c \sim 2$ is about three orders of magnitude smaller (Meylan 1989). $\omega$ Cen could then mantain for a much longer time the imprinting of its initial conditions, as noticed among others by Merritt, Meylan \& Mayor (1997). This fact discloses the possibility to use the observed distribution of stars of different populations within the cluster in order to study the cluster formation and evolution.

The abundance distribution in $\omega$ Cen is clearly not uniform. Indeed, early attempts to reveal radial abundance gradients based on integrated spectra (Smith
1981) and colors (Pastoriza et al. 1986) revealed some trends, but their meaning was not clear. As mentioned above, the spectroscopic studies showed that most metal-rich stars are more centrally concentrated. The strong concentration of the metal-rich population was then confirmed by Pancino et al. (2000): These authors also showed that this population has an elliptical distribution, in analogy with that found for the metal-poor stars in the cluster, but with a completely different (orthogonal) major semiaxis.

Large, kinematic studies of $\omega$ Cen have been presented by Meylan \& Mayor (1986) and Merritt et al. (1997), based on radial velocities; and van Leeuwen et al. (2000) from proper motions. These studies are very useful to derive the most important dynamical information for the cluster (total mass, mass distribution, rotation, and triaxality). However, they did not correlate their results with abundances. Such a correlation was presented by Norris et al. (1997). This study is based on radial velocities for about 400 stars, mainly in the outer part of the cluster, from Meylan \& Mayor (1986), and the metal abundances from spectroscopy by Norris et al. (1996). Norris et al. (1997) found that the metal-rich population is not only more concentrated but also kinematically cooler than the metal-poor one. An even more extensive study (radial velocity data for 4728 giants), this time considering the inner central region ( 3.5 arcmin ) of the cluster, has been done recently by Xie et al. (2002). Abundance information was obtained from Strömgren photometry. Whereas these abundances are more uncertain than the spectroscopic values considered by Norris et al. (1997), these authors were able to show that the metal-poor sample shows systematic rotation with high confidence, but the most metal-rich group does not. Although the measured projected rotation is not significant, it is suggestive that the position angle of the best-fitting rotation axis of the metal-rich group is about 90 degrees from that of the metal-poor group, consistent with the spatial flattening difference in the metal-poor and metal-rich groups as suggested by Pancino et al. (2000).

Various authors have considered asymmetries both in the distribution and velocity of the stars in $\omega$ Cen (Jurcsik 1998; Ferraro, Bellazzini \& Pancino 2002; Platais et al. 2003; Xie et al. 2002). Such asymmetries would be important because they could signal past accretion events within $\omega$ Cen. Results are controversial, and for the time being, we consider evidence for asymmetries as not definitive.

### 4.4. Element-to-Element Abundance Ratios

Whereas photometry and low-resolution spectroscopy may provide important information about the abundance distribution within $\omega$ Cen, detailed evolution of the different elements, providing constraints on the involved nucleosynthesis, can only be obtained from high-resolution spectroscopic studies. The first such studies were presented by Mallia \& Pagel (1981), Cohen (1981), and Gratton (1982). These studies confirmed the presence of star-to-star abundance variations in all the elements surveyed and suggested that variations are larger for those elements possibly involved in H -burning at high temperatures, and those produced by neutron-capture.

Results obtained by later studies are now examined in detail for different groups of elements.
4.4.1. ELEMENTS PRODUCED IN H-BURNING AT HIGH TEMPERATURES First, detection of spreads in the elements produced by H -burning at high temperature in $\omega$ Cen was obtained using DDO intermediate band photometry and low-dispersion spectroscopy (Norris \& Bessel 1975, 1977; Dickens \& Bell 1976; Lloyd-Evans 1977). More extensive data were presented by Persson et al. (1980); by correlating $V-K$ colors with CO indices, this study showed that variations in C abundances were not correlated with those of the Fe -peak elements, and that C -rich and C -poor stars exist at different values of the Fe -peak abundance. This result was confirmed by the spectroscopic studies of Cohen \& Bell (1986) and Caldwell \& Dickens (1988), who determined quantitative abundances of C, N, and O; they found that the range of variation of C and N is typical of those seen in other GCs.

Whereas these early results were based on C-molecule bands ( $\mathrm{CH}, \mathrm{CN}$, and CO ), Norris \& Smith (1983a), Norris \& Pilachowski (1985), Paltoglou \& Norris (1989), Brown et al. (1991b), and Milone et al. (1992) studied Na and Al abundances. The most extensive study was presented by Norris \& Da Costa (1995a), who considered a (biased) sample of 40 red giants. As in other clusters, they found strong $[\mathrm{Na} / \mathrm{Fe}]-[\mathrm{O} / \mathrm{Fe}]$ and $[\mathrm{Al} / \mathrm{Fe}]-[\mathrm{O} / \mathrm{Fe}]$ anticorrelations, and a strong positive correlation between $[\mathrm{Na} / \mathrm{Fe}]$ and $[\mathrm{Al} / \mathrm{Fe}]$. These anticorrelations are present in stars of different metallicities. Hence, whatever is the mechanism responsible for the O-Na anticorrelation and related phenomena, it is also active in stars of $\omega$ Cen over a broad range of metal abundances.

Zucker, Wallerstein \& Brown (1996) concentrated on the oxygen-poor stars. All of the stars show large Al excesses, and all but one reveal an excess of Na . They found ${ }^{12} \mathrm{C} /{ }^{13} \mathrm{C}$ ratios which are similar to those obtained for oxygen-rich stars. Smith, Terndrup \& Suntzeff (2002b) measured carbon isotopic ratios in 11 bright giants selected to span a substantial fraction of the range of iron and $[\mathrm{O} / \mathrm{Fe}]$, $[\mathrm{Na} / \mathrm{Fe}]$, and $[\mathrm{Al} / \mathrm{Fe}]$ abundance ratios. In all stars the ${ }^{12} \mathrm{C} /{ }^{13} \mathrm{C}$ abundance ratio is found to be close to the equilibrium ratio of 3.5 . There is no correlation between the ${ }^{12} \mathrm{C} /{ }^{13} \mathrm{C}$ and the abundance of iron. The derived abundances of $\left[{ }^{12} \mathrm{C} / \mathrm{Fe}\right]$ show a positive correlation with $[\mathrm{O} / \mathrm{Fe}]$ and an anticorrelation with $[\mathrm{Na} / \mathrm{Fe}]$. Finally, Origlia et al. (2003) obtained an average ${ }^{12} \mathrm{C} /{ }^{13} \mathrm{C} \approx 4$ from near-IR spectra of 21 giants spanning the whole range of metallicities observed in this cluster. All these results indicate that nonstandard deep mixing is occurring in bright red giants of $\omega$ Cen.
4.4.2. $\alpha$ - AND Fe-PEAK ELEMENTS In the past ten years various papers based on high-resolution and high-S/N spectra for a rather large number of stars in $\omega$ Cen have been published (Brown \& Wallerstein 1993; Smith, Cunha \& Lambert 1995; Norris \& Da Costa 1995b; Pancino et al. 2002). The first three papers deal with the metal-poor and intermediate-metallicity populations: Results obtained by different investigations agree very well with each other. The basic conclusion is that the run of $\alpha(\mathrm{Mg}, \mathrm{Si}, \mathrm{Ca}$, and Ti$)$ and $\mathrm{Fe}-\mathrm{peak}(\mathrm{Cr}$, and Ni$)$ [metal/Fe] is flat as a function of


Figure 12 (Upper panel) Run of the average abundance ratios of the $\alpha$-elements Si and Ca with respect to Fe for stars in $\omega$ Cen. (Middle panel) The same for Cu (with abundances from Cunha et al. 2002 and Pancino et al. 2002). (Lower panel) The same for the average abundance ratio of the $n$-capture elements Ba and La . Filled symbols represent data from Norris \& Da Costa (1995b); open symbols, data from Smith et al. (2000); crosses, data from Pancino et al. (2002). All abundances were corrected to the scale of Norris \& Da Costa using stars in common.
$[\mathrm{Fe} / \mathrm{H}]$ and is consistent with primordial enrichment from stars having mass greater than $10 M_{\odot}$, as has been found for field halo stars (see upper panel of Figure 12).

An element of particular interest is Cu (see Section 2): Examining the results for field stars obtained by Sneden et al. (1991a), Matteucci et al. (1993) concluded that Cu can be used as a sensitive tracer of the contribution by Type Ia SNe to nucleosynthesis. Smith et al. (2000) and Cunha et al. (2002) determined Cu abundances for 40 red giants in $\omega$ Cen (spanning the range from $[\mathrm{Fe} / \mathrm{H}] \sim-2.0$ to -0.8 ), as well as 15 red giants in other clusters. $\omega$ Cen displays a constant ratio of $[\mathrm{Cu} / \mathrm{Fe}] \sim-0.5$ all the way to $[\mathrm{Fe} / \mathrm{H}]=-0.8$ (see middle panel of Figure 12).

The lack of an increase in $[\mathrm{Cu} / \mathrm{Fe}]$ in $\omega$ Cen would suggest very little contribution from SNe Ia to its chemical evolution in this metallicity range.

Pancino et al. (2002) studied three stars of the very metal-rich red giant branch (RGB-a as defined by Pancino et al. 2000) and three of the metal-intermediate population (RGB-MInt). $\mathrm{Fe}, \mathrm{Cu}$, and $\alpha$-element ( Ca and Si ) abundances have been derived and discussed. The metallicity of this sequence is $[\mathrm{Fe} / \mathrm{H}]=-0.60 \pm$ 0.15 . The $\alpha$-element enhancement of the two populations is quite different (see Figure 12). The three RGB-MInt stars have the expected overabundance, typical of halo and GC stars: $[\alpha / \mathrm{Fe}]=0.29 \pm 0.01$. The three RGB-a stars show, instead, a significantly lower $\alpha$-enhancement: $[\alpha / \mathrm{Fe}]>=0.10 \pm 0.04$. Pancino et al. have also detected an increasing trend of $[\mathrm{Cu} / \mathrm{Fe}]$ with metallicity similar to the one observed for field stars. The low $\alpha$ enhancement for the metal-rich population has been confirmed by Origlia et al. (2003). These facts suggest that SNe Ia ejecta have contaminated the medium from which the metal-rich RGB-a stars have formed.
4.4.3. NEUTRON-CAPTURE ELEMENTS Mallia (1976) first discovered the presence of stars very rich in $n$-capture elements in $\omega$ Cen. Several S-stars (at the luminous, cool end of the RGB) were found by Evans (1983). The high-dispersion studies of red giants by Cohen (1981), Gratton (1982), and François, Spite \& Spite (1988) indicated that large abundances of these elements are common among stars of $\omega$ Cen. However, the first to show that there is a clear correlation between metallicity and abundance of the $n$-capture elements were Smith, Cunha \& Lambert (1995) and Norris \& Da Costa (1995b). These authors noticed that the abundance of the heavy $n$-addition elements (in particular Y, Ba, La, and Nd ) rises as $[\mathrm{Fe} / \mathrm{H}]$, in sharp contrast with what is found in the normal clusters, whereas the relative abundances as a function of atomic number are suggestive of $s$-processing (see lower panel of Figure 12).

An extensive study was presented by Smith et al. (2000), who considered 22 chemical elements in 10 red giants plus published literature values, spanning the range from $[\mathrm{Fe} / \mathrm{H}] \sim-1.8$ to -0.8 . At the lowest metallicity, the heavy-element abundance is found to be well characterized by a scaled solar system $r$-process distribution, as found in other stellar populations at this metallicity. As Fe increases, the $s$-process heavy-element abundances increase dramatically. Models of $s$-process nucleosynthesis in $1.5-3 M_{\odot}$ AGB fit the heavy-element abundance distributions well. This indicates that AGB ejecta were more efficiently retained in the cluster relative to the much faster moving Type II SN ejecta. This requires that the cluster was active in star formation for quite a long interval of time, of the order of $2-3 \mathrm{Gyr}$, in order to allow the low-mass stars to evolve to the AGB.

Similar conclusions were drawn by Vanture, Wallerstein \& Suntzeff (2002), who determined the abundance of heavy elements for five stars classified as S stars by Evans (1983). These stars are all variable and among the most luminous in the cluster; however, as Evans noticed, these stars are much fainter than S stars in the Magellanic Clouds and are not associated with C-stars as the latter are. It is
then likely that they represent the top of the range of metal abundance in $\omega$ Cen and that the strong Ba II and ZrO features result from a primordial excess of $s$-process elements.

### 4.5. Chemical/Dynamical Evolution Models

Various authors constructed chemo-dynamical models of $\omega$ Cen. Dopita \& Smith (1986) studied the effects of SN explosions within a cluster. They found that clouds less massive than about $10^{5} M_{\odot}$ are completely disrupted by SN explosions. In clouds of greater mass, SN explosions occurring near the tidal radius tend to lose their hot gas and metals to the intercloud medium. For explosions occurring closer to the mass center, the ejecta must be slowed below the escape velocity, and this can only occur in clouds more massive than about $3 \times 10^{6} M_{\odot}$. If this condition is met, then the slow isothermal momentum-conserving shocks generated by the SN explosions may eventually induce secondary star formation. For such shocks converging on the mass center, it is found that a cloud mass of at least $10^{7} M_{\odot}$ is required for this process to be efficient. From the observed properties of $\omega$ Cen, a primordial mass of order $10^{8} M_{\odot}$ is estimated.

Several authors have speculated on the possibility that $\omega$ Cen is the nucleus of a now-dissolved nucleated dwarf galaxy (Zinnecker et al. 1988, Freeman 1993, Lee et al. 1999, Hilker \& Richtler 2000, Meylan et al. 2001, Ferraro et al. 2002), based on various circumstantial arguments: the similarity of abundance properties with those of dwarf spheroidal galaxies; the possible large range in ages within the cluster; and the fact that other massive clusters may also be the nucleus of other galaxies (see, for instance, the case of M54 in the Sagittarius Dwarf Galaxy). An argument favoring an accretion origin is its present orbit close to the Galactic plane and center (Dinescu et al. 1999): Intracluster gas should have been likely swept out of the cluster long time ago, halting its chemical evolution. Similarly, Gnedin et al. (2002) noticed that $\omega$ Cen escape velocity is not especially large, and that its exceptional ability to retain the ejecta of AGB stars likely required that it should have been very different in the past. Carraro \& Lia (2000) modeled the evolution of a primordial $10^{8} M_{\odot}$ density peak that ends up in an object closely resembling the present-day $\omega$ Cen by means of N-body/hydrodynamical simulations. They suggested that $\omega$ Cen might be a cosmological dwarf elliptical, evolved in isolation and self-enriched, and eventually fallen inside the potential well of the Milky Way. They suggested that $\omega$ Cen is probably surrounded by an extended Dark Matter halo that perhaps can be found by studying the kinematics of stars outside about 20 arcmin. A similar $N$-body capture scenario has been recently presented by Tsuchiya, Dinescu \& Korchagin (2003), who found that the present orbital and structural parameters of $\omega$ Cen are compatible with the cluster being originally the nucleus of a nucleated dwarf elliptical with a Hernquist (1990) density profile, a mass of $8 \times 10^{9} M_{\odot}$, and a half-mass radius of 1.4 kpc , launched from 58 kpc from the Galactic center on a radial low-inclination orbit. In their simulation, the non-nucleated dwarf is destroyed in less than 3 Gyr .

On the contrary, other authors moved more conservatively without any assumption about the early environment of $\omega$ Cen, trying to derive its properties from observational data alone. Models for the chemical evolution have been presented by Suntzeff \& Kraft (1996), and more recently by two Japanese groups (Ikuta \& Arimoto 2000, Tsujimoto \& Shigeyama 2003). All these models consider selfenrichment scenarios, following ideas initially proposed by Cayrel (1986). General agreement is found for the need of significant outflow from the cluster, reducing the effective yield per stellar generation, and requiring a much larger original mass ( $\sim 10^{8}$ rather than a few $10^{6} M_{\odot}$ ). Ikuta \& Arimoto suggest that observations are better explained by adopting a bimodal initial mass function. Tsujimoto \& Shigeyama divide star formation into three epochs. At the end of the first epoch, $\sim 70 \%$ of the gas was expelled by supernovae. AGB stars then supplied $s$-process elements to the remaining gas during the first interval of $\sim 300$ Myr. This explains the observed sudden increase in $\mathrm{Ba} / \mathrm{Fe}$ ratios. SNe at the end of the second epoch were unable to expel the gas, because their explosion energy did not exceed the gravitational energy of the cluster. Eventually, SN Ia initiated SN-induced star formation, and the remaining gas was stripped when the cluster passed through the newly formed disk of the Milky Way.

Tsujimoto \& Shigeyama (2003) also discussed the formation of $\omega$ Cen in the framework of GC formation triggered by cloud-cloud collisions. In this scenario, the relative velocity of clouds in the collision determines the later chemical evolution in the clusters. A head-on collision of protocluster clouds with a low relative velocity would have converted less than $1 \%$ of the gas into stars and promoted the subsequent chemical evolution by SN-driven star formation. This would be consistent with the present observed form of $\omega$ Cen. In contrast, the other Galactic GCs are expected to have formed from more intense head-on collisions, and the resultant clouds would have been too thin for supernovae to accumulate enough gas to form the next generation of stars. This would explain the absence of chemical evolution in these other GCs.

## 5. STARS WITH PECULIAR ABUNDANCES

In this section we review results for different classes of stars exhibiting peculiar abundances. GCs host a variety of such stars. Some of these peculiarities arise owing to the evolutionary phases crossed by stars during their evolution: In this case, sometimes the chemical peculiarities seen for stars in GCs are analogous to those found for field stars of similar mass, age, and metallicity. Observations of large numbers of stars in clusters offer unique chances for accurate determination of properties, like mass and surface gravity, that are not easily determined for field stars. For some peculiar classes of objects, stars in GCs may have slightly different properties owing to the peculiar dynamical conditions met. However, a number of stars owe their peculiar chemical composition to their membership in binary systems, or even simply to their membership in the cluster. In this second case, the
very peculiar dynamical conditions met in dense systems like GCs play a basic role, so that the properties of objects found in GCs may be very different from those usually found for field stars.

Excellent reviews covering part of the topics discussed here have been given by Bailyn (1995), who discusses the manifestations of the interaction between GC dynamics and stellar evolution; and Moehler (2001), where the reader may find an exhaustive discussion of those aspects relative to the hot stars. Only a few points about such objects are summarized here.

### 5.1. Stars in Peculiar Evolutionary Phases

5.1.1. MICROSCOPIC DIFFUSION AND RADIATION LEVITATION IN HOT MAIN-SEQUENCE STARS Microscopic diffusion is a basic physical mechanism that should be included in stellar models. Several years of investigations have shown that it must be included in solar interior models in order to adequately reproduce the run of the sound speed as derived from the extremely precise helioseismological data (see Basu, Pinsonneault \& Bahcall 2000). Diffusion causes sedimentation of heavy elements. The timescale $\tau$ for sedimentation is given by:

$$
\tau \approx K M_{c z} /\left(M T_{c z}^{3 / 2}\right)
$$

where $K$ is a constant, $M_{c z}$ is the mass of the convective zone, $T_{c z}$ the temperature at its base, and $M$ is the stellar mass (Chaboyer et al. 2001). Owing to the small mass of the convective envelope, in low-mass ( $M \sim 0.8 M_{\odot}$ ), metal-poor stars $([\mathrm{Fe} / \mathrm{H}] \leq$ $-2)$ the sedimentation time is comparable to the MS lifetime, so that its effects can be noticed in stars near the TO, that is, the same stars from which inferences on the primordial Li abundance can be derived (the Spite plateau: Spite \& Spite 1982). The expected effects of sedimentation depend on its treatment: Models like those of Straniero, Chieffi \& Limongi (1997), Castellani, degl'Innocenti \& Marconi (2000), Chaboyer et al. (2001), which assume complete ionization (and then negligible effects of radiation pressure), predict depletions for all elements heavier than H , including not only He , but also among others $\mathrm{Li}, \mathrm{O}$, and Fe . On the other hand, recent models by Richard et al. (2002) that take into detailed account the effect of partial ionization and radiation pressure, show that whereas some elements like He and Li are expected to be depleted, others (like Fe ) are expected to be significantly enhanced.

Microscopic diffusion is the most important source of theoretical uncertainty in cluster ages: These are about 1 Gyr smaller if the effect of diffusion is taken into account, with respect to those obtained by neglecting it. Also, microscopic diffusion might help to explain the discrepancy between the observed value of the abundance of Li for stars on the Spite plateau, and that expected from primordial nucleosynthesis, using the latest Wilkinson Microwave Anisotropy Probe (WMAP) results (Cyburt et al. 2003).

An early observation of a few stars slightly brighter than the TO in the very metal-poor cluster M92 (King et al. 1998) suggested a depletion of Fe in these
stars with respect to red giants, a result in agreement with the predictions of models with complete ionization, but not with those of Richard et al. (2002). However, temperatures adopted in these two separate analyses are not consistent each other, so that it is not clear that the abundances may be directly compared. More recently, Gratton et al. (2001) obtained consistent and precise abundances for stars at the TO and at the base of the subgiant branch in NGC 6397: Whereas this cluster is slightly more metal-rich than M92, it has $[\mathrm{Fe} / \mathrm{H}]=-2$, so that the impact of diffusion should still be measurable. Gratton et al. (2001) obtained practically identical values of $[\mathrm{Fe} / \mathrm{H}]$ for stars in the two groups, suggesting that no effect of diffusion is visible.

There may be various explanations for this discrepancy between models and observations. (a) The analysis of observational data may contain some error: For instance, the relative temperature scales between TO and subgiants may be incorrect, or the structure of the model atmospheres may not correctly reproduce the real ones (for instance, because they neglect three-dimensional effects, Asplund, Carlsson \& Botnen 2003), or departures from LTE may act differently, canceling a real difference. Because the expected effect of microscopic diffusion on abundances is not very large in the case of NGC 6397, this is possible, although, on the whole, not very probable. (b) As suggested by the same Richard et al. (2002) some turbulence at the base of the convective envelope may act, thereby canceling the effect of diffusion. If the second explanation is valid, then the Li abundance for stars on the Spite plateau would be only 0.15 dex smaller than the original value (Richard et al. 2002), not enough to explain the discrepancy with expectations from primordial nucleosynthesis.

More observations on more critical, very metal-poor clusters (like M92), where the expected impact of diffusion is larger than in NGC 6397, are required to definitely settle this issue.
5.1.2. Li-RICH RED GIANTS Lithium is easily destroyed in relatively low-temperature proton-capture reactions, via ${ }^{7} \mathrm{Li}+\mathrm{p} \rightarrow{ }^{8} \mathrm{Be} \rightarrow 2{ }^{4} \mathrm{He}$. In typical mainsequence stars, the observed Li exists in only a thin outer part of the surface layers. The deepening convective envelope that develops with evolution off the main sequence dilutes this surface Li with the Li -free interior regions. Thus at the end of the standard first dredge-up, the observed Li abundances are factors of 10 to 30 times less than their initial values. An evolved metal-poor subgiant or red giant typically exhibits a very weak or undetectable $6707 \AA$ Li I resonance doublet in its spectra. For such stars, a clearly defined decline in Li with advancing evolutionary state (decreasing $T_{\text {eff }}$ and/or increasing $L$ ) has been shown by Pilachowski, Sneden \& Booth (1993), Ryan \& Deliyannis (1998), and Gratton et al. (2000). In the Gratton et al. paper, the correlation of Li abundances with $L$ demonstrates that the Li drop is a two-step process: a decrease by a factor of 10 to 20 owing to convective dilution on the subgiant branch, followed by an additional factor of at least ten at the onset of the canonical mixing episode along the RGB. Whereas MS turn-off metal-poor stars exhibit an almost uniform Spite plateau
abundance of $\log \epsilon(\mathrm{Li}) \simeq+2.2$, their luminous giant star counterparts usually have $\log \epsilon(\mathrm{Li}) \leq 0.0 .{ }^{5}$

One expects a similar situation to exist in globular clusters, and indeed most RGB cluster members surveyed to date have undetectable Li I features. There are, however, a few exceptions. Carney, Fry \& Gonzalez (1998) found an AGB variable star in M5 with $\log \epsilon(\mathrm{Li}) \simeq+1.8$, and Smith, Shetrone \& Keane (1999) reported a moderately large abundance, $\log \epsilon(\mathrm{Li}) \simeq+1.2$, in an RGB-tip variable star in NGC 362. The high Li abundances of these two stars were probably produced after the He-flash, probably during AGB evolution itself. But the most Li-rich globular cluster giant discovered to date is an apparently normal first-ascent RGB star of M3. Kraft et al. (1999) found that M3 IV-101 has $\log \epsilon(\mathrm{Li}) \sim+3$, much larger than the Spite-plateau Li abundance that one guesses was the star's initial Li content. Pilachowski et al. (2003) investigated the carbon isotopic ratios of this and two other M3 giant stars of M3 that reside at nearly the same CMD locations of the cluster. They discovered that M3 IV-101 has ${ }^{12} \mathrm{C} /{ }^{13} \mathrm{C} \simeq 11$, relatively high for globular cluster giants, and in particular nearly double that of the two other M3 giants of their study. The combined Li and carbon isotopic ratio information suggests strongly that the Li is a recent addition to the M3 IV-101 envelope, having been generated in hydrogen shell fusion and mixing (e.g., Charbonnel \& Balachandran 2000) perhaps associated with an extra-mixing episode at the RGB bump phase.

The Li-rich phenomenon apparently is quite rare. Pilachowski et al. (2000a) surveyed 261 giants in M3, M13, M15, and M92, finding no stars with strong Li I lines, and setting abundance upper limits of $\log \epsilon(\mathrm{Li})<+1.0$ in all cases. But in preliminary reports of more extended surveys, Pilachowski et al. (2000b) and Thompson \& Pilachowski (2003) found that about $2 \%$ of nearly 800 giants studied in more than 10 globular clusters have detectable Li I lines, yielding abundances mostly in the $\log \epsilon(\mathrm{Li}) \sim+1$ domain. Most of these are lower RGB stars, having completed the standard first dredge-up mixing but prior to the canonical extramixing episode. Ramírez \& Cohen (2002) also find no Li abundance anomalies in the subgiants and RGB stars of the relatively metal-rich cluster M71. These low but detectable Li abundances are consistent with those of lower RGB field giants. Thus, the true incidence of anomalously very high Li abundances in globular cluster giants appears to be $<1 \%$.
5.1.3. WARM HORIZONTAL BRANCH STARS The HB (the locus occupied in the CMD by core He-burning stars after the core He-flash) corresponds to a phase crossed by all stars with a mass lower than about $2.3 M_{\odot}$ (Greggio, Renzini \& Sweigart 1995). The mass of the He-core is nearly independent of the stellar mass and chemical composition. HB stars of different masses would all lie at essentially the same luminosity, with a large range in surface temperature depending on the efficiency

[^4]of the H-burning shell (that gives a minimal contribution to the total luminosity): For this reason the HB is a mass-sequence (in analogy with the MS). In nearly coeval systems like GCs, it is expected that most metal-poor stars, of smaller total mass, should occupy a bluer location on the HB than stars of larger mass. However, observations show that the location of stars along the HB is not a simple function of metallicity, and additional parameters are needed to explain observations (the second parameter problem: Sandage \& Wildey 1967; van den Bergh 1967). This issue has resisted 36 years of intense efforts: Clearly there cannot be a single second parameter, although in some cases this is likely to be the age, as in the GC Ruprecht 106 (Buonanno et al. 1990).

Among the various unclear aspects of the HB is the presence of gaps in the stellar distribution (see Moehler 2001). Some of these gaps are certainly real. In particular, a gap at about $11,500 \mathrm{~K}$ present in a large number of clusters can be attributed to the disappearance (at higher temperatures) of the subatmospheric convection zone owing to the large opacities related to H and He ionization (Caloi 1997). Stars warmer than this value have deep radiative envelopes, where microscopic diffusion and radiation levitation is free to act over the whole lifetime of HB stars ( $\sim 210^{8}$ years). The expectations from models that include these effects (Michaud, Vauclair \& Vauclair 1983, Hui-Bon-Hoa, Leblanc \& Hauschildt 2000) agree well with observation of large chemical peculiarities in warm HB stars (Heber 1987; Glaspey et al. 1989; Peterson et al. 1995, 2000; Behr et al. 1999, 2000a; Moehler et al. 2000; Behr 2003a; Fabian et al. 2003): large He depletions, and large overabundances of selected elements (Fe, Ti, Cr, and Mn, etc.) (see Figure 13); abundances for other elements (like $\mathrm{Ca}, \mathrm{Mg}$, and Si ) are much closer to those found in red giants. However, as expected, stars cooler than this limit display a surface chemical composition similar to that observed in much cooler red giants (Glaspey et al. 1986, 1989; Lambert, McWilliam \& Smith 1992; Cohen \& McCarthy 1997; Behr et al. 1999, 2000a; Peterson et al. 2000; Behr 2003a; Fabian et al. 2003).

The chemical composition of warm HB stars also helps to explain other peculiarities: In particular, the anomalous bright $u$ magnitudes (Grundahl et al. 1999), and the low surface gravities (and hence masses) obtained from analysis of the H-line profiles (Crocker, Rood \& O’Connel 1988; Moehler 1999). In both cases, adoption of larger atmospheric metal abundances (as obtained from the abundance analysis) largely improve the agreement between observed and predicted properties (Hui-Bon-Hoa et al. 2000, Moehler et al. 2003).

In contrast, other features are still not adequately understood. The 11,500 K threshold corresponds to a gap in the star distribution only in some clusters. Moreover, whereas HB stars warmer than the $11,500 \mathrm{~K}$ threshold do not rotate (as found for GC stars in other evolutionary phases: Lucatello \& Gratton 2003), significant rotations, up to a few tens of $\mathrm{km} / \mathrm{s}$ are widespread among HB stars cooler than this limit (Peterson 1983, 1985a, 1985b; Peterson et al. 1995; Behr et al. 2000a, 2000b; Recio-Blanco et al. 2002; Behr 2003a). The reason some HB stars rotate is unclear (see the review by Moehler 2001), as it is the fact that stars warmer than the 11,500 K threshold do not. Yong, Demarque \& Yi (2000) proposed that mass loss


Figure 13 Difference between either $[\mathrm{Fe} / \mathrm{H}]$ values (upper panel) or $[\mathrm{He} / \mathrm{H}]$ values (lower panel) obtained for stars on the blue HB and average values for the clusters as a function of effective temperature. Filled squares are results from Behr (2003a) for M3, M13, M15, M68, M92, and NGC288; open squares are results from Fabian et al. (2003) for NGC1904.
along the HB may originate from extremely blue HB stars. Vink \& Cassisi (2002) found that radiation pressure on spectral lines is not enough to cause such an effect, but it may explain that the lack of rotation in the warmer stars may be related to loss of angular momentum by wind. Finally, we note that whereas statistics are still not very large, possibly there are puzzling systematic cluster-to-cluster variations in the incidence of rotating stars (Recio-Blanco et al. 2002). Nevertheless, it is remarkable that both abundance anomalies and rotation pattern for cluster HB stars are similar to those found in analogous field stars (Behr 2003b), hence the origin of these peculiarities is not to be found in the large densities of GCs.
5.1.4. POST-EHB AND POST-AGB STARS Once He is nearly exhausted at the center, the star evolves off the HB. If its residual mass is larger than about $0.6 M_{\odot}$, the star may reach the AGB, burning H in a shell. The mass of stars in GCs is so small that they leave the AGB before the thermal pulse phase may develop. Cool post-AGB stars in GCs are then not expected to show peculiar abundances. This is indeed the case for RV Tau stars (see review and discussion by Russell 1998). It should be noted that whereas cluster RV Tau's do not display any significant abundance peculiarity, this is not the case for the corresponding field (Pop. I) objects (Luck \& Bond 1989), where large underabundances of Fe and a few other elements are considered as evidence for depletion onto dust grains. This difference might possibly be due to a much smaller incidence of (wide) binaries in GCs (Russell 1998). On the other hand, there may be peculiar post-AGB stars, as shown by the analysis of V42 in M5 by Carney, Fry \& Gonzalez (1998: a large and unexpected Li abundance of $\log \epsilon(\mathrm{Li})=1.8$, but no other peculiarity), and of star 1412 in M4 by Whitmer et al. (1995: strong TiO bands and a gross deficiency in C, and again no further anomaly).

Whereas cool post-AGB stars in GCs do not display evidences for depletion onto dust grains, such a process has been called to explain the observed pattern of hot post-AGB stars (Moehler et al. 1998b, Dixon \& Hurwitz 1998, Mooney et al. 2002). These stars generally display very large N excesses and low C abundances (Conlon, Dufton \& Keenan 1994; Mooney et al. 2002; Landsman et al. 2002), indicating that they evolved off the AGB before the first thermal pulse, although stars with large C abundances (Dixon, Brown \& Landsman 2002), and even with spectacularly high O abundances (Klochkova \& Samus 2001) have also been found. These last objects are unexpected, and suggest some peculiarities (e.g., binarity).

Hot post-AGB stars display a wide range of He abundances, but generally some He is indeed observed (Adelman et al. 1994; Moehler, Landsman \& Napiwotzki 1998a). Nonetheless, stars that have a mass not large enough to reach the AGB and evolve directly from the HB toward hot temperatures (EHB stars) do not display any He (Moehler et al. 1998a). Again, this pattern is expected, owing to He sedimentation during the HB phase.

### 5.2. Stars in Binary Systems

5.2.1. CH AND Ba-STARS CH -stars are characterized by strong bands of CH and $\mathrm{C}_{2}$, Ba-stars by strong Ba II lines (Keenan 1942). Both groups of stars are the result of mass transfer (generally by wind) from a thermally pulsing AGB star onto a less evolved companion, the star that is currently observed (McClure, Fletcher \& Nemec 1980; McClure 1984). The binary system should have been originally wide enough to allow evolution of the primary up to the AGB.

A catalog of CH stars, including objects in GCs, has been prepared by Bartkevicius (1996). A few other objects have been discovered since then (Côté et al. 1997; Buss, Shetrone \& Briley 1998): The total number of objects known is about 20. However, a large fraction of these objects can be misclassified, not being truly CH- or Ba-stars (see III-106 in M22: Vanture \& Wallerstein 1992). All
$\mathrm{CH}-$ and Ba-stars discovered thus far in GCs are bright giants. This is certainly an observational selection effect because most CH -stars in the field are subgiants or MS stars (Bartkevicius 1996). Hence we expect the census of CH- and Ba-stars in GCs to be largely incomplete. Furthermore, all known CH and Ba-stars in GCs are in low concentration clusters. This is likely due to the fact that in highly concentrated clusters, the possible progenitor systems (with a binding energy only a few times larger than the kinetic energy of individual stars) are destroyed on a timescale shorter than the evolution of intermediate-small mass stars (see Giersz \& Spurzem 2000).

Whereas CH - and Ba -stars are thought to originate in binaries, it is not obvious that we should still observe them as members of binary systems in GCs. Owing to the large mass lost by the former primary at the end of its AGB phase, the system should appear very loose, and would have likely been disrupted on a short timescale. As a matter of fact, there is no evidence for radial velocity variations, at least in the case of the CH-stars in M22 studied by Côte et al. (1996).

The chemical composition of the few CH - and Ba -stars with adequate studies agrees with typical values found for field CH-stars. This is, for instance, the case of stars RGO 55 (Bell \& Dickens, 1974) and RGO 70 (Bell \& Dickens 1974, Gratton 1982) in $\omega$ Cen. These stars have $[\mathrm{Fe} / \mathrm{H}]=-1.9$ (RGO70), ${ }^{12} \mathrm{C} /{ }^{13} \mathrm{C} \sim 10$, $[\mathrm{C} / \mathrm{H}] \sim-0.8,[\mathrm{O} / \mathrm{H}] \sim-1.3,[\mathrm{~N} / \mathrm{H}] \sim 0$, and overabundance of the elements produced by the $s$-process. Unluckily, these stars not only have been polluted by a previous companion, but they have also been quite severely mixed, so that details of the composition of the AGB wind have been partly lost. Detection and detailed observations of dwarf CH-stars in GCs would be highly welcome.
5.2.2. BLUE STRAGGLERS Blue straggler stars (BSSs) (that is MS stars bluer than the TO: Sandage 1953) are known to be present in all GCs surveyed (De Angeli \& Piotto 2003). They are the result of the evolution of close binary systems. Different channels may be active to create BSSs (for a comprehensive discussion see Bailyn 1995). In the field and in open cluster, the dominant channel is mass transfer in a binary system when the primary fills the Roche lobe while evolving on the RGB, creating a system composed of massive MS stars and a white dwarf (McCrea 1964), a process very similar to that creating CH-stars, but with a smaller initial separation. As a result, virtually all field BSSs are in binary systems (Preston \& Sneden 2000). The surface chemical composition of field BSSs exhibits the signatures of material coming from deep regions of the former primary, that is an incomplete CN cycle (Preston \& Sneden 2000). Li is expected to be strongly depleted: This is indeed confirmed by observations (Ryan et al. 2001), so that these authors turned around the argument, suggesting that all Li-poor metal-poor field stars (with temperatures within the Spite's plateau) actually are BSSs, even if their color is bluer than the TO for the corresponding isochrone.

BSSs in GCs may be formed not only by the McCrea mass-transfer mechanism from primordial binaries (that is expected to be efficient only in the less concentrated cluster because it requires rather large initial separations in order for the
primary to evolve along the RGB), but also through stellar encounters in the very dense stellar cores. These may form BSSs by direct stellar collisions, resulting in a merged star, as well as from tidal capture and then mass transfer. The radial distribution of BSSs within GCs shows that both mechanisms are active, one favored in the cluster core, and the other in the outermost regions (Fusi Pecci et al. 1992, Ferraro et al. 1993). On the whole, BSSs are more frequent in loose clusters than in dense ones (De Angeli \& Piotto 2003), suggesting that direct collisions are not the dominant channel.

The chemical composition could help to separate the two origins: BSSs created by direct collisions should undergo very little mixing between the inner cores and the outer envelopes of the colliding stars (Lombardi, Rasio \& Shapiro 1995). In the mass-transfer production channel the gas from the donor star instead is expected to come from deep regions (Sarna \& de Greve 1996), and the resulting BSSs should show signatures of mixing with incomplete CN-products, and an overabundance of He. Very little is known thus far about the composition of cluster BSSs. In principle, insights into the chemical composition of pulsating BSSs (SX Phoenicis variables) can be obtained from their pulsational parameters. However, this is not practically easy because in most cases the mode of pulsation cannot be determined, and because the period-luminosity relation is not affected much by details of the chemical composition (Templeton, Basu \& Demarque 2002). Santolamazza et al. (2001) propose to use secular period changes in order to derive He abundances in the stellar envelope, thus gaining insight into the physical mechanisms that trigger BSSs formation. In contrast, BSSs in the closest GCs are accessible to highdispersion analysis from $8-10 \mathrm{~m}$ telescopes, and exciting results are expected in the near future.
5.2.3. MILLISECOND PULSAR COMPANIONS The GCs host a large population of millisecond pulsars (MSP) (about 50 objects known; half of the total Galactic population), their formation is clearly favored by the dense environment (for a review of the properties of millisecond pulsars, see Lorimer 2001). In most systems the companion to a binary MSP is either a white dwarf or a very light $\left(0.01 \div 0.03 M_{\odot}\right)$ almost exhausted star (Hansen \& Phinney 1998, Stappers et al. 2001) with an MS star, perhaps acquired via dynamical encounters in the cluster core, orbiting MSP 47 Tuc-W in 47 Tuc (Edmonds et al. 2002). These stars are optically very faint objects, inaccessible to an abundance analysis; however, recently Ferraro et al. (2001) identified the optical counterpart of the MSP J1740-5340 in NGC 6397 with a rather bright variable having a luminosity similar to that of TO stars and an anomalous red color (COM J1740 5340). The shape of the optical curve is a clear signature of tidal distortion, providing strong evidence that the pulsar is orbiting a companion that has almost completely filled its Roche lobe. The mass of COM J1740 5340 (accurately determined at $\sim 0.3 M_{\odot}$ : Ferraro et al. 2003; Kaluzny, Rucinski \& Thompson 2003) is too high for a very light companion. The nature of this binary system is very intriguing (Burderi, D'Antona \& Burgay 2002; Possenti 2002; Orosz \& van Kerkwijk 2003; Grindlay et al. 2002): COM J1740 5340 could be an MS star acquired by exchange interaction in the cluster core, or alternatively,
the same star that spun up the MSP. Sabbi et al. (2003) showed that whereas the abundances of several elements ( $\mathrm{Fe}, \alpha$-elements) agree with those of the cluster, COM J1740 5340 lacks C, indicating that the star has been peeled down to regions where incomplete CNO burning occurs, favoring a scenario where the companion is a TO star that has lost most of its mass (Burderi et al. 2002, Ergma \& Sarna 2003). Finally, the presence of Li suggests that some fresh Li was produced on the stellar surface, possibly by high-energy particles coming from the pulsar.

## 6. CONCLUSIONS

In this review we have considered the most important results about star-to-star abundance variations in GCs, and variations depending on apogalactic distance. Summarizing, they may be due to a large variety of phenomena:

- GCs have an initial composition which depends on previous evolution of the matter from which they formed. Systematic trends with galactocentric distance like those shown in Figure 5 suggest that large-scale phenomena on a galactic scale played an important role. However, it is well possible that a significant amount of the metals we presently observe in clusters were manufactured within the same episode that later led to the cluster formation.
- Changes in the surface chemical composition occur during the evolution of single stars, both in GCs and in the general field. Such changes include standard mixing effects for intermediate- and low-mass stars like the first dredge-up and Li dilution at the base of the RGB, the third dredge-up during the AGB phase (although stars evolving through this phase are now white dwarfs in GCs), as well as nonstandard mixing that occurs after a star has passed through the RGB bump. In clusters and field stars, the effects of microscopic diffusion and levitation owing to radiation pressure become obvious whenever enough time is left for them to take place. The timescale is short enough to be effective in warm HB stars, as well as possibly in stars close to the MS TO in the most metal-poor clusters. Finally, possible evidence for the effects of depletion on dust grains may be visible in hot post-AGB stars. All these effects are not peculiar to GCs, and there is no strong evidence that their effects on typical GC stars is much different from what occurs in field stars of similar mass, metallicity, and age; however, GCs offer unique possibilities to study them in detail, in particular for those phases having short duration. An additional phenomenon that may strongly affect evolution of single stars is mass loss: Whereas the picture is far from being clearly set, there are several observations (lack of bright red giants, excess of B-subdwarfs) suggesting that mass loss may be significantly different from stars in the core of GCs (see the review by Bailyn 1995). More observations and theoretical modeling are urgently needed in this area.
- Mass transfer in binary systems is an effective way to cause abundance changes in a minority of stars. It occurs in GC as well as in field stars.

However, formation and evolution of binaries is strongly affected by the overall density of the medium: Hence, characteristics of binaries in GCs are much different from those in field stars. Wide binaries, that originate CHand Ba-stars, as well as BSSs owing to Roche-lobe overflow, are underrepresented in GCs, apparently found only in clusters of low concentration. Despite this, GCs host a numerous population of close binaries, partly primordial and partly owing to dynamical interactions within its dense cores. Little is known about the chemical composition of these stars; the only example studied so far is the companion of the millisecond pulsar COM J1740-5340. A wealth of new data may shortly appear thanks to the use of powerful 8-10-m telescopes.

- Finally, GCs as a whole may have a complex chemical history. In the case of $\omega$ Cen, different generations of stars are clearly present, allowing enrichment by different contributors (core collapse SNe, AGB stars, and likely also thermonuclear SNe for the most metal-rich population). This might be due to a special history of this cluster that in the past could have been the nucleus of a dwarf elliptical galaxy; however, it is possible that $\omega$ Cen is not unique in this respect. However, most if not all GCs show evidence of a much shorter but not negligible chemical enrichment history. Whereas the contribution of core collapse SNe in the very early phases of the protocluster evolution is still controversial, there is increasing evidence that massive AGB stars may have significantly contributed to the metal enrichment of part of the GC stars. This last event is peculiar to GCs-in other stellar populations characterized by less dense environments the contribution by these stars cannot be separated from those of other objects.

This large variety of phenomena makes the picture complicated but exciting. We are in fact progressively gaining more and more insights into the early phases of evolution of one of the building blocks of the Universe.

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Figure 8 Run of the abundance of Li ; of the abundance ratios $[\mathrm{C} / \mathrm{Fe}],[\mathrm{N} / \mathrm{Fe}],[\mathrm{O} / \mathrm{Fe}]$, and $[\mathrm{Na} / \mathrm{Fe}]$; and of the isotopic ratio ${ }^{12} \mathrm{C} /{ }^{13} \mathrm{C}$ with luminosity for stars with $-2<[\mathrm{Fe} / \mathrm{H}]<-1$. Upper limits (lower limits for the isotopic ratios) are indicated. The RGB bump occurs near $\log L / L_{\odot} \sim 1.8$ (from Gratton et al. 2000).


Figure 9 Abundance profile for $\mathrm{O}, \mathrm{Na}$, and Ne in and near the H -burning shell (adapted from Weiss et al. 2000).

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## ERRATA

An online log of corrections to Annual Review of Astronomy and Astrophysics chapters may be found at http://astro.annualreviews.org/errata.shtml


[^0]:    ${ }^{1}$ In this section the symbols $\rangle$ are reserved to represent means computed from multiple cluster abundance sets. Mean values computed from ensembles of stars within individual clusters will appear without the enclosing brackets but with the cluster name as a subscript.

[^1]:    ${ }^{2}$ Catalog is available at http://physun.memaster.ca/harris/mwgc.dat.

[^2]:    ${ }^{3}$ Gratton et al. (2001) apparently found constant abundances of O in low-luminosity stars of NGC 6397. However, Thévenin et al. (2001) discovered one turn-off star in this cluster with an Na abundance quite different from the others of their sample, and a new survey of NGC 6397 (E. Carretta, R. Gratton, A. Bragaglia, unpublished manuscript) with an expanded sample does recover the typical $\mathrm{O}-\mathrm{Na}$ anticorrelation seen in giant stars of other clusters.

[^3]:    ${ }^{4}$ The presence of deep mixing dredging-up to the surface of MS stars the light metals $\mathrm{C}, \mathrm{N}$, $\mathrm{O}, \mathrm{Na}, \mathrm{Mg}$, and A1 should also bring fresh fuel (hydrogen) to the cores. Because the MS lifetime depends on the H exhaustion in the stellar cores, the effect should be visible in the CMD and in LF around the TO region, at odds with observations.

[^4]:    ${ }^{5}$ Here and in the following, $\epsilon(\mathrm{A})$ is the abundance by number of atoms of the element A , in a scale where the abundance of H atoms is $10^{12}$.

