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THE RATIO OF TITANIUM TO ZIRCONIUM IN LATE-TYPE STARS

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ABSTRACT

High-dispersion (4–15 Å mm^{-1}) spectrograms of thirty-six K–M stars, five Ba II stars, six MS stars, and nine S stars have been analyzed by a curve-of-growth technique to yield the atomic-abundance ratio of Ti to Zr. The correction arising from formation of the molecular oxide is considered. The Ti/Zr ratio for the K and M giants is similar to the solar value In the Ba II and S stars, this ratio is 3–30 times lower than in the normal stars; the average value is about 6 times less. The average for the MS stars is intermediate between the normal stars and the Ba II and S stars The abundance results are compared with those of other investigators to examine the evolutionary interrelationships of the various types of red giants. The discussion is in the context of nucleosynthesis.

I. INTRODUCTION

Three major classes of late-type giants are distinguished by their spectra: (1) normal K and M stars having nearly solar composition, with M stars containing molecular oxide bands from the fourth period of the periodic table, e.g., TiO; (2) heavy-metal giants, the Ba II and S stars, with the S stars showing molecular oxides of elements from the fifth period, e.g., ZrO; and (3) the carbon stars showing bands of C_2, CN, and CH. The difference in the appearance of the three types of spectra has been thought to be due to the ratio of oxygen to carbon resulting from the high dissociation potential of the CO molecule (Russell 1934). The less abundant of the two species will be almost exclusively tied up in CO, while the more abundant is available to form other compounds. Fujita (1939) has suggested that a low O/C ratio in S stars would lead to a low partial pressure of O, which in turn would favor the formation of ZrO over TiO, since the dissociation energy of ZrO is greater than that of TiO.

Qualitative studies of Merrill (1947), Keenan and Aller (1951), and Buscombe and Merrill (1952) have suggested that atomic Zr is more abundant than Ti in the S star R And. From molecular-equilibrium calculations and an analysis of two S stars in the infrared region, Tsuji (1962) concludes that, in addition to a low O/C ratio, the S stars have a higher abundance of Zr than M stars.

Titanium is formed primarily by the α- and e-processes, and its abundance is not expected to change as the star evolves. Since Zr is produced by the s-process, its abundance should increase with neutron exposures in the interiors of red giants according to the theory of nucleosynthesis presented by Burbidge *et al.* (1957) and the neutron-irradiation calculations of Seeger, Fowler, and Clayton (1965). Thus, the ratio Ti/Zr can yield information on nucleosynthesis and the relative phase of evolution of a late-type giant. In this study, actual Ti/Zr abundance ratios have been determined in Ba II, K, M, MS, and S stars. Both in numbers of stars and in stellar types, a broad base is provided on which to compare the neutron-irradiation predictions of nucleosynthesis with observations.

II. OBSERVATIONS AND MEASUREMENTS

Fifty-six stars have been observed with the coudé spectrographs of the 100-, 120-, and 200-inch reflectors. The dispersions used at each telescope are: 100-inch, 6.7 and 15 Å mm^{-1}; 120-inch, 4 and 8 Å mm^{-1}; 200-inch, 6.8 and 13.5 Å mm^{-1}. All spectrograms were taken on Eastman 103a-F or IIa-F emulsions and, in general, were widened to at

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least 0.6 mm. The S-star spectrograms secured at Palomar were kindly made available for this study by Dr. Jesse L. Greenstein. The stars observed are listed in Table 1. The seven stars listed below Table 1 were used as standards representative of, respectively, Ba II, K, M0–M1, M2–M4, M supergiants, MS, and S stars.

Step-slit calibration exposures were made at the time of the stellar exposure on each plate obtained with the 100- and 120-inch telescopes; the auxiliary calibration spectrograph at the 200-inch reflector provided the intensity calibration for those plates. Direct-intensity microphotometer tracings were made for all plates with a magnification of 100–200 covering the wavelength region λλ5650–6720. The resolving slit of the microphotometer was set at 10 μ, a setting consistent with the narrow slit widths used at the telescope.

The position of the continuum was established with little difficulty in the K and Ba II stars. To assure a degree of consistency, the continua in the later-type stars were positioned with reference to each other and to the relatively unblended spectra of the K and Ba II stars. Equivalent widths of twenty Ti I lines and seven Zr I lines were measured on each tracing where possible. Readings were made in two coordinates along the line profile with either a Gerber or a Benson-Lehner digital recorder; a computer program then added the areas of trapezoids and calculated the equivalent width of each line. At the time of measurement, a number from 1 to 5 was assigned to each equivalent width to represent the accuracy of the measurement (1 = highest accuracy; 5 = lowest); these numbers reflect factors such as blending effects and uncertainty in the continuum level and indicate which lines have the greatest reliability when the curve of growth is constructed.

The equivalent-width measurements from the Lick Observatory spectrograms have been previously published (Merchant 1967*a*). The equivalent widths determined from the Mount Wilson and Palomar material are given in Table 2. Where there is more than one spectrogram, the equivalent width given is a weighted mean determined by the quality and dispersion of the spectra.

III. DATA ANALYSIS

The analysis procedure followed the standard curve-of-growth method. The determination of the atmospheric parameters for the M stars is discussed in the paper by Merchant (1967*b*). The only difference between that procedure and the method used for the MS, S, and Ba II stars is the use of the Ti I rather than the V I lines to determine the excitation temperature.

The analysis of the initial standard star, α Hya, was done with the abscissa of the curve of growth equal to $\log (gf\lambda) - \theta_{\rm exc}\,\chi - \log \alpha_\lambda(H^-)$, where the gf-values are from Corliss and Bozman (1962) and the continuous absorption coefficient for H^-, $\alpha_\lambda(H^-)$, is taken from Gingerich (1961). Once the excitation temperature ($\theta_{\rm exc} = 5040/T_{\rm exc}$) was determined, values of the abscissa, $\log \eta'_0(\alpha$ Hya), were read off the curves of growth of the different elements by entering the curve with the measured $\log W/\lambda$. These values were used to make the preliminary curve and then determine $\theta_{\rm exc}$ and the velocity parameter for the K stars in the α Hya group. These $\log \eta'_0(\alpha$ Hya) values were also used to construct the first curve for the next standards, HR 2392 (K0 Ba3) and γ Eri (M1 III). Excitation temperatures and microturbulent velocities were found for these standards, and new $\log \eta'_0(2392)$ and $\log \eta'_0(\gamma$ Eri) were determined. Again, these values of the abscissa were used for the preliminary curves for the stars in their respective group and for the next standards, i.e., δ Vir and δ Sge from γ Eri. In like manner, a succession was made from δ Vir (M3 III) to the standard MS star, HR 2967 (M3S), then to the standard S star, HR 8714 (S5,1).

This method of successive evaluation of the $\log \eta'_0$'s has two special features to recommend it: (1) Every star is analyzed relative to a standard star to which it is very similar. The scatter in the resultant curves of growth is greatly reduced by comparing an S star

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TABLE 1

SPECTROSCOPIC DATA

Star	HD	Spectral Type *	Standard(s)+	No. of Plates	Dispersion A/mm
χ Peg	1013	M3 III	D	1	8
	1613	M2 II: S?	F	1	13.5
T Cet	1760	M5-6S	G	2	6.7
R And	1967	S6,6e	G	1	6.8
η Cet	6805	K2 III	B	1	4
β And	6860	M0 III	C	3	4,4,8
HR 363	7351	M2S	F	1	6.7
υ Cet	12274	M1 III	C	1	8
α Cet	18884	M2 III	D	1	8
HR 1105	22649	S5,3	G	1	6.8
γ Eri	25025	M1 III	B	3	8
o[1] Ori	30959	M3S	D,F	1	8
	35155	S4,1	G	2	6.7,15
119 Tau	36389	M2 Ib	E	1	8
HR 2018	39045	M3 III	D	1	8
HR 2028	39225	M3 III	D	1	8
α Ori	39801	M2 Iab	E	2	8
π Aur	40239	M3.5 II	D	2	8
HR 2275	44131	gM1	C	1	8
HR 2392	46407	K0 Ba3	B	2	6.7
R CMi	54300	pec‡	G	1	13.5
HR 2902	60414	M2ep Iab	E	1	8
HR 2967	61913	M3S	D	3	6.7
SU Mon	62164	S 3,6	G	1	15
HR 3288	70652	M1	C	1	8
α Lyn	80493	M0 III	C	1	8
α Hya	81797	K4 III	-	1	4
HR 3820	83069	gM1	C	1	8
ψ UMa	96833	K1 III	B	1	4
ν Vir	102212	M1 III	C	1	4
ψ Vir	112142	M3 III	D	1	4
δ Vir	112300	M3 III	C	2	4,8
HR 5219	120933	gM2	D	1	8
	121447	K7 Ba5	B,C	1	15
σ Lib =					
γ Sco	133216	M4 III	D	1	4
δ Oph	146051	M1 III	C	1	8
α Sco	148478	M2 Ib	E	1	8
δ[2] Lyr	175588	M4 II	D	1	4
	178717	K4 Ba4	B,C	1	15
T Sgr	180196	S5,8e	G	1	6.8
α Vul	183439	M0 III	C	1	8
	183915	K1 Ba2	A	1	15
R Cyg	185456	S5,8e	G	1	6.8
δ Sge	187076	M2Ib-II	C	2	4
γ Sge	189319	K5+ III	C	2	4,8
	191589	early S:	C	1	13.5
	196673	K0 Ba2	A	1	15
24 Cap	200914	M1 III	C	1	8
29 Cap	202369	gM3	D	2	4,8
HR 8164 A	203338	M1ep Ib	E	1	8
5 Lac	213310	M0Ib-II	E	1	8
λ Aqr	216386	M2 III	D	1	8
HR 8714	216672	S5,1	F	2	6.7
β Peg	217906	M2+ II-III	D	1	8
57 Peg	218634	M4S	F	2	6.7
ψ Peg	224427	M3 III	D	1	8

*From Yale Catalog of Bright Stars, Keenan (1954), Bidelman (1957), Warner (1965).

+Standards: A=HR 2392, B=α Hya, C=γ Eri, D=δ Vir, E=δ Sge, F=HR 2967, G=HR 8714

‡R CMi has an atomic spectrum similar to an S1 star, but shows no bands ZrO or LaO; the C_2 Swann bands are present. Keenan (1950) calls it a red carbon star.

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TABLE 2 (Continued)

λ	HD 121447		HD 178717		T Sgr		HD 183915		R Cyg		HD 191589		HD 196673		HR 8714		57 Peg	
	wt	$-\log \frac{W}{\lambda}$	wt	$-\log \frac{W}{\lambda}$	wt	$-\log \frac{W}{\lambda}$	wt	$-\log \frac{W}{\lambda}$	wt	$-\log \frac{W}{\lambda}$	wt	$-\log \frac{W}{\lambda}$	wt	$-\log \frac{W}{\lambda}$	wt	$-\log \frac{W}{\lambda}$	wt	$-\log \frac{W}{\lambda}$
TiI																		
6599	2	4.30	2	4.33	3	4.21	3	4.75	3	4.16	2	4.58	4	5.03	2	4.39	2	4.75
6556	3	4.43	-	--	4	4.33	3	4.70	-	--	2	4.59	3	4.81	2	4.34	2	4.59
6554	3	4.36	3	4.36	4	4.46	4	4.61	-	--	2	4.67	4	4.90	3	4.44	2	4.73
6546	2	4.48	-	--	4	4.43	1	4.51	-	--	1	4.59	1	4.55	2	4.39	1	4.63
6498	-	--	5	4.50	-	--	5	4.89	-	--	3	4.70	4	5.07	4	4.52	2	4.96
6419	-	--	3	4.66	-	--	4	4.94	-	--	3	5.02	4	5.23	3	4.78	3	5.08
6366	2	4.31	3	4.38	4	4.57	3	4.82	-	--	1	4.70	2	4.69	3	4.47	2	4.64
6336	4	4.50	4	4.58	3	4.88	4	4.99	3	4.54	3	4.79	3	5.06	3	4.80	3	5.05
6146	3	4.50	3	4.72	3	4.75	3	5.02	4	4.44	2	4.88	5	5.34	2	4.72	2	4.91
6126	2	4.31	3	4.41	-	--	3	4.63	3	4.31	2	4.73	-	--	2	4.53	1	4.56
6093	4	4.45	4	4.49	-	--	4	4.94	5	4.45	-	--	4	4.91	3	4.64	3	5.00
6091	3	4.63	3	4.54	-	--	4	5.01	5	4.59	2	4.83	4	5.14	2	4.68	3	4.78
6065	4	4.47	3	4.53	-	--	4	4.99	3	4.27	2	4.66	3	4.93	3	4.37	3	4.60
5866	3	4.40	3	4.33	3	4.28	3	4.73	4	4.24	2	4.42	3	4.52	2	4.35	3	4.64
5740	3	4.79	3	4.59	4	5.01	4	5.10	4	4.59	4	4.69	4	4.97	4	4.61	4	5.09
5739	4	4.69	4	4.76	3	4.80	4	5.21	4	4.73	-	--	4	5.03	4	4.54	4	4.98
5720	3	4.79	3	4.83	-	--	4	5.20	-	--	4	4.97	4	5.14	-	--	4	5.07
5716	3	4.86	4	4.74	3	5.10	4	5.06	3	4.96	3	4.96	4	5.16	5	4.74	4	5.27
5714	3	4.87	3	4.68	3	4.94	4	5.19	3	4.84	3	4.82	4	5.22	4	4.63	4	5.10
5689	4	4.87	4	4.30	3	4.94	4	4.87	5	4.46	-	--	4	4.92	-	--	3	4.91
ZrI																		
6446	3	4.96	3	5.07	3	4.92	4	5.42	3	4.51	3	5.43	4	5.49	2	4.96	2	5.15
6407	3	4.75	3	4.83	4	4.95	4	5.34	4	4.64	4	5.63	3	5.32	2	5.03	3	5.35
6143	2	4.30	2	4.37	-	--	3	4.66	3	3.93	1	4.63	-	--	2	4.44	1	4.76
6135	3	4.39	3	4.45	-	--	4	4.95	4	3.99	3	4.66	4	5.48	3	4.33	2	4.52
5886	3	4.62	3	4.62	-	--	3	5.66	-	--	2	4.71	4	5.31	4	4.69	3	4.82
5880	3	4.26	3	4.30	3	4.15	3	4.98	-	--	-	--	4	4.91	4	4.48	4	4.93
5737	2	4.45	3	4.52	3	4.03	4	5.32	5	4.06	2	4.56	-	--	3	4.34	3	4.77

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TABLE 2

EQUIVALENT WIDTHS

λ	HD 1613		T Cet		R And		HR 363		HR 1105		HR 35155		HR 2392		R CMi		HR 2967		SU Mon	
	wt	$-\log \frac{W}{\lambda}$	wt	$-\text{lot} \frac{W}{\lambda}$	wt	$-\log \frac{W}{\lambda}$	wt	$-\log \frac{W}{\lambda}$	wt	$-\log \frac{W}{\lambda}$	wt	$-\log \frac{W}{\lambda}$	wt	$-\log \frac{W}{\lambda}$	wt	$-\log \frac{W}{\lambda}$	wt	$-\log \frac{W}{\lambda}$	wt	$-\log \frac{W}{\lambda}$
TiI																				
6599	1	4.26	4	4.73	3	4.29	3	4.44	3	4.41	-	--	3	5.15	3	4.16	2	4.48	1	4.05
6556	2	4.28	2	4.60	4	4.37	2	4.45	3	4.46	3	4.52	4	4.87	3	4.36	2	4.39	3	4.02
6554	2	4.39	3	4.77	-	--	2	4.46	3	4.52	3	4.55	3	4.88	3	4.38	2	4.51	3	4.10
6546	2	4.28	4	4.82	4	4.52	2	4.42	3	4.59	3	4.49	1	4.60	3	4.30	1	4.45	3	4.10
6498	3	4.40	4	5.13	-	--	3	4.54	4	4.55	3	4.65	4	4.98	-	--	2	4.69	4	4.15
6419	3	4.73	4	4.99	4	4.67	3	4.75	4	4.73	-	--	3	5.19	-	--	2	4.93	4	4.40
6366	2	4.40	5	4.61	-	--	2	4.48	4	4.41	4	4.64	2	4.74	3	4.28	2	4.54	3	4.42
6336	-	--	4	4.98	4	5.00	2	4.77	4	4.66	-	--	3	5.20	-	--	2	4.81	3	4.83
6146	2	4.58	4	5.04	-	--	2	4.72	3	4.78	3	4.76	4	5.19	3	4.58	1	4.75	3	4.58
6126	2	4.37	3	4.78	2	4.34	1	4.46	3	4.48	-	--	2	4.64	3	--	1	4.52	3	4.21
6093	4	4.70	2	5.02	3	4.63	3	4.77	4	4.83	3	4.82	4	5.21	3	4.71	2	4.73	3	4.43
6091	2	4.60	3	4.96	4	5.01	2	4.59	3	4.77	3	4.72	2	5.00	4	4.85	1	4.68	3	4.53
6065	3	4.49	4	4.67	3	4.45	2	4.51	2	4.42	3	4.55	3	5.08	-	--	2	4.52	2	4.21
5866	2	4.38	3	4.64	3	4.22	2	4.36	3	4.33	1	4.46	2	4.61	3	4.23	2	4.35	-	--
5740	4	4.66	-	--	4	4.69	3	4.65	-	--	4	4.71	4	4.99	4	4.42	4	4.76	-	--
5739	4	4.53	4	4.65	-	--	3	4.57	-	--	4	4.78	4	5.20	4	4.40	4	4.70	-	--
5720	4	4.61	-	--	-	--	3	4.57	-	--	-	--	5	5.57	-	--	4	4.88	-	--
5716	3	4.73	-	--	4	5.18	3	4.71	3	4.89	3	4.97	4	5.00	-	--	-	--	-	--
5714	4	4.84	-	--	-	--	3	4.66	4	4.70	3	4.77	5	5.54	-	--	4	4.85	5	4.56
5689	3	4.67	-	--	4	4.84	-	--	4	4.65	3	4.69	-	--	-	--	-	--	-	--
ZrI																				
6446	1	4.99	3	5.07	3	4.98	1	4.94	3	4.83	2	4.84	2	5.30	3	4.57	1	5.09	4	4.60
6407	4	5.33	4	5.35	4	5.32	2	4.94	3	4.84	4	4.87	4	5.63	3	4.83	2	5.17	3	4.68
6143	1	4.47	3	4.67	3	4.13	1	4.38	2	4.40	2	4.50	2	4.74	3	4.27	2	4.64	2	4.04
6135	3	4.39	4	4.45	3	4.12	2	4.40	3	4.34	2	4.44	2	4.92	3	4.23	2	4.57	3	3.93
5886	3	4.94	3	4.60	3	4.40	3	4.91	3	4.55	3	4.64	3	5.25	4	4.26	4	5.01	5	4.12
5880	3	4.56	4	4.63	3	4.23	3	4.50	4	4.30	3	4.42	3	4.87	3	4.30	3	4.66	5	4.35
5737	3	4.46	-	--	3	4.24	3	4.32	4	4.20	3	4.49	4	5.34	3	4.12	2	4.69	5	3.87

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with a standard S star rather than the standard M star. Examples of the curves of growth are given in Figure 1. Samples for the M stars appear in the paper by Merchant (1967*b*). (2) It is unnecessary to know explicitly the cause or the value of the continuous absorption coefficient. It is represented implicitly in the changing values of the abscissa in the progression from standard star to standard star.

The final form for the atomic-abundance ratio is:

$$\log \frac{N(\mathrm{Ti})}{N(\mathrm{Zr})} = \Delta \log \eta_0 + \log \frac{v(\mathrm{Ti})}{v(\mathrm{Zr})} + \log \frac{u(\mathrm{Ti\ I})}{u(\mathrm{Zr\ I})} + \log \frac{(1+a)}{(1+b)}\,, \quad (1)$$

where $\Delta \log \eta_0$ is the horizontal shift of the Zr I curve to the Ti I curve, v is the thermal and turbulent velocity found from the vertical shift of the curve of growth, u is the partition function, and $a = N(\mathrm{Ti\ II})/N(\mathrm{Ti\ I})$ and $b = N(\mathrm{Zr\ II})/N(\mathrm{Zr\ I})$. The values of log

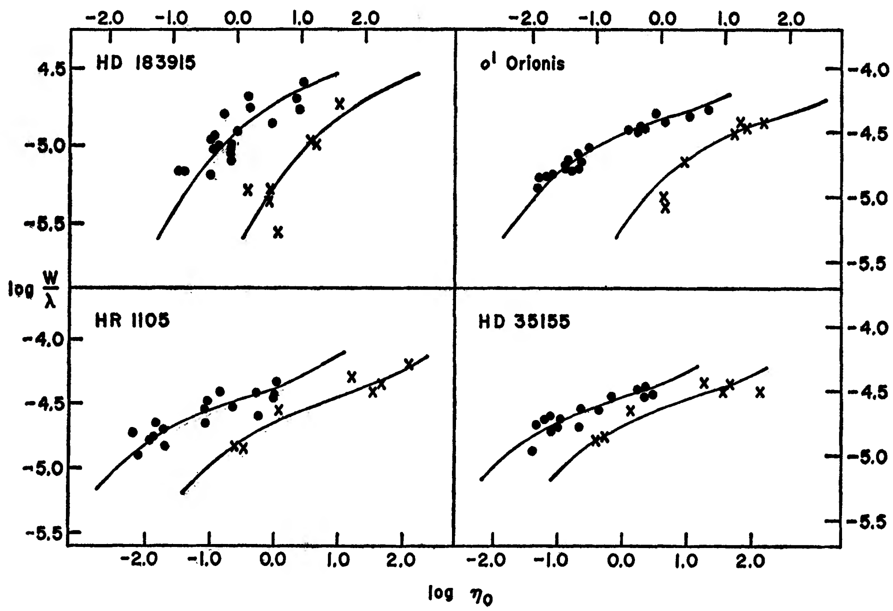

FIG. 1.—Examples of the curves of growth. *Filled circles*, lines of Ti I; *crosses*, Zr I lines. Data for the K0 Ba star HD 183915 is from a 15 Å mm⁻¹ Mount Wilson spectrogram. The star o¹ Ori is an M3S star; data are from an 8 Å mm⁻¹ Lick spectrogram. HR 1105 and HD 35155 are both S stars. The plate dispersion for HR 1105 is 6.8 Å mm⁻¹. There are two plates for HD 35155: 6.7 and 15 Å mm⁻¹. *Solid line*, appropriate curve of growth calculated by Wrubel (1949).

$v(\mathrm{Ti})/v(\mathrm{Zr})$ were found to be $\sim$0.01–0.02. The log of the ratio of the partition functions varies slightly with θ in this temperature range from about -0.02 to $+0.02$. Since the ionization potentials of Ti I and Zr I differ by only 0.02 eV, the values of a and b are very similar. With the guidance of the ionization temperatures and electron pressures found previously for the M stars (Merchant 1967*b*), $\log (1 + a)/(1 + b)$ was found to vary slightly with temperature between $\sim$0.06 and 0.01. None of the final three terms in equation (1) is large enough to have a significant effect on the final answer, but appropriate values were selected for each star from tabulations of both the partition function and the ionization degree as a function of temperature; the velocity term was individually determined.

The term $\theta_{\mathrm{exc}}\,\chi$ in $\log \eta_0$ contributes an error to $\Delta \log \eta_0$ in equation (1), since the average excitation potential (χ) of the twenty Ti I lines is 1.7 eV and of the seven Zr I lines is 0.2 eV. Thus, a probable error of 0.1 in θ_{exc}, not atypical for the cooler stars, leads

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to a temperature-induced error in log N(Ti)/N(Zr) of 0.15. The probable errors for θ_{exc} in the M stars are smaller, since the excitation temperature for them was found from thirty-eight lines of V I.

Intensity measures in terms of the continuum absorption were made of the TiO band head at λ6680.6 if the $\gamma(1, 0)$ system and of the ZrO head of the $\gamma(0, 0)$ band at λ6473.5. The intensity ratio I(TiO)/I(ZrO) was later compared with the atomic-abundance ratio.

IV. RESULTS

a) Atomic Abundances

Results obtained for the atomic-abundance ratio and the atmospheric parameters are presented in Table 3. The last column gives the intensity ratio of the molecular-oxide bands. For comparison, the solar log N(Ti)/N(Zr) is 2.27, with log N(Ti) = 4.50 taken from the recent work of Warner (1968) and log N(Zr) = 2.23 from Goldberg, Müller, and Aller (1960).

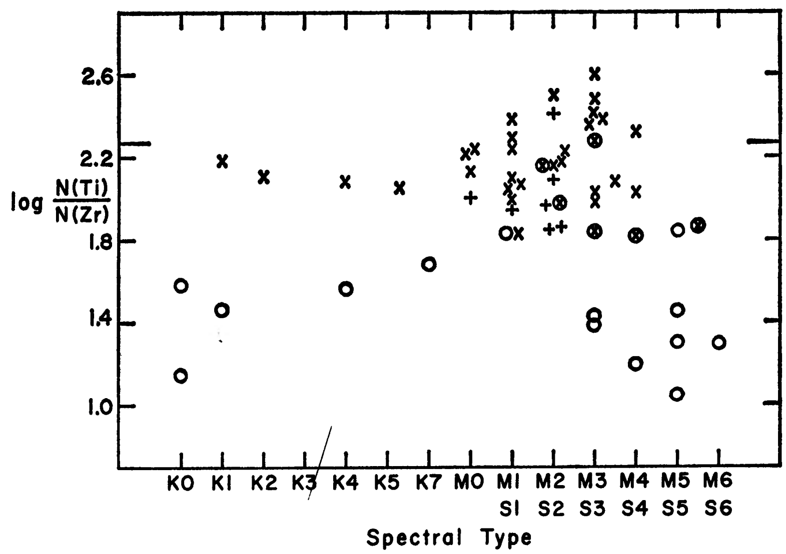

FIG. 2.—Logarithm of the atomic-abundance ratio Ti/Zr plotted against spectral type. *Crosses*, normal giants; *plus signs*, supergiants; *open circles*, Ba II and S stars; *circled crosses*, MS stars. Horizontal line at +2.27 shows the solar log N(Ti)/N(Zr). Note the clear distinction between the normal stars and the heavy-metal-rich stars.

The atomic-abundance ratio is plotted against spectral type in Figure 2, which shows a clear delineation between the normal K and M giants and the heavy-metal Ba II and S stars. Both the M-supergiant group and the MS star group seem to fall at intermediate values of log Ti/Zr. This result is less certain, however, since there are fewer stars in these groups.

This study, based on a large number of stars, shows conclusively that the heavy-metal stars have a lower Ti/Zr ratio than normal stars. Comparison of the line strengths in the two classes of stars at similar temperatures shows little difference in the Ti lines, but stronger Zr lines are found in the heavy-metal stars. Thus, the decrease in the Ti/Zr ratio in the heavy-metal stars is attributed to an increase in Zr. This work also demonstrates the similarity between Ba II and S stars in this abundance feature.

b) Molecular Effects

Since the dissociation potential for ZrO (7.8 eV) is higher than that for TiO (6.8 eV), more Zr will be in the molecular-oxide form than Ti. If a considerable portion of these

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TABLE 3

ATMOSPHERIC PARAMETERS AND ABUNDANCES

Star	Spectral Type	θ_{exc}	ξ km/sec	$\log \frac{N(Ti)}{N(Zr)}$	$\frac{I(TiO)}{I(ZrO)}$
Ba II Stars					
HD 196673	K0 Ba2	1.27	2.9	1.58	-
HR 2392	K0 Ba3	1.19	2.8	1.26	-
HD 183915	K1 Ba2	1.32	2.6	1.46	-
HD 178717	K4 Ba4	1.57	2.8	1.56	-
HD 121447	K7 Ba5	1.78	3.7	1.68	-
K Giants					
ψ UMa	K1 III	1.41	3.2	2.19	-
η Cet	K2 III	1.43	2.5	2.11	-
α Hya	K4 III	1.55	2.8	2.08	-
γ Sge	K5+ III	1.70	2.4	2.05	0.84
M0 - M1 Giants					
β And	M0 III	1.61	2.3	2.24	0.89
α Lyn	M0 III	1.63	2.5	2.13	1.09
α Vul	M0 III	1.57	2.3	2.22	1.35
υ Cet	M1 III	1.65	2.8	2.05	0.79
γ Eri	M1 III	1.66	2.9	2.24	1.01
HR 2275	M1 III	1.87	2.3	2.39	0.74
HR 3288	M1 III	1.61	2.3	2.00	0.90
HR 3820	M1 III	1.65	2.0	2.29	1.15
ν Vir	M1 III	1.63	2.1	2.10	1.08
δ Oph	M1 III	1.58	2.4	2.06	1.02
24 Cap	M1 III	1.48	2.8	1.83	0.69
M0 - M2 Supergiants					
5 Lac	M0Ib-II+A	1.65	4.0	2.00	0.78
HR 8164 A	M1Ib+B	1.66	2.6	1.95	0.86
δ Sge	M2Ib-II+A	1.64	2.8	1.97	0.99
119 Tau	M2Ib	1.64	4.4	2.09	0.78
HR 2902	M2Iab+B	1.63	4.1	1.86	0.83
α Ori	M2Iab	1.76	3.8	2.41	0.87
α Sco	M2Ib	1.63	3.8	1.85	0.86

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TABLE 3 (Continued)

ATMOSPHERIC PARAMETERS AND ABUNDANCES

Star	Spectral Type	θ_{exc}	ξ km/sec	$\log \frac{N(Ti)}{N(Zr)}$	$\frac{I(TiO)}{I(ZrO)}$
M2 - M4 Giants					
α Cet	M2 III	1.70	3.3	2.19	0.89
HR 5219	M2 III	1.71	3.0	2.17	1.02
λ Aqr	M2 III	1.81	3.1	2.50	1.15
β Peg	$M2^+$ II-III	1.71	3.3	2.22	1.21
χ Peg	M3 III	1.71	3.0	2.60	1.15
HR 2018	M3 III	1.74	3.0	2.41	1.10
HR 2028	M3 III	1.81	3.4	2.48	1.45
ψ Vir	M3 III	1.58	2.2	1.98	1.06
δ Vir	M3 III	1.70	2.7	2.38	1.16
29 Cap	M3 III	1.70	3.4	2.03	0.92
ψ Peg	M3 III	1.72	2.7	2.36	1.00
π Aur	M3.5 III	1.69	3.5	2.08	0.87
σ Lib	M3 III	1.69	2.4	2.32	0.96
δ^2 Lyr	M4 II	1.68	2.8	2.03	0.89
MS Stars					
HR 363	M2 S	1.65	2.3	1.98	0.72
HD 1613	M2 II: S?	1.61	3.7	2.16	1.11
o^1 Ori	M3 S	1.86	2.8	1.84	0.78
HR 2967	M3 S	1.80	2.6	2.28	1.04
57 Peg	M4 S	1.80	1.8	1.82	0.92
T Cet	M5-6 S	1.79	1.8	1.87	0.97
S Stars					
HD 191589	S1 ?	1.66	1.6	1.83	0.64
R CMi	pec	1.90	3.7	1.40	-
SU Mon	S3,6	1.80	4.9	1.43	0.45
HD 35155	S4,1	1.72	1.7	1.20	0.58
HR 8714	S5,1	1.80	2.8	1.84	0.86
HR 1105	S5,3	2.03	2.2	1.46	0.58
T Sgr	S5,8e	1.93	4.2	1.05	0.32
R Cyg	S5,8e	2.27	3.2	1.31	0.42
R And	S6,6e	2.01	2.9	1.30	0.34

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elements is in the molecular form, then our atomic-abundance ratio will not represent the true elemental-abundance ratio. The Zr would be underestimated relative to Ti, and the log $N(\mathrm{Ti})/N(\mathrm{Zr})$ would thus be too large. This effect should be greater in the cooler stars. Thus, the points on the right of Figure 2 would be too high.

The ratio of the molecular-oxide form to free atoms depends on the temperature, pressure, and chemical composition of the atmosphere as given by

$$\log \frac{N(XO)}{N(X)} = \log P_{\mathrm{O}} - \log K_{X\mathrm{O}}(\theta)\ , \qquad (2)$$

where X denotes the atom (here either Ti or Zr), P_{O} is the partial pressure of oxygen, and $K_{X\mathrm{O}}(\theta)$ is the dissociation constant. Tsuji (1964) has given values for P_{O} for sixteen different chemical compositions and many values of the effective temperature and gas pressure. Tsuji also calculates log K for both TiO and ZrO for a variety of temperatures. His composition models I–V (varying O/C only) have been used to determine the ratios log TiO/Ti and log ZrO/Zr here. Values of the gas pressure were selected to

TABLE 4

MOLECULAR OXIDES

Spectral Type	θ_{eff}	O/C=5.0		O/C=3.33		O/C=2.0		O/C=1.25		O/C=1.0	
		log TiO/Ti	log ZrO/Zr	log TiO/Ti	log ZrO/Zr	log TiO/Ti	log ZrO/Zr	log TiO/Ti	log ZrO/Zr	log TiO/Ti	log ZrO/Zr
						log P_g=3.0					
M1...	1.4	−2.83	−1.56	−2.89	−1.62	−3.03	−1.76	−3.40	−2.13	−3.95	−2.68
M4...	1.6	−1.44	+0.04	−1.50	−0.02	−1.64	−0.16	−2.04	−0.86	−3.77	−2.19
M6...	1.8	−0.13	+1.54	−0.19	+1.48	−0.33	+1.41	−0.87	+0.94	−3.41	−1.74
						log P_g=4.0					
M1...	1.4	−1.84	−0.57	−1.90	−0.63	−2.04	−0.77	−2.44	−1.17	−3.45	−2.18
M4...	1.6	−0.54	+0.94	−0.59	+0.89	−0.74	+0.74	−1.17	+0.31	−3.19	−1.71
M6...	1.8	+0.35	+2.02	+0.29	+1.96	+0.15	+1.82	−0.25	+1.42	−3.00	−1.33

bracket the numbers given by Aller (1960) for normal M giants. The results of these calculations appear in Table 4 for five O/C ratios, three values of the effective temperature, and two values of the gas pressure. The spectral types corresponding to the effective temperatures are taken from Johnson (1966). It can be seen from Table 4 that the formation of the molecular oxide is enhanced as the temperature decreases, as the pressure increases, and as the O/C ratio increases.

From calculations designed to give physical meaning to Keenan's (1954) classification for S stars, Tsuji (1962) has suggested that the O/C ratio is 3.0 for M stars, 2.8 for MS stars, and from 2.5 to 1.0 for S stars. (An S star classified as S6,1 would have O/C = 2.5, whereas an S star of similar temperature but different abundance class, S6,9, would have O/C = 1.0.) Spinrad and Vardya (1966) have derived an O/C ratio of 1.05 for M giants from an observational and model-atmosphere study of the molecular-band strengths. They were, however, somewhat puzzled by the smallness of this ratio. The O/C ratio found in the Sun is 1.66 (Lambert 1968).

For a giant star with $\theta = 1.4$, Aller (1960) gives a rough value of log $P_g = +3.50$. Interpolations in Table 4 for an M1 giant show that the atomic abundances of both Ti and Zr are more than an order of magnitude greater than their molecular-oxide abundances for any O/C ratio between 1.0 and 3.0. For the M1 and warmer stars then, the molecular correction is considered negligibly small.

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None of the M giants is cooler than M4 where Aller suggests log $P_g = +3.12$. If the O/C ratio is 3.0, an M4 giant still has much more atomic Ti than TiO, but Zr and ZrO are present in nearly equal numbers. The atomic-abundance ratio would thus be too large by a factor of 2 to represent the elemental-abundance ratio. If the O/C ratio is between 1.0 and 2.0, however, as suggested by the work of Spinrad and Vardya and by the solar value, then the molecular correction for the M2–M4 stars would be smaller, probably less than a factor of 1.4 (<0.15 in the log).

The points representing the M3 and M4 stars in Figure 2 do not show a pronounced upward displacement from those representing M0–M1 stars. However, the averages of log $N(\mathrm{Ti})/N(\mathrm{Zr})$ for the eleven M0–M1 stars (+2.16) and for the ten M3–M4 stars (+2.31) do differ by 0.15, which in both magnitude and direction is about the correction to be expected for the effect of the molecular oxides. In Figure 2 the horizontal line at +2.27 shows the Ti/Zr abundance ratio in the Sun. If the cooler M stars have a molecular correction applied that is much larger than 0.15, they will fall considerably below

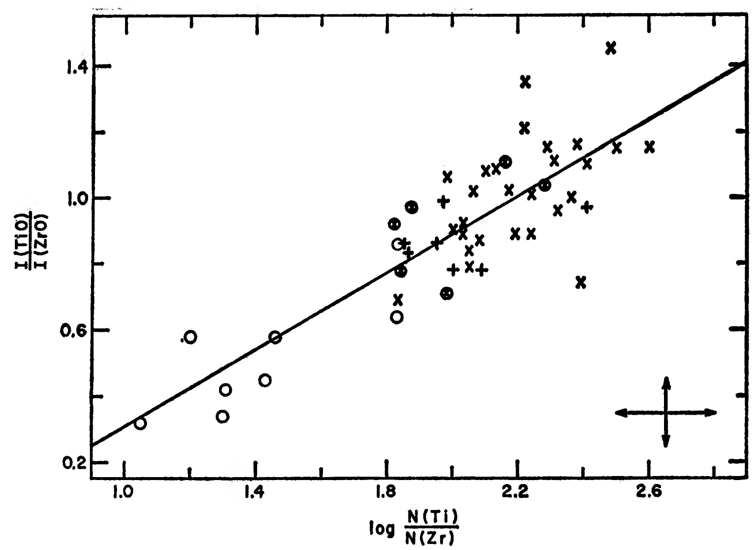

FIG. 3.—The intensity ratio TiO/ZrO plotted as a function of the log of the atomic-abundance ratio Ti/Zr. Symbols have the same meaning as in Fig. 2. Indications of the size of the errors in both coordinates are given by the arrows in the lower right. *Straight line*, least-squares fit.

the solar value and the values for the K and early M stars and values for other K giants (Helfer and Wallerstein 1964, 1968).

With the assumption of uniform composition for the Sun and the K and M stars, the above *empirical* arguments suggest that the total molecular correction is likely to be quite small, probably not greater than a factor of 2, even for the coolest M stars. On this basis, most of the molecular correction appears to be explained by the presence of molecular oxides rather than hydrides, carbides, etc.

Table 4 indicates that the correction is smaller with decreasing O/C ratio, which implies that the correction will be smaller for the extreme S stars than for the more "normal" S stars. Thus, even though the effective temperatures of many of the S stars studied here are lower than those of the M stars, the lower O/C ratio assists somewhat in reducing the molecular correction. The values for the O/C ratio and the gas pressure in the layer where the molecules are formed are too uncertain to assess accurately the size of the correction. It can be stated that the atomic-abundance ratios here are upper limits—close to the true values—for the S stars. Even so, the composition distinction between the S and M stars is clear.

Figure 3 shows the measured band-intensity ratio TiO/ZrO plotted against the

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atomic-abundance ratio Ti/Zr. The observed strengthening of the ZrO band appears to be due to the increase in the Zr abundance. As indicated by the least-squares straight-line fit, the band ratio TiO/ZrO can be used as a reliable indicator of the atomic-abundance ratio of Ti/Zr and, on the basis of the comments of the preceding paragraphs, as a fairly good indicator of the elemental-abundance ratio.

c) Comparison with Titanium and Zirconium in Other Stars

Several other abundance analyses of late-type stars have yielded abundances of both Ti and Zr, although such analyses were not specifically directed at determining the ratio Ti/Zr. It is of interest to compare the results found here with those in other investigations both to assess the validity of this work and to place all the stars in a broader context to study the possible evolutionary interrelationships.

Results of several abundance studies are summarized in Table 5, which gives [Ti/Zr], the stellar log Ti/Zr minus the solar log Ti/Zr. The solar value was selected as the most

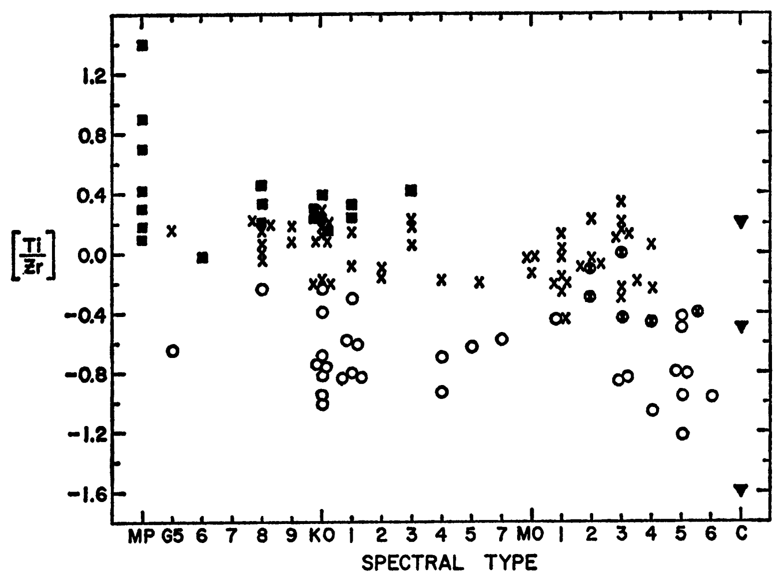

FIG. 4.—The logarithm of Ti/Zr relative to the Sun plotted as a function of spectral type for the data summarized in Table 5. *Crosses*, normal stars; *circled crosses*, MS stars; *open circles*, heavy-metal stars; *filled squares*, metal-poor stars (*MP*) and the high-velocity stars; *filled triangles*, carbon stars (*C*).

universal comparison base. The stars are grouped in four categories: normal, metal-deficient, heavy-metal-rich, and carbon stars.

The results found in this study for the K and M giants are slightly, but probably not significantly, lower than those found by Helfer and Wallerstein (1968). Two of Helfer and Wallerstein's (1964) Hyades K giants have also been analyzed by Griffin (1969). She finds lower [Ti/Zr]-values for these two stars. The present investigation and Warner's (1965) have three stars in common. The agreement is well within a factor of 2; values of [Ti/Zr] obtained by Boesgaard and by Warner are as follows: HD 46407 (−1.01, −0.75), HD 178717 (−0.71, −0.94), and HD 183915 (−0.81, −0.83). The abundance ratios found by Tsuji (1962) for the two S stars are in the same range as those determined here.

The [Ti/Zr]-values summarized in Table 5 are plotted individually against spectral type in Figure 4. The methods of analysis of the various authors differ, so completely consistent results cannot be expected; we will assume that the errors are typically factors of 2–3 for this intercomparison. Spectral types for some of the metal-poor stars are not known; these are plotted linearly on the left side of Figure 4. The three carbon stars are similarly plotted on the right side of Figure 4.

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TABLE 5

Ti/Zr ABUNDANCE RATIOS IN LATE-TYPE GIANTS

Type	No.	Mean [Ti/Zr]	Range [Ti/Zr]	Source
Normal				
G Giant - Field	1	+0.08	-	Cayrel and Cayrel, 1963
K Giants - Field	4	-0.16	-0.22 - -0.08	This paper
K Giants - Field	13	+0.15	-0.03 - +0.22	Helfer and Wallerstein, 1968
K Giant - Field	1	-0.04*	-	Griffin, 1969
K Giants - Hyades	4	+0.16	+0.1 - +0.3	Helfer and Wallerstein, 1964
K Giants - Hyades	2	-0.21*	-	Griffin, 1969
Galactic Cluster Giants	9	-0.09	-0.2 - 0.0	Wallerstein and Conti, 1964
M Giants - Field	25	-0.02	-0.44 - +0.33	This paper
M Supergiants	7	-0.21	-0.42 - +0.14	This paper
Metal Deficient				
K Giants - Pop.II	4	+0.99	+0.1 - +1.4	Helfer, Wallerstein, Greenstein, 1959
G-K - high velocity	2	+0.30	+0.17, +0.42	Koelbloed, 1967
Very metal poor HD 122563	1	+0.30	-	Wolff and Wallerstein, 1967
K Giants - high Velocity	12	+0.29	-0.02 - +0.45	Helfer and Wallerstein, 1968
Heavy Metal				
Ba II K0-K7	5	-0.74	-1.01 - -0.59	This paper
Ba II G5-K5	9	-0.70	-0.95 - -0.40	Warner, 1965
Ba II K0,K1	2	-0.6+ (-0.4)	-0.8,-0.4 (0.6,-0.2)	Danziger, 1965
Ba II K0	1	-0.77‡	-	Burbidge and Burbidge, 1957
Ba II G8	1	-0.24	-	Cowley, 1968
Ba II K1	1	-0.30	-	Helfer and Wallerstein, 1968
Ba II K1	1	-0.84	-	Griffin, 1969
MS Stars	6	-0.32	-0.45 - +0.01	This paper
S Stars	9	-0.77	-1.22 - -0.43	This paper
S stars	2	-0.65	-0.8, -0.5	Tsuji, 1962
Carbon				
Y CVn $C5_4$	1	-1.6	-	Fujita and Tsuji, 1964, 1965
HD 26, CH	1	-0.5	-	Wallerstein and Greenstein, 1964
RU Cam, CO_1	1	+0.2	-	Faragiana and Hack, 1967

* Using [Ti/Zr] for α Boo = +0.20 from values of Griffin from neutral lines, $[\frac{Ti}{Zr}]=0.28$ and ionized lines $[\frac{Ti}{Zr}]=+0.12$

+ relative to α Boo; values in parentheses are relative to the sun where [Ti/Zr]=+0.20 for α Boo

‡ relative to κ Gem

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V. DISCUSSION

a) *Abundances*

The metal-poor stars—Population II K giants, high-velocity stars—have a tendency to show higher Ti/Zr ratios than normal stars. This result is to be expected, since they are thought to have been formed at an early era or outside the galactic plane and therefore to have little enrichment of heavy metals; a low Fe abundance provides few seed nuclei for the *s*-process product, Zr.

The K and M field stars and the Hyades stars show the solar-abundance ratio within a factor of 3. The carbon variable, RU Cam, which Faraggiana and Hack (1967) found to have solar abundances, has solar Ti/Zr, too.

The MS stars seem to fall preferentially below the solar value; the average for the six stars is a factor of 2 smaller. Both the Ba II and the S stars in this enlarged sample show values 3–30 times smaller than the Sun. In addition, the CH star, HD 26, seems to fall in this group. This Population II star shows enrichment of the *s*-process elements (Wallerstein and Greenstein 1964), a characteristic similar to the Ba II and S stars.

The carbon star, Y CVn, shows the lowest Ti/Zr ratio (Fujita and Tsuji 1964, 1965). Utsumi (1967) has pointed out that U Hya, a $C7_3$ star, has even stronger lines of Zr I than Y CVn. Table 4 indicates that the molecular correction is expected to be less in carbon stars than in S stars. Therefore, the elemental-abundance ratio Ti/Zr appears to be less for carbon stars than for S stars. More Ti/Zr abundances in carbon stars are necessary to assure this point.

b) *Nucleosynthesis*

The *s*-process products such as Zr are built up by the slow addition of neutrons to Fe and its successive products. A plot of the product of the abundance and the neutron-capture cross-section as a function of atomic weight ($\sigma_c N$-curve) shows several discontinuities. Seeger *et al.* (1965) have shown that the greater the neutron exposure, the smaller the discontinuities. Since Zr falls near the bottom of one of these discontinuities, an increase in the Zr abundance implies an increase in neutron exposure and a flatter $\sigma_c N$-curve. Warner (1965) and Wallerstein (1968) have suggested that the abundances in Ba II stars can be accounted for by greater neutron exposure than in the solar material. Wallerstein and Greenstein (1964) have interpreted the surface abundances in the CH stars in terms of successive interior compositions including *s*-process products which are then diluted by a factor of 100 to represent mixing to the stellar surface. The agreement of their model with the observed abundances is very good, which thus implies a greater neutron exposure in the CH stars, too.

The differences in the Ti/Zr ratios found for the various types of red giants can be ascribed to the variation in the buildup of Zr by the *s*-process. During post–main-sequence evolution, a star may experience several stages of neutron irradiation and thus several increases in the *s*-process elements. Reeves (1966) discusses the various neutron sources and the evolutionary stages at which they occur. Before He burning $^{12}C(p, \gamma)^{13}N \rightarrow {}^{13}C(\alpha, n)^{16}O$ can be a source of neutrons with $T_8 \sim 1$ (T_8 represents temperature in units of 10^8 ° K). During He burning, $^{22}Ne(\alpha, n)^{25}Mg$ at $T_8 > 2$ and $^{18}O(\alpha, n)^{21}Ne$ at $T_8 > 3.5$ will produce neutrons. In later evolutionary stages, neutrons can come from the energy-producing reactions of carbon burning and oxygen burning: $^{12}C(^{12}C, n)^{23}Mg$, $9 < T_8 < 11$, and $^{16}O(^{16}O, n)^{31}S$, $14 < T_8 < 20$. Neutrons produced here are very plentiful, and neutron captures by heavy elements take 10^5 and 10^4 sec, respectively.

The Ba II and S stars may have experienced more stages of irradiation than the normal stars, and the carbon stars are perhaps at an even more advanced stage of evolution. This would imply that the peculiar abundances seen in the heavy-metal and carbon stars result from the evolutionary phase of these stars. Data from more than one ele-

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ment and estimates of the time to mix *s*-process products to the surface are necessary to confirm this idea. Anders (1957) suggests that the Nb underabundance and the Tc decay can be used as indicators of the mixing time. Reeves presents information for the addition of neutron-irradiation calculations to stellar-evolution models.

VI. CONCLUSIONS

The abundance results for Ti/Zr in the nine S stars and the twenty-five M giants studied here show conclusively that there is a heavy-metal composition difference between these two classes of stars in addition to the accepted O/C difference. The average values for the atomic-abundance ratio show that Ti/Zr is about 6 times smaller in the S stars. The six MS stars have an average value about 2 times smaller than the M giants.

The Ti/Zr ratio in the Ba II stars studied here and by the other investigators is similar to the ratio in S stars both in the average value and the range. Thus, the Ba II stars and S stars would appear to have similar structure and neutron irradiation. The data for the carbon star Y CVn and the inference for U Hya suggest that additional irradiation has taken place in carbon stars.

The Population II CH star has a Ti/Zr ratio in the upper part of the range for Ba II and S stars. It may have undergone similar irradiation but had a smaller initial amount of Zr than the Population I stars. The rather high Ti/Zr ratio in the metal-poor stars can be understood in terms of little or no irradiation and/or mixing and low initial values of the Fe peak and heavy metals.

The composition of these stars must contain clues to the nuclear reactions taking place in the interiors. It would be of interest to identify, from model-star calculations which include Reeves's neutron-irradiation information, the positions in the H-R diagram and the stellar masses where the nuclear reactions and neutron irradiation take place which, through mixing, result in the observed differences in the surface compositions.

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