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## THE CHEMICAL EVOLUTION OF PHOSPHORUS\*

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### ABSTRACT

Phosphorus is one of the few remaining light elements for which little is known about its nucleosynthetic origin and chemical evolution, given the lack of optical absorption lines in the spectra of long-lived FGK-type stars. We have identified a P I doublet in the near-ultraviolet (2135/2136 Å) that is measurable in stars of low metallicity. Using archival *Hubble Space Telescope*–Space Telescope Imaging Spectrograph spectra, we have measured P abundances in 13 stars spanning  $-3.3 \leq [\text{Fe}/\text{H}] \leq -0.2$ , and obtained an upper limit for a star with  $[\text{Fe}/\text{H}] \sim -3.8$ . Combined with the only other sample of P abundances in solar-type stars in the literature, which spans a range of  $-1 \leq [\text{Fe}/\text{H}] \leq +0.2$ , we compare the stellar data to chemical evolution models. Our results support previous indications that massive-star P yields may need to be increased by a factor of a few to match stellar data at all metallicities. Our results also show that hypernovae were important contributors to the P production in the early universe. As P is one of the key building blocks of life, we also discuss the chemical evolution of the important elements to life, C–N–O–P–S, together.

**Key words:** stars: abundances – stars: fundamental parameters – stars: Population II

### 1. INTRODUCTION

The production of chemical elements over cosmic time is mapped out well by the element abundances of different metal-poor stars. The previous decades have seen an accumulation of abundance data for most of the element groups in the Periodic Table in large samples of stars over a wide metallicity range, including the most metal-poor stars. In contrast, stellar phosphorus (P) abundances have been striking in their absence. The paucity of abundance information for phosphorus is due to the scarcity of P absorption features in the spectra of FGK-type stars. The only study to trace the P abundances of stars over a range of metallicity (and thus “time” in the chemical evolution of the universe) is that of Caffau et al. (2011), who analyzed weak P features in the near-IR. However, these features become too weak to be measurable in stars with  $[\text{Fe}/\text{H}] \lesssim -1$ , which means little is known of the chemical evolution of P in the universe at the earliest times. (The P abundances of some metal-poor damped Ly $\alpha$  (DLA) systems give a hint, but the sample size is very small; see later sections.)

The results of Caffau et al. (2011) show that  $[\text{P}/\text{Fe}]$  increases with decreasing  $[\text{Fe}/\text{H}]$  from roughly solar metallicity down to  $[\text{Fe}/\text{H}] \sim -1$ , with hints that it may plateau at  $[\text{P}/\text{Fe}] \approx +0.2$  below that. A comparison of these results to chemical evolution models of phosphorus has indicated that current massive star yields of P must be increased in order to match the

stellar abundance distribution (Cescutti et al. 2012) at  $\sim$ solar metallicity. However, firm conclusions could not be made at the time without knowledge of the P abundances in more metal-poor stars, which are necessary to better constrain the nucleosynthetic origin of P and its early chemical evolution in the universe.

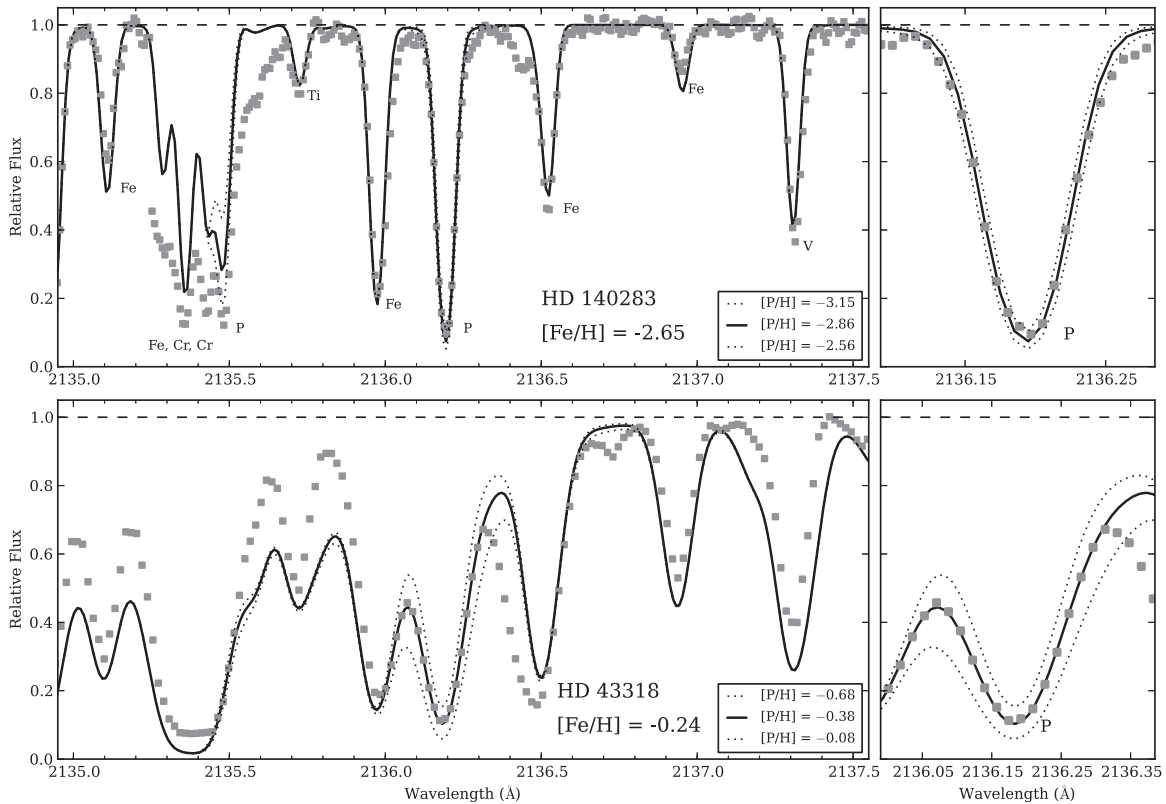
We have identified a P I doublet in the ultraviolet (UV; 2135/2136 Å) that remains strong and measurable even in very low-metallicity stars. A search of the *Hubble Space Telescope* (HST) MAST data archive for high-resolution Space Telescope Imaging Spectrograph (STIS) spectra of Milky Way stars spanning this wavelength region uncovered spectra of 13 stars with a metallicity range of  $-3.3 \leq [\text{Fe}/\text{H}] \leq -0.2$ , or three orders of magnitude in metallicity. This covers almost the entire range of cosmic chemical evolution. The P I doublet is present in the spectra of all these stars, allowing us to measure its abundance in stars with  $[\text{Fe}/\text{H}] \lesssim -1$  for the first time.

### 2. THE P I 2135/2136 Å DOUBLET

The P I doublet at 2135.47 Å and 2136.18 Å (E.P. = 1.41 eV; Kramida et al. 2014) connects the lower  $3s^2 3p^3 \ ^2D^\circ$  level to the upper  $3s^2 3p^2(^3P)4s \ ^2P$  level. The 2135 Å feature is often blended with a nearby Cr II line, but the stronger 2136 Å is free of blends, even in the solar metallicity stars. Though this line becomes saturated in the higher metallicity stars in our sample, comparisons to synthetic spectra show that it remains sensitive enough to abundance to be a useful abundance indicator (see the next section and Figure 1). Therefore, we have used this feature to measure P abundances in our entire stellar sample.

We have adopted the NIST log  $gf$  value for this line,  $-0.11$ , for which they report an accuracy of 25%. The 2136 Å feature can exhibit strong damping wings in the more metal-rich stars. We have calculated the van der Waals damping constant,  $\Gamma_6$ , for

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**Figure 1.** P I 2136 Å region in the STIS spectra of HD 140283 (spectral resolution  $R = (\lambda/\Delta\lambda) = 110,000$ ) and HD 43318 ( $R = 30,000$ ). The data are represented by gray squares. Absorption features are identified in the top panels. Synthetic spectra of different P abundances are plotted over each spectrum, with the best fit indicated by a bold line. A zoom-in on the 2136 Å line is shown in the right panels. Note that the P abundances shown here include the empirical 0.23 dex correction described in the text.

this line using the collisional cross-section information from the work of Anstee & O’Mara (1995).

To our knowledge, no non-LTE calculations have been performed for P I features. A comparison of the abundances of Fe I and Fe II lines in the near-UV (NUV) spectra of six stars in our sample shows abundance differences of 0.07 dex in the mean, indicating that relatively small non-LTE effects may be present, at least for Fe I. If non-LTE effects of similar magnitude are present for P I, they have little impact on our results and are a small component of our total error budget (see the next section). Non-LTE calculations for P I are desirable for future studies.

### 3. ANALYSIS

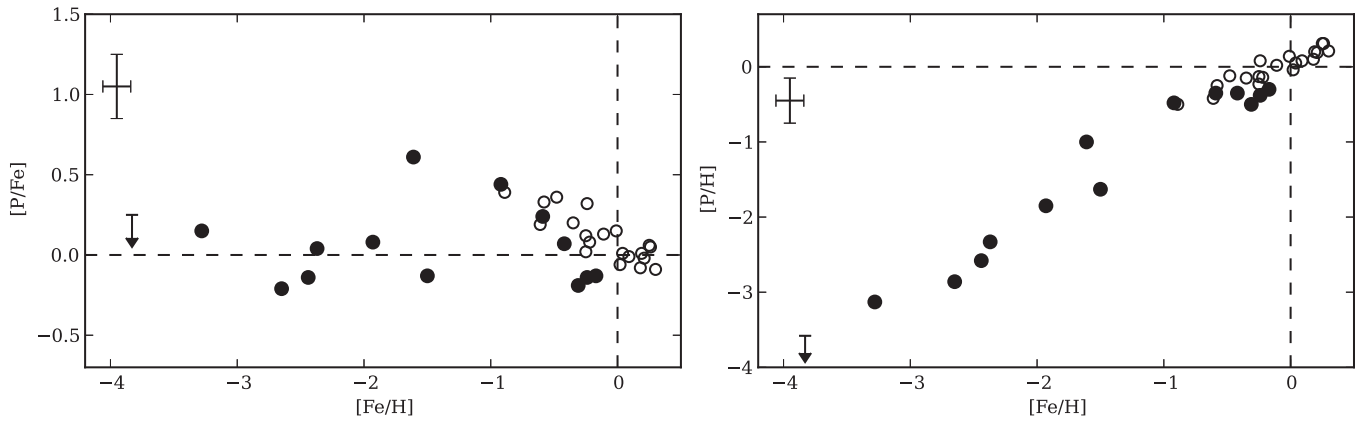
This work has made use of both NUV and optical high-resolution spectra available in a number of archive facilities, as well as spectra obtained by us on the Magellan 6.5 m Clay and 2.7 m Harlan J. Smith Telescopes at Las Campanas Observatory and the McDonald Observatory, respectively. The NUV spectra are in two spectral resolution groups:  $R = (\lambda/\Delta\lambda) = 110,000$  and 30,000. The signal-to-noise ratio (S/N) of each spectrum ranges from 10 to 100, with a mean value of 64. We refer the reader to Roederer et al. (2014) for more details about the data.

Although stellar parameters exist in the literature for all stars in our sample, we performed our own analysis to ensure homogeneity. We determined stellar parameters and element abundances from the optical spectra following the method described in Frebel et al. (2013), and using software developed by A. Casey (Casey 2014). This method employs standard classical spectroscopic techniques for determining parameters, but applies an empirical correction to stellar effective temperature to

place it on a scale consistent with photometric temperature determinations. Our analysis uses the model atmosphere grid of Castelli & Kurucz (2004) and the LTE analysis code MOOG (Snedden 1973), which accounts for Rayleigh scattering as described in Sobeck et al. (2011). Throughout, we adopt the solar abundances of Asplund et al. (2009).

Abundances for 13 elements (Na, Mg, Al, Si, Ca, Sc, Ti, Cr, Mn, Fe, Co, Ni, and Zn) with optical absorption lines were determined from these spectra, using line lists in Roederer et al. (2010) and Ramírez et al. (2013). Together with the stellar parameters, these abundances were used as inputs to create detailed synthetic spectra of the region around the P I doublet for each star. The P abundance in each synthetic spectrum was varied until it best matched the P I 2136 Å feature in the stellar spectrum. The best match was determined by inspection of the residuals of the difference between the observed and synthetic spectra. Figure 1 illustrates this for two stars in our sample. Several other species (predominantly Fe-peak elements) are also detected in this spectral region, which motivated our use of the abundances determined from the optical spectra to generate the synthetic spectra of this region. As indicated in Figure 1, the overall agreement between the synthetic and observed spectra was relatively poorer for the more metal-rich stars. However, the quality of the fit to these other lines did not affect measurement of the P feature, and they are largely shown for illustration.

As previous studies of NUV stellar spectra have uncovered systematic offsets in element abundances compared to those found from optical lines (e.g., Roederer et al. 2012), we also determined NUV Fe I and Fe II abundances for a subset of our sample. In order to avoid potential non-LTE effects on the NUV Fe I abundances, we restricted the optical-NUV abundance



**Figure 2.** [P/Fe] and [P/H] vs. [Fe/H] for the current study (filled circles and upper limit symbol) along with the sample of Caffau et al. (2011; open circles). A representative error bar for an individual star is given in the top left corner of each panel.

**Table 1**  
Stellar P and Fe Abundances

Star	[Fe/H] <sup>a</sup>	$\sigma$	[P/H]	$\sigma$	[P/Fe]	$\sigma$
BD +44 493	-3.83 <sup>b</sup>	0.19	< -3.58	...	< +0.25	...
G 64-12	-3.28	0.09	-3.13	0.34	+0.15	0.26
HD 2454	-0.42	0.12	-0.35	0.27	+0.07	0.21
HD 16220	-0.31	0.11	-0.50	0.26	-0.19	0.20
HD 43318	-0.24	0.11	-0.38	0.26	-0.14	0.20
HD 76932	-0.92	0.12	-0.48	0.29	+0.44	0.20
HD 94028	-1.61	0.13	-1.00	0.29	+0.61	0.21
HD 107113	-0.59	0.11	-0.35	0.26	+0.24	0.20
HD 108317	-2.44	0.11	-2.58	0.35	-0.14	0.20
HD 128279	-2.37	0.12	-2.33	0.36	+0.04	0.22
HD 140283	-2.65	0.08	-2.86	0.30	-0.21	0.19
HD 155646	-0.17	0.07	-0.30	0.25	-0.14	0.19
HD 160617	-1.93	0.08	-1.85	0.27	+0.07	0.17
HD 211998	-1.50	0.11	-1.63	0.33	-0.13	0.21

#### Notes.

<sup>a</sup> These values were determined from the optical spectra.

<sup>b</sup> From Ito et al. (2013).

comparison to Fe II lines that are thought to be unaffected. Based on six stars in which a minimum of five NUV Fe II lines could be measured, the mean (optical–NUV) offset in Fe II abundances was found to be  $+0.23 \pm 0.02$  ( $\sigma = 0.09$ ). The difference between this offset and that found by Roederer et al. (2012) in a similar exercise is 0.14 dex (for Fe II). To test that this correction is appropriate for the NUV P abundances, we adjusted the NUV continuous opacity to force agreement between NUV and optical Fe I and Fe II abundances and remeasured P abundances. [P/Fe] ratios agreed within an average of 0.04 dex with those found by applying the 0.23 dex offset, indicating that this empirical correction is sufficient.

Table 1 gives the P abundances of our stellar sample, with this empirical NUV–optical correction applied. The errors in the [P/H] and [P/Fe] abundances take into account all relevant statistical and systematic uncertainties due to errors in atomic data, stellar parameters, continuum fitting, and the empirical correction described above. Such uncertainties include 0.12 dex for the log  $gf$ , 0.05 dex for the damping constant, and a 0.14 dex zero-point uncertainty in the NUV–optical abundance correction. P abundance sensitivities due to uncertainties in atmospheric parameters were assessed for each star, and the means are 0.07 dex for  $\Delta T_{\text{eff}} = 100$  K, 0.04 dex for  $\Delta \log g = 0.3$  dex, and 0.06 dex for  $\Delta v_t = 0.2$  km s<sup>-1</sup>. Sensitivity due to errors in continuum placement is typically no more than 0.07 dex, save

for G 64–12, which has S/N  $\sim 10$  and the weakest P feature. For this star, uncertainty in the continuum normalization can vary the P abundance by as much as 0.15 dex.

Finally, we supplement our sample with BD +44 943, the STIS spectrum of which was recently presented by Placco et al. (2014). For the analysis, we have adopted the stellar parameters and metallicity of Ito et al. (2013). Only an upper limit to its P abundance could be determined from the P I 2553 Å line.

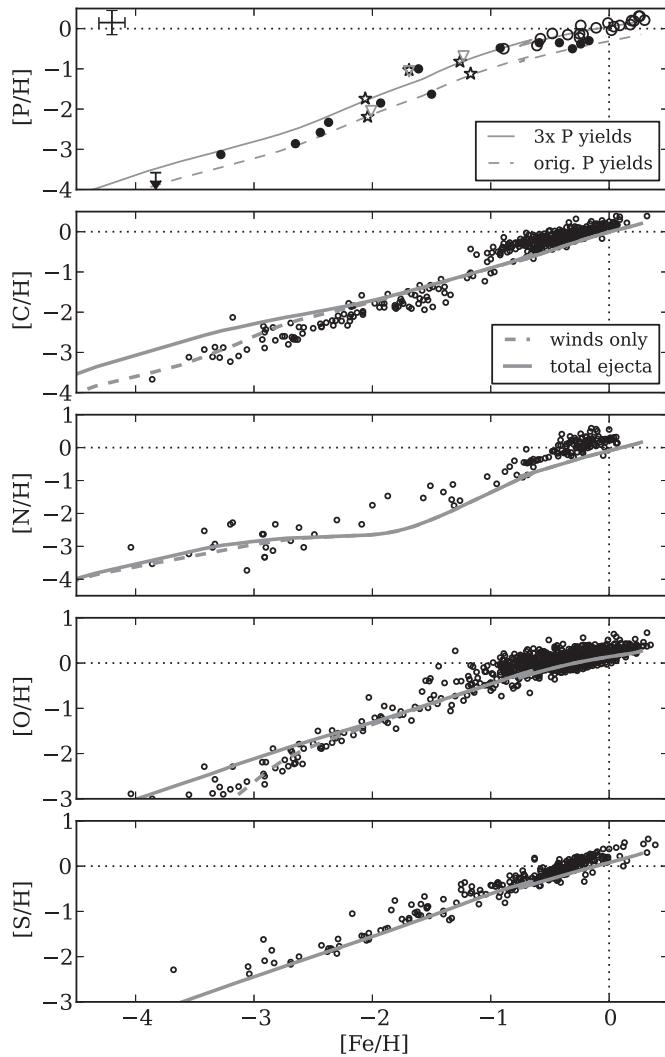
## 4. RESULTS AND DISCUSSION

### 4.1. The Nucleosynthetic Origin(s) of P

Figure 2 shows the P abundance results of the current sample (filled symbols and upper limit) and those of Caffau et al. (2011; open circles). Below [Fe/H]  $\sim -2$ , the [P/Fe]  $\sim +0.0$  trend (albeit with a large scatter) depicts the production of P from massive stars. From [Fe/H]  $\sim -1.5$ , [P/Fe] then starts to increase with increasing metallicity before returning down to [Fe/H]  $\sim 0$  near solar metallicity. This behavior is very similar to that predicted by the chemical evolution models of Kobayashi et al. (2006) and Cescutti et al. (2012). Perhaps more striking is the distribution of [P/H] versus [Fe/H] (right panel), which clearly shows a smooth and very well defined buildup of over  $\sim 4$  orders of magnitude in P with chemical time (increasing [Fe/H]). There is reasonable agreement ( $\sim 0.25$  dex,  $\approx 2\sigma$ ) with the Caffau et al. (2011) sample P abundances for stars of similar metallicity, with our values being lower. This comes after applying the 0.23 dex offset to our NUV abundance scale. The UV–IR agreement thus depends on this offset. However, we have assumed that no additional offset must be applied to place our abundances on the same scale as their near-IR abundances.

The top panels of Figures 3 and 4 show the stellar P abundance distributions again, this time with the results of chemical evolution models from Cescutti et al. (2012). The lines in each panel present chemical evolution model results for the Milky Way, based on a two-infall model (Chiappini et al. 1997), and adopting P yields for massive stars from Kobayashi et al. (2006). Also shown here are the P abundances of four DLA systems, with upper limits for three more (Molaro et al. 1998, 2001; Outram et al. 1999; Levshakov et al. 2002; Lopez et al. 2002; Fenner et al. 2004; Rix et al. 2007; R. Cooke 2014, private communication). The agreement of the independently determined DLA P abundances with those of the stars is remarkable.

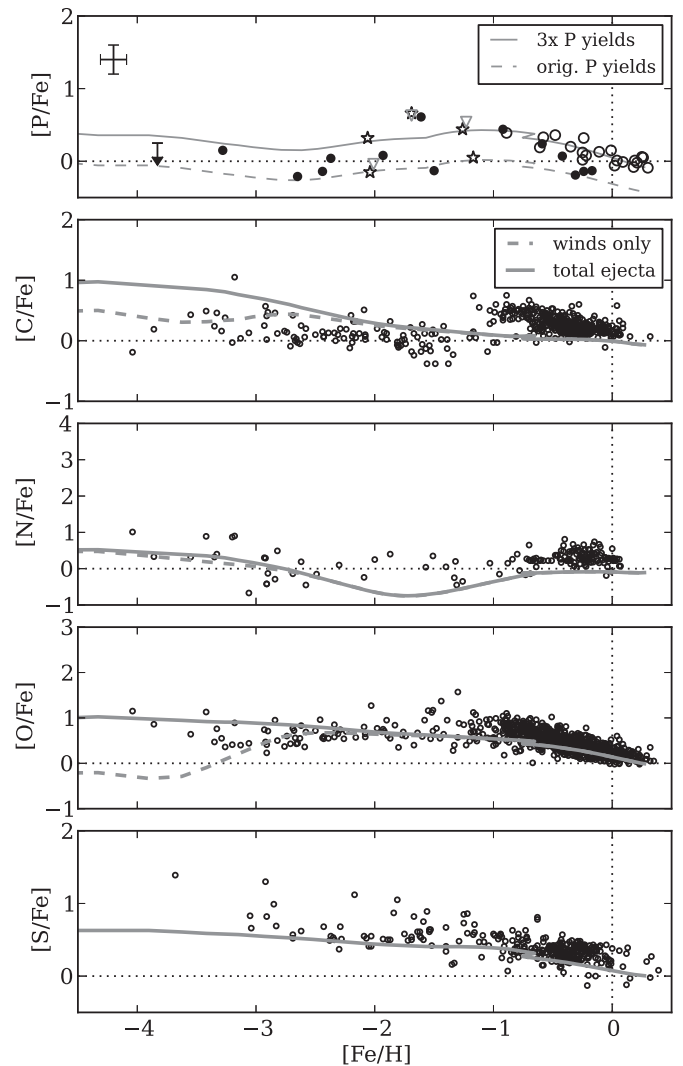
As mentioned in the Introduction, Cescutti et al. (2012) indicated that current supernovae (SNe) P yields must be enhanced



**Figure 3.** Top panel: stellar  $[P/H]$  vs.  $[Fe/H]$  as in Figure 2, with the addition of DLA measures (stars) and DLA upper limits (triangles). Also shown are the chemical evolution model of Cescutti et al. (2012), with massive-star P yields from Kobayashi et al. (2006; dashed line) and the yields increased by a factor of three (solid line). These correspond to “Model 6” and “Model 8” in Cescutti et al. (2012), respectively. Remaining panels: the same for elements C, N, O, and S, with stellar abundances taken from the literature. Also in each panel is the prediction for the chemical evolution model for each element. For C, N, and O, two models are shown, the only difference being the treatment of yields from massive stars with  $Z < 10^{-5}$  (spin stars). The solid lines indicate total C, N, O ejecta (winds plus supernovae (SNe)), while the dashed lines represent element production in spin star winds only; see Cescutti & Chiappini (2010) for details. References for the literature stellar samples shown here are Israelian et al. (2004), Ramírez et al. (2013), Nissen et al. (2004, 2007), Caffau et al. (2005), Spite et al. (2005, 2011), Lai et al. (2008), Takada-Hidai et al. (2002), Carbon et al. (1987), Reddy et al. (2003, 2006), Fabbian et al. (2009), Shi et al. (2002), Takeda & Takada-Hidai (2011), Ryde & Lambert (2004), Hansen et al. (2011), and Israelian & Rebolo (2001).

by a factor of  $\sim 3$  to match the then-available abundance data (Caffau et al. 2011), and especially to obtain  $[P/Fe] = 0$  at solar metallicity. As can be seen in Figures 3 and 4, most of the stars in our sample indicate that while some enhancement to the yields is needed, the exact factor is difficult to derive, especially at low  $[Fe/H]$  and given the sizable (0.3 dex) error bar on our P abundances. In agreement with Cescutti et al. (2012), factors of 1–3 are likely and we rule out a decreased yield.

However, even though our results cannot definitely say how much the P yields must be increased, they do allow us to



**Figure 4.**  $[X/Fe]$  vs.  $[Fe/H]$  for elements P, C, N, O, and S. Symbols and models are the same as in Figure 3.

better constrain the nucleosynthetic origin for P. In their work, Cescutti et al. (2012) found that two versions of their chemical evolution model, both with P yields enhanced by  $\sim 3$ , fit the Caffau et al. (2011) data equally well: the main difference between the two models, “Model 7” and “Model 8,” was the inclusion of hypernovae. “Model 7” assumed an energy of  $10^{51}$  erg for all massive stars, while “Model 8” adopted  $10^{52}$  erg for stars with masses  $> 20 M_{\odot}$  (hypernovae). While exhibiting similar P abundances at  $\sim$ solar metallicity, these models showed very different behavior at low  $[Fe/H]$ , with “Model 7” having  $[P/Fe] > 0.5$  at all  $[Fe/H]$  below  $-1$ . Our results, most of which have  $[P/Fe] \sim 0$ , clearly support “Model 8” and indicate that hypernovae were important sources of P in the early universe. This is consistent with results of studies fitting other element abundance patterns of  $[Fe/H] \sim -3$  stars, which also found that regular core-collapse SNe were insufficient to reproduce the data and required contributions from more energetic events (e.g., Cayrel et al. 2004; Tominaga et al. 2007).

#### 4.2. The Chemical Evolution of C–N–O–P–S, the Building Blocks of Life

Phosphorus serves a crucial role in forming and sustaining life: P ions form the backbone of DNA and are the primary



constituents in energy exchange in cells, in the form of ATP and ADP. Recent research indicates that P, in the form of polyphosphates, may have played a key role in chaperoning protein folding when life first formed on Earth billions of years ago (Gray et al. 2014). Now that we have a clearer view of its formation history, we can review the chemical evolution of all the building blocks of life, C–N–O–P–S, together. The remaining panels of Figures 3 and 4 show the cosmic evolution of C, N, O, and S, based on literature data, and compared to the same chemical evolution model as for P. For C–N–O, we follow the prescription of Cescutti & Chiappini (2010): the dashed and solid lines in those panels indicate different spin star (massive stars with  $Z < 10^{-5}$ ) yields (dashed: from winds only; solid: ejecta from winds and SNe). We also limit the stellar samples for these elements to dwarfs and “unmixed” giant stars, as in Cescutti & Chiappini (2010). Finally, for S we use the hypernovae yields from Kobayashi et al. (2006). Contrary to yield predictions for P until now, the yields of C, N, O, and S are relatively well understood, having been verified by stellar abundances from many previous studies (Cescutti & Chiappini 2010; Spite et al. 2005; Caffau et al. 2005).

We present Figures 3 and 4 to highlight a couple of points. First, they illustrate the accumulation of these elements in the universe over cosmic time (right panels), as well as highlight the importance of massive stars as the main sources of C–N–O–P–S production at early epochs in the universe (the generally enhanced  $[X/Fe]$  values at low metallicities that then decline with the advent of Type Ia SNe that produced much Fe, but relatively smaller amounts of the lighter elements). Second, it also emphasizes the relative degrees to which we understand the origin and production of these elements: chemical evolution models with current yields match the observational data well for C, O, and S, and now P. This is less true for N, for which it is difficult to measure primordial abundances in metal-poor stars, and which (along with C) is subject to variations due to stellar rotation and stellar evolution.

## 5. CONCLUSIONS

We have identified a P I doublet in the NUV that allows for the measure of P abundances in stars with  $[Fe/H] \lesssim -1$  for the first time. Using archival high-resolution *HST*–STIS spectra of fourteen stars, we have presented P abundances (and an interesting upper limit) for stars in the range  $-3.8 \leq [Fe/H] \leq -0.2$ , which spans nearly the entire chemical evolution history of the universe. Comparison to chemical evolution models utilizing current core-collapse SNe P yields allows us to test previous indications that P yields must be increased by a factor of three to match stellar abundances at all metallicities. Our results indicate that a factor of three may be too large to match the observations at low  $[Fe/H]$ , but that at least some enhancement (a factor of  $\sim 1.5$ ) is likely necessary. Independent of the yield discussion, our results clearly imply that hypernovae were important sources of P production in the early universe, in line with other results.

Finally, our findings highlight the interdependence of observations of stars in our galaxy with chemical evolution modeling and nuclear physics: observations are needed to constrain and revise theoretical models and nucleosynthesis calculations. Our results also emphasize the importance of finding bright ( $V < 10$ ) very metal-poor stars observable at high spectral resolution in the UV for work such as this. The study of P and other elements with features in the UV is entirely dependent on the existence of samples bright enough for such observations, highlighting the

necessity of dedicated surveys to find these objects (Schlaufman & Casey 2014).

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*Facilities:* *HST* (STIS), Magellan:Clay (MIKE), Smith (Tull)

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