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# The Pristine survey - XII. Gemini-GRACES chemo-dynamical study of newly discovered extremely metal-poor stars in the Galaxy 

Collin L. Kielty ${ }^{\circledR}$, ${ }^{1 \star}$ Kim A. Venn ${ }^{\circledR},{ }^{1}$ Federico Sestito ${ }^{\circledR}$, $1,2,3$ Else Starkenburg, ${ }^{3,4}$ Nicolas F. Martin ${ }^{\circledR}$, ${ }^{2,5}$ David S. Aguado, ${ }^{6}$ Anke Arentsen ${ }^{\odot},{ }^{2,3}$ Sébastien Fabbro, ${ }^{7}$ Jonay I. González Hernández, 8,9 Vanessa Hill, ${ }^{10}$ Pascale Jablonka, ${ }^{10,11}$ Carmela Lardo ${ }^{\oplus},{ }^{11}$ Lyudmila I. Mashonkina ${ }^{\odot},{ }^{12}$ Julio F. Navarro, ${ }^{1}$ Chris Sneden, ${ }^{13}$ Guillaume F. Thomas, ${ }^{7}$ Kris Youakim ${ }^{\ominus},{ }^{14}$ Spencer Bialek ${ }^{1}$ and Rubén Sánchez-Janssen ${ }^{15}$<br>${ }^{1}$ Department of Physics and Astronomy, University of Victoria, Victoria, BC V8W 3P2, Canada<br>${ }^{2}$ CNRS, Observatoire astronomique de Strasbourg, Université de Strasbourg, UMR 7550, F-67000 Strasbourg, France<br>${ }^{3}$ Leibniz-Institut für Astrophysik Potsdam (AIP), An der Sternwarte 16, D-14482 Potsdam, Germany<br>${ }^{4}$ Kapteyn Astronomical Institute, University of Groningen, Landleven 12, NL-9747 AD Groningen, the Netherlands<br>${ }^{5}$ Max-Planck-Institut für Astronomie, Königstuhl 17, D-69117 Heidelberg, Germany<br>${ }^{6}$ Institute of Astronomy, University of Cambridge, Madingley Road, Cambridge CB3 0HA, UK<br>${ }^{7}$ National Research Council of Canada, Herzberg Astronomy \& Astrophysics Program, 5071 West Saanich Road, Victoria, BC V9E 2E7, Canada<br>${ }^{8}$ Instituto de Astrofísica de Canarias, Vía Lactea, E-38205 La Laguna, Tenerife, Spain<br>${ }^{9}$ Departamento de Astrofísica, Universidad de La Laguna, E-38206 La Laguna, Tenerife, Spain<br>${ }^{10}$ GEPI, Observatoire de Paris, Université PSL, CNRS, Place Jules Janssen, F-92190 Meudon, France<br>${ }^{11}$ Dipartimento di Fisica e Astronomia, Universitá degli Studi di Bologna, Via Gobetti 93/2, I-40129 Bologna, Italy<br>${ }^{12}$ Institute of Astronomy, Russian Academy of Sciences, RU-119017 Moscow, Russia<br>${ }^{13}$ Department of Astronomy, University of Texas at Austin, Austin, TX 78712, USA<br>${ }^{14}$ Department of Astronomy, Stockholm University, SE-106 91 Stockholm, Sweden<br>${ }^{15}$ UK Astronomy Technology Centre, Royal Observatory Edinburgh, Blackford Hill, Edinburgh EH9 3HJ, UK

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#### Abstract

High-resolution optical spectra of 30 metal-poor stars selected from the Pristine survey are presented, based on observations taken with the Gemini Observatory GRACES spectrograph. Stellar parameters $T_{\text {eff }}$ and $\log g$ are determined using a Gaia DR2 colour-temperature calibration and surface gravity from the Stefan-Boltzmann equation. GRACES spectra are used to determine chemical abundances (or upper limits) for 20 elements ( $\mathrm{Li}, \mathrm{O}, \mathrm{Na}, \mathrm{Mg}, \mathrm{K}, \mathrm{Ca}, \mathrm{Ti}, \mathrm{Sc}, \mathrm{Cr}, \mathrm{Mn}, \mathrm{Fe}, \mathrm{Ni}, \mathrm{Cu}, \mathrm{Zn}$, $\mathrm{Y}, \mathrm{Zr}, \mathrm{Ba}, \mathrm{La}, \mathrm{Nd}, \mathrm{Eu})$. These stars are confirmed to be metal-poor $([\mathrm{Fe} / \mathrm{H}]<-2.5)$, with higher precision than from earlier medium-resolution analyses. The chemistry for most targets is similar to other extremely metal-poor stars in the Galactic halo. Three stars near $[\mathrm{Fe} / \mathrm{H}]=-3.0$ have unusually low Ca and high Mg , suggestive of contributions from few SN II where alphaelement formation through hydrostatic nucleosynthesis was more efficient. Three new carbon-enhanced metal-poor (CEMP) stars are also identified (two CEMP-s and one potential CEMP-no star) when our chemical abundances are combined with carbon from previous medium-resolution analyses. The GRACES spectra also provide precision radial velocities ( $\sigma_{\mathrm{RV}} \leq 0.2 \mathrm{~km} \mathrm{~s}^{-1}$ ) for dynamical orbit calculations with the Gaia DR2 proper motions. Most of our targets are dynamically associated with the Galactic halo; however, five stars with $[\mathrm{Fe} / \mathrm{H}]<-3$ have planar-like orbits, including one retrograde star. Another five stars are dynamically consistent with the Gaia-Sequoia accretion event; three have typical halo $[\alpha / \mathrm{Fe}]$ ratios for their metallicities, whereas two are $[\mathrm{Mg} / \mathrm{Fe}]$-deficient, and one is a new CEMP-s candidate. These results are discussed in terms of the formation and early chemical evolution of the Galaxy.


Key words: nuclear reactions, nucleosynthesis, abundances - Galaxy: formation - stars: Population II.

## 1 INTRODUCTION

The oldest and most metal-poor stars contain a fossil record of the star formation processes in the early Universe. These first stars would have been composed solely of hydrogen, helium, and trace amounts of lithium (Steigman 2007; Cyburt et al. 2016); without

[^0]metals to efficiently cool the gas, large Jeans masses, and thereby very massive stars ( $M_{*} \gtrsim 100 \mathrm{M}_{\odot}$ ) are predicted to have formed (Silk 1983; Tegmark et al. 1997; Bromm, Coppi \& Larson 1999; Abel, Bryan \& Norman 2002; Yoshida et al. 2006). In addition, improved gas fragmentation models (e.g. Clark et al. 2011; Schneider et al. 2012) and the discovery of very low-mass ultrametal-poor stars $([\mathrm{Fe} / \mathrm{H}]<-4$; Keller et al. 2014; Starkenburg et al. 2017b; Schlaufman, Thompson \& Casey 2018; Nordlander et al. 2019) have
suggested that lower mass, long-lived stars may have also formed in these pristine environments (e.g. Nakamura \& Umemura 2001; Wise et al. 2012). Notably, if $\leq 0.8 \mathrm{M}_{\odot}$ stars were to form, they could still exist today on the main sequence, and are expected to have undergone very little surface chemical evolution over their lifetimes. Detailed studies could provide invaluable constraints on (1) the nucleosynthetic yields from the first stars and the earliest supernovae (e.g. Heger \& Woosley 2010; Ishigaki et al. 2014; Tominaga, Iwamoto \& Nomoto 2014; Clarkson, Herwig \& Pignatari 2018; Nordlander et al. 2019), (2) the physical conditions in the high-redshift universe (where stars are too faint to be observed individually; Tegmark et al. 1997; Freeman \& Bland-Hawthorn 2002; Cooke \& Madau 2014; Hartwig et al. 2018; Salvadori et al. 2019), (3) the primordial initial mass function (e.g. Greif et al. 2012; Susa, Hasegawa \& Tominaga 2014), and (4) early Galactic chemical evolution processes (see Sneden, Cowan \& Gallino 2008; Tolstoy, Hill \& Tosi 2009; Roederer et al. 2014; Yoon et al. 2016; Wanajo et al. 2018; Kobayashi, Karakas \& Lugaro 2020, and references therein).

Dedicated searches for old, metal-poor stars in the Milky Way (MW) and in its dwarf galaxy satellites were initiated over two decades ago (e.g. Bond 1980; Carney \& Peterson 1981; Beers, Preston \& Shectman 1985; Beers et al. 1999). Chemical abundances have now been measured for hundreds of extremely metal-poor stars (EMP), where $[\mathrm{Fe} / \mathrm{H}]^{1} \leq-3$ (e.g. Aoki et al. 2013; Cohen et al. 2013; Yong et al. 2013a; Frebel \& Norris 2015; Matsuno et al. 2017; Aguado et al. 2019) and over a dozen stars with $[\mathrm{Fe} / \mathrm{H}]<-4$ (see Starkenburg et al. 2017b; Bonifacio et al. 2018; Aguado et al. 2018a,b, 2019; Frebel et al. 2019; Nordlander et al. 2019, and references therein). Most of the Galactic EMP stars show enhanced [ $\alpha / \mathrm{Fe}]$ abundances and a diversity of neutron capture element ratios, interpreted as the yields from core-collapse supernovae with different progenitor masses and explosion prescriptions. More recently, the importance of compact binary mergers to the r-process abundance ratios has also been revealed (Ji et al. 2016; Roederer et al. 2016; Hansen et al. 2017). In dwarf galaxies, the abundance ratios of hydrostatic elements (e.g. O, Na, Mg), explosive elements (e.g. Si, $\mathrm{K}, \mathrm{Mn}$ ), complex elements (like Zn ), and heavy elements (as $\mathrm{Ba}, \mathrm{Y}$ ) tend to be lower than those of their Galactic counterparts of similar metallicity. This reflects a range of differences in their star formation histories, including interstellar mixing efficiencies, star formation efficiencies, star formation rates, and effective mass functions of the dwarf galaxy systems (Venn et al. 2004; Tolstoy et al. 2009; Nissen \& Schuster 2010; McWilliam, Wallerstein \& Mottini 2013; Frebel \& Norris 2015; Hasselquist et al. 2017; Hayes et al. 2018; Lucchesi et al. 2020). The diversity of chemical abundance profiles seen in this sparse population of objects makes for challenging statistical studies. Targeted programs are needed to uncover larger samples of these (nearly) pristine stars.

The present-day locations of metal-poor stars also a diagnostic of early galaxy formation. Based on cosmological simulations of the Local Group, it is thought that the Galactic halo was formed through the accretion and disruption of dwarf galaxies at early epochs. Consequently, properties of the old, metal-poor stars seen in the halo manifest in the properties of their dwarf galaxy hosts (e.g. Ibata, Gilmore \& Irwin 1994; Helmi et al. 1999; Johnston et al. 2008; Wise et al. 2012; Starkenburg et al. 2017a; El-Badry et al. 2018). The arrival of precision proper motions from Gaia DR2 (Gaia

[^1]Collaboration 2018), and increasingly large data sets of stars with precision radial velocities from high-resolution spectroscopy, has enabled the determination of orbits for halo stars. The majority of the EMP halo stars have been shown to have high-velocities and eccentric orbits, consistent with accretion from a dwarf galaxy (Sestito et al. 2019, 2020; Di Matteo et al. 2020; Cordoni et al. 2021). A large population of halo stars has also been found with retrograde orbits and kinematics consistent with a halo merger remnant, e.g. GaiaEnceladus/Sausage (Meza et al. 2005; Belokurov et al. 2018; Helmi et al. 2018; Myeong et al. 2018) and Gaia-Sequoia (Matsuno et al. 2017; Barbá et al. 2019; Myeong et al. 2019; Monty et al. 2020; Cordoni et al. 2021).

The Galactic halo is not the only place to look for old stars. Curiously, some EMP stars have been found on nearly circular, planar orbits (Caffau et al. 2012; Schlaufman et al. 2018; Sestito et al. 2019, 2020; Venn et al. 2020). Since the Galactic plane is thought to have formed $\sim 10 \mathrm{Gyr}$ ago (Casagrande et al. 2016), these stars challenge the idea that the metal-poor stars are amongst the oldest stars accreted from the mergers of dwarf galaxies. The Galactic bulge is another environment to look for relics of first stars (White \& Springel 2000; Guo et al. 2010; Starkenburg et al. 2017a; El-Badry et al. 2018). To date, $\sim 2000$ very metal-poor stars ( $[\mathrm{Fe} / \mathrm{H}]<-2.0$ ) associated with the bulge have been found (García Pérez et al. 2015; Howes et al. 2015, 2016; Lamb et al. 2017; Arentsen et al. 2020b). Detailed chemical abundance analyses for these objects are limited, especially at the lowest metallicities, but they indicate that many of the metal-poor bulge candidates are chemically similar to halo stars (Lucey et al. 2019). In fact, estimates of their orbital properties using the exquisite astrometry from Gaia DR2 (Gaia Collaboration 2018) suggests that up to 50 per cent of these stars may be normal halo stars with highly elliptical and plunging orbits, a fraction that increases with decreasing metallicity (Lucey et al. 2020). However, while Gaia DR2 proper motions are extremely valuable in eliminating foreground metal-poor non-bulge members, the uncertainties on the parallax measurements for most stars in the bulge are currently too large for reliable distance estimates.

Regardless of where metal-poor stars are found, the union of stellar dynamics and chemical cartography provides a foundation for studies of Galactic Archaeology (e.g. Freeman \& Bland-Hawthorn 2002; Carney et al. 2003; Venn et al. 2004; Hayden, Bovy \& Holtzman 2015; Bovy et al. 2016; Hasselquist et al. 2017). Dedicated surveys have been successful in finding most of the metal-poor stars; these include the HK and Hamburg-ESO surveys (Beers, Preston \& Shectman 1992; Christlieb, Wisotzki \& Graßhoff 2002; Beers \& Christlieb 2005), the SDSS SEGUE, BOSS, and APOGEE surveys (Yanny et al. 2009; Eisenstein et al. 2011; Majewski et al. 2015), LAMOST (Cui et al. 2012), and more recently the narrow band imaging surveys SkyMapper (Keller et al. 2007; Da Costa et al. 2019; Onken et al. 2020) and Pristine (Starkenburg et al. 2017b). The discovery of more EMP stars is necessary to build a statistically significant sample to study the metal-poor Galaxy, and also to overcome cosmic variance in the chemo-dynamic analysis of stellar populations within it.

In this paper, 30 new candidate EMP stars have been selected from the Pristine survey for follow-up high-resolution spectroscopy. Pristine is based on a MegaPrime/MegaCam imaging survey at the 3.6-m Canada-France-Hawaii Telescope, using a unique narrowband filter centered on the Ca II H\&K spectral lines ( CaHK ). When CaHK is combined with the broad-band SDSS gri photometry (York et al. 2000) or Gaia DR2 photometry, this CaHK filter can been calibrated to find metal-poor candidates with $4000<$ $T_{\text {eff }}<7000 \mathrm{~K}$ (Youakim et al. 2017; Starkenburg et al. 2017b;

Arentsen et al. 2020a). The Pristine survey has been shown to successfully predict stellar metallicities. A total of $\sim 56$ per cent of stars with $[\mathrm{Fe} / \mathrm{H}]_{\text {Phot. }}<-2.5$ are confirmed to have $[\mathrm{Fe} / \mathrm{H}]<-2.5$ ( $\sim 23$ per cent when $[\mathrm{Fe} / \mathrm{H}]_{\text {Phot. }}<-3.0$ ) based on follow-up spectroscopic studies (Caffau et al. 2017; Youakim et al. 2017; Aguado et al. 2019; Bonifacio et al. 2019b; Venn et al. 2020). The target stars for this paper were selected from the medium-resolution spectroscopic follow-up studies of EMP candidates found within the initial $\sim 2500 \mathrm{deg}^{2}$ footprint ${ }^{2}$ of the Pristine survey (Martin et al., in preparation). In Section 4, we improve upon the the previous stellar parameter determinations; in Section 5, we calculate the chemical abundances or upper limits for $\sim 15$ elements; and in Section 6, we estimate the orbits using the Gaia DR2 data base for a chemodynamical analysis. Together, these properties permit a study of the origins of these metal-poor stars themselves, ultimately to unravel the formation history of the MW Galaxy.

## 2 TARGET SELECTION

Targets in this paper have been selected from the original $2500 \mathrm{deg}^{2}$ Pristine photometric survey (Starkenburg et al. 2017b; Youakim et al. 2017) and medium-resolution spectroscopic follow-up survey (Youakim et al. 2017; Aguado et al. 2019). All of the mediumresolution spectra (hereafter MRS) were observed at the Isaac Newton Telescope (INT), and were analysed using the FERRE data analysis pipeline (Prieto et al. 2006) and the ASSET grid of synthetic stellar spectra as described and published by Aguado et al. 2017. FERRE searches for the best fit to the observed spectrum by simultaneously deriving the main stellar atmospheric parameters (effective temperature, surface gravity, and metallicity $[\mathrm{Fe} / \mathrm{H}]$ ), and it also determines the carbonicity, $[\mathrm{C} / \mathrm{Fe}]$. Uncertainties are found via Markov Chain Monte Carlo (MCMC) sampling around the best-fitting stellar parameters. Stars with a very high probability ( $>90$ per cent) for a Pristine metallicity $[\mathrm{Fe} / \mathrm{H}]_{\text {phot }}<-2.75$ in both the $(g-i)$ and $(g-r)$ calibrations are shown in Fig. 1 (in grey). The metallicities from the INT medium-resolution spectral analyses by FERRE for those same stars are also shown in Fig. 1 (in red). Clearly some of our initial Pristine metallicities were too low; however, significant improvements in the Pristine selection function have been made since our original MRS spectroscopic follow-up programs, in anticipation of providing targets for the WEAVE survey (Dalton et al. 2014, 2018).

Targets in this paper with high-resolution spectroscopy have been selected with $[\mathrm{Fe} / \mathrm{H}]_{\text {MRS }}<-3$ and low temperatures ( $T_{\text {eff }}<6500 \mathrm{~K}$ ) in the magnitude range $14.8<V<16.4$. These are noted in blue in Fig. 1. We have observed $<5$ per cent of the full sample from the original footprint area, showing that a spectroscopic survey like WEAVE is necessary to reach all of them. Some stars with enhanced carbon were included ( $[\mathrm{C} / \mathrm{Fe}]_{\text {FERRE }}>1$ ); however, stars with non-normal carbon abundances were not given a higher priority in the target selection because the carbon abundances are typically unreliable when low $\operatorname{SNR}(<25)$ and low-resolution data are analysed with the FERRE pipeline (see below, also Aguado et al. 2019; Arentsen et al., in preparation).

The targets analysed in this paper are listed in Table 1. The stellar identifications (IDs) are a combination of their SDSS RA and Dec. coordinates and $V$ are in observer magnitudes calculated from SDSS $u, g, r, i, z$ given the calibration by (Lupton et al.

[^2]

Figure 1. The metallicity distribution for the full sample of metal-poor stars found in the original Pristine footprint. The grey and pink distributions are for the same sample of stars ( $V<18$, Aguado et al. 2019), showing that medium-resolution spectral follow-up found slightly higher metallicities for this sample. GRACES metallicities from this paper are shown in blue (inset included for higher detail). Clearly, there are many more EMP candidates available for high-resolution spectroscopic analyses.
2005). The other SDSS and Pristine filter magnitudes have been dereddened using $E(B-V)$ from (Schlegel et al. 1998). Table 1 also lists the information on the exposures and the SNR of the final combined spectrum for each target. Stellar parameters from the Pristine survey are listed in Table 2. This includes the photometric Pristine metallicities $\left([\mathrm{Fe} / \mathrm{H}]_{\text {phot }}\right)$ and the colour temperatures ( $T_{\text {phot }}$ ), which are an average of the dwarf and giant solutions from SDSS gri and Pristine CaHK photometry (see Starkenburg et al. 2017b). Table 2 also includes the stellar parameters from the FERRE analysis of the INT medium-resolution spectroscopic survey by Aguado et al. (2019) for our sample. The average SNR $=28$ for the MRS of our targets, with a range $7<\mathrm{SNR}<79$. As mentioned above, the FERRE pipeline simultaneously determines the effective temperature ( $T_{\text {eff }}$ ), surface gravity ( $\log \mathrm{g}$ ), metallicity $[\mathrm{Fe} / \mathrm{H}]_{\mathrm{MRS}}$, and carbonicity $[\mathrm{C} / \mathrm{Fe}]_{\text {MRS }}$ for each star. Radial velocities are also derived from MRS ( $\Delta \mathrm{RV} \sim 1 \mathrm{~km} \mathrm{~s}^{-1}$ ). Aguado et al. (2019) investigated the FERRE carbonicity measurements as functions of both surface gravity and SNR. They find that carbon abundances are more reliably determined (systematic uncertainties of $\sim 0.2$ dex) for cool, lower gravity giants, primarily due to the increased strength of spectral lines at lower temperatures. Likewise, increased line strength means lower SNR is needed for a detection of the $G$ band. Conversely, the uncertainties in the carbon abundances increases up to $\sim 0.6$ dex for the hotter, higher gravity stars, where weaker spectral features and less reliable surface gravities are expected. Since the carbon measurement is so heavily dependent on both SNR and gravity, we do not report individual values for $[\mathrm{C} / \mathrm{Fe}]_{\text {MRS }}$ in Table 2, and instead flag stars as C -rich candidates if $[\mathrm{C} / \mathrm{Fe}]_{\text {MRS }}>1.0$. The stars are flagged further to note whether the carbon abundances are reliable, based on the SNR of the medium-resolution INT spectra analysed by FERRE.

## 3 GEMINI-GRACES OBSERVATIONS

High-resolution spectra have been collected for 30 EMP candidates with the Gemini Remote Access to CFHT ESPaDOnS Spectrograph (GRACES; Chene et al. 2014; Pazder et al. 2014). A 270-m optical fibre links the Cassegrain focus at the Gemini-North telescope to

Table 1. Stellar identifications, positions, and CaHK and SDSS dereddened magnitudes for our GRACES targets, selected from the Pristine survey (Starkenburg et al. 2017a; Aguado et al. 2019). $E(B-V)$ values from Schlegel, Finkbeiner \& Davis (1998), and the observer $V$ magnitudes from the SDSS conversions. Total exposure times (number of exposures), observation dates, and final SNR (at $6000 \AA$ ) are also provided. The full table is available as online supplementary material.

| ID | RA <br> $(\mathrm{deg})$ | Dec. <br> $(\mathrm{deg})$ | $V$ <br> $(\mathrm{mag})$ | $E(B-V)$ | $C a H K_{0}$ <br> $(\mathrm{mag})$ | $g_{0}$ <br> $(\mathrm{mag})$ | $r_{0}$ <br> $(\mathrm{mag})$ | $i_{0}$ <br> $(\mathrm{mag})$ | $t_{\text {exp }}(\mathrm{s}, \#)$ | SNR |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2018A: |  |  |  |  |  |  |  |  |  |  |
| P191.8535+12.0508 | 191.8535 | 12.0508 | 15.21 | 0.03 | 15.52 | 15.26 | 15.05 | 14.98 | $5580(3)$ | 121 |
| P209.0986+09.8244 | 209.0986 | 9.8244 | 15.50 | 0.03 | 15.79 | 15.51 | 15.32 | 15.25 | $6300(3)$ | 75 |
| P224.8444+02.3043 | 224.8444 | 2.3043 | 15.21 | 0.05 | 15.64 | 15.27 | 14.91 | 14.76 | $4500(3)$ | 91 |
| P237.8589+12.5660 | 237.8589 | 12.5660 | 15.58 | 0.04 | 15.84 | 15.58 | 15.37 | 15.30 | $8100(4)$ | 95 |
| P244.8986+10.9310 | 244.8986 | 10.9310 | 15.58 | 0.07 | 15.76 | 15.48 | 15.28 | 15.22 | $7200(4)$ | $8 / 17 / 2018$ |

Table 2. Stellar parameters from the Pristine photometric survey (PRIS, Starkenburg et al. 2017b) and follow-up medium resolution spectroscopy (MRS) analysed with FERRE Aguado et al. (2019) are shown. Carbonicity is also determined from the medium resolution spectra, with the exception of P207.3454+14.1268 that was observed with a medium-resolution ESO 3.6 m -EFOSC spectrum (Buzzoni et al. 1984). The C-rich flag denotes whether the star has [C/Fe] $>1.0$, and an asterisk denotes that the SNR was too low for a reliable determination. Radial velocities from medium resolution spectroscopy (from Sestito et al. 2020) are compared to our more precise GRACES values. The full table is available as online supplementary material.

| ID | PRIS <br> $T_{\text {phot }}$ <br> (K) | PRIS $[\mathrm{Fe} / \mathrm{H}]_{\text {phot }}$ (dex) | $\begin{gathered} \text { MRS } \\ S N R \end{gathered}$ | MRS <br> $T_{\text {eff }}$ <br> (K) | MRS <br> $\log g$ <br> (dex) | MRS <br> [ $\mathrm{Fe} / \mathrm{H}$ ] <br> (dex) | MRS <br> C-rich? | $\begin{gathered} \text { MRS } \\ \text { RV } \\ \left(\mathrm{km} \mathrm{~s}^{-1}\right) \end{gathered}$ | $\begin{gathered} \text { GRACES } \\ \text { RV } \\ \left(\mathrm{km} \mathrm{~s}^{-1}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P} 008.5638+28.1855$ | 6173 | -3.04 | 34 | $6169 \pm 17$ | $5.00 \pm 0.07$ | $-2.84 \pm 0.05$ | N* | $-266.4 \pm 7.4$ | $-272.3 \pm 0.5$ |
| P016.2907+28.3957 | 5583 | -3.02 | 21 | $5378 \pm 24$ | $1.13 \pm 0.10$ | $-3.27 \pm 0.04$ | Y | $-384.5 \pm 10.8$ | $-374.3 \pm 0.5$ |
| P021.6938 + 29.0039 | 6184 | -3.31 | 25 | $5789 \pm 20$ | $1.09 \pm 0.09$ | $-3.40 \pm 0.04$ | Y* | $-91.0 \pm 8.4$ | $-85.4 \pm 0.5$ |
| P021.9576+32.4131 | 5408 | -3.53 | 55 | $5379 \pm 147$ | $2.40 \pm 0.84$ | $-2.67 \pm 0.19$ | N* | - | $-152.6 \pm 0.1$ |
| P031.9938 + 27.7363 | 6465 | -3.27 | 25 | $6477 \pm 35$ | $4.93 \pm 0.04$ | $-2.83 \pm 0.04$ | N* | $-215.1 \pm 11.1$ | $-209.4 \pm 0.6$ |

the Canada-France-Hawaii Telescope ESPaDOnS spectrograph (a cross-dispersed high-resolution échelle spectrograph that covers the whole visible spectrum; Donati et al. 2006). We note that the exposure times we used were in good agreement with the GRACES ITC provided by Gemini Observatory. In the 2 -fibre (object+sky) mode, spectra are obtained with resolution R $\sim 65000$; however, light below $\sim 4800 \AA$ is severely limited by poor transmission through the optical fibre link.

The GRACES spectra have been reduced using the Gemini 'Open-source Pipeline for ESPaDOnS Reduction and Analysis' tool (OPERA; Martioli et al. 2012). This includes standard calibrations (images are bias subtracted, flat-fielded, extracted, wavelength calibrated, and heliocentric corrected). Starting from the individually extracted and normalized échelle orders (the $*$ i.fits files), one continuous spectrum is stitched together by weighting the overlapping wavelength regions by their error spectrum, and co-adding as a weighted average. All visits for a given star are examined for radial velocity (RV) variations, potentially indicating binarity; no evidence for binary systems was found based on the criteria $\Delta \mathrm{RV} \leq 1 \mathrm{~km} \mathrm{~s}^{-1}$, although we note radial velocity variations are unlikely to be measured due to the short cadence of our observations. All visits for a given star have then been co-added via a weighted mean using the error spectrum. The co-added spectrum has then been radial velocity corrected through cross-correlation with a high SNR comparison spectrum of the metal-poor standard star HD 122563. Other radial velocity standards were examined (e.g. Arcturus and a synthetic spectrum for a typical metal-poor RGB), however, the solutions had the smallest uncertainties ( $\sigma \mathrm{RV} \leq 0.2 \mathrm{~km} \mathrm{~s}^{-1}$ ) when compared to HD 122563. As a final step, the RV-corrected spectra were re-normalized using k-sigma clipping with a non-linear filter (a combination of a median and a boxcar). The effective scale length of the filter ranged from 8 to $15 \AA$, dependent on the crowding of the
spectral lines, which was sufficient to follow the continuum when used in conjunction with iterative clipping. The portion of the stellar spectra that was used in this analysis in shown in Fig. A1.

## 4 STELLAR PARAMETERS AND RADIAL VELOCITIES

The stellar temperatures ( $T_{\text {eff }}$ ) have been determined using the colour-temperature relation for Gaia photometry from Mucciarelli \& Bellazzini (2020; MB2020). This calibration was selected based on their inclusion of very metal-poor stars (from González Hernández \& Bonifacio 2009). When calculating temperatures from MB2020, it is necessary to know if the star is a dwarf or giant (two sets of calibrations) and to have a metallicity estimate a priori. Using the Gaia parallaxes, we were able to estimate the likelihood of an individual star as a dwarf or giant (see below), and we adopted the initial metallicities determined from the Pristine survey photometry and INT medium-resolution spectroscopic analysis (Aguado et al. 2019). Colours were dereddened using Schlafly \& Finkbeiner (2011), adapted for Gaia DR2 photometry. ${ }^{3}$ A comparison of our temperatures from the MB2020 calibration to those from the Casagrande et al. (2020) calibration showed very good agreement, even though the latter had very few standard stars at very low metallicities.

Surface gravities $(\log g)$ were determined using the StefanBolzmann equation (e.g. Kraft \& Ivans 2003; Venn et al. 2017). This method requires (i) a distance, which we calculate from the Gaia DR2 parallax assuming the parallax zero-point offset from Lindegren et al. (2018), (ii) the solar bolometric magnitude ${ }^{4}$ of $\mathrm{M}_{\mathrm{bol}}=4.74$,

[^3]and (iii) bolometric corrections for Gaia DR2 photometry (Andrae et al. 2018).

Uncertainties in $T_{\text {eff }}$ and $\log g$ were determined from a Monte Carlo analysis on the uncertainties from the input parameters, as well as assuming a flat prior on the stellar mass, spanning $0.5-1.0 \mathrm{M}_{\odot}$. The final stellar parameter, microturbulence $\xi$, was determined from the surface gravity values, using the calibrations by Sitnova et al. (2015) for dwarf stars and Mashonkina et al. (2017) for giants.

This method was selected over the use of isochrones due to significant differences between the MIST/MESA (Paxton et al. 2011; Choi et al. 2016; Dotter 2016) and Yale-Yonsei isochrones (Lejeune, Cuisinier \& Buser 1998; Demarque et al. 2004) for old, metal-poor stars shown in Fig. 2. The quality of the spectral parameters using the MIST/MESA isochrones for metal-poor stars has been questioned. For example, Monty et al. (2020) found good agreement between spectroscopic and isochrone-mapping temperature determinations for stars with $[\mathrm{Fe} / \mathrm{H}]>-2$. However, for lower metallicities, the temperatures determined from isochrone-mapping tended to be hotter, by up to $\Delta T_{\text {eff }}=+500 \mathrm{~K}$ when $[\mathrm{Fe} / \mathrm{H}]=-3.5$. A similar result has been seen by Joyce \& Chaboyer $(2015,2018)$ due to a range of (optimized) values for the convective mixing length parameter. Nevertheless, a comparison of our temperatures from the MB2020 calibrations to those from the Bayesian inference method using MIST/MESA isochrones developed by Sestito et al. (2019) showed good agreement for dwarfs and red giants. Where we found significant deviations were for our EMP stars on the sub-giant branch and those predicted to be carbon-rich.

A comparison of our stellar parameters (Table 3) to those determined from our medium-resolution FERRE analysis (Table 2) are shown in the bottom row of Fig. 3. The FERRE stellar parameter errors are the FERRE MCMC fitting errors to the spectra. The SDSS photometric colour estimates for temperature (Table 1) are also shown for comparisons in the top row of Fig. 3, where separate dwarf and giant solutions have been averaged together. We note that the MB2020 calibrations appear to be well constrained for EMP stars on the red giant branch and the main sequence (see their fig. 2). Nevertheless, for hotter stars, which are typically the main-sequence or main-sequence turn-off stars, there are larger temperature uncertainties as seen in Fig. 3. From tests in our MCMC analysis of temperature, we find this is simply due to a nearly constant uncertainty in the colours that scales to a slightly larger temperature uncertainty as the temperature increases.

Overall, the agreement between our temperatures from MB2020 and the FERRE MRS analysis are in good agreement $\left(\sigma T_{\text {eff }} \sim\right.$ 200 K ). The SDSS photometric temperatures tend to be hotter than our temperatures or those from the FERRE MRS analysis, by $\Delta T_{\text {eff }} \sim 200 \mathrm{~K}$. Only the hottest stars show photometric and FERRE MRS temperatures that are cooler than ours. On the other hand, our values for $\log g$ are more precise then those from the FERRE MRS analysis. Due to the low SNR of the MRS, FERRE is forced to make a dwarf/giant distinction, forcing the gravities to values to be near the edges of their synthetic grid $(\log g=1.0$ or 5.0$)$. Similar trends in gravity have been seen when comparing the FERRE MRS results to other high-resolution spectral analyses of EMP stars in our group (Bonifacio et al. 2019a; Venn et al. 2020; Arentsen et al. 2020b).

A comparison of radial velocity values from the MRS and our high-resolution GRACES spectra is shown in Fig. 4. There has been significant improvement in the radial velocity determinations between our initial MRS results (in Pristine VI, Aguado et al. 2019) and the most recent MRS analysis (in Pristine X, Sestito et al. 2020). The most recent MRS radial velocities show a mean offset of only


Figure 2. $T_{\text {eff }}$ and $\log g$ derived from Mucciarelli \& Bellazzini (2020) and the Stefan-Boltzmann law. MIST/MESA (the grey-dashed line) and YaleYonsei (the black-dotted line) isochrones with $[\mathrm{Fe} / \mathrm{H}]=-3.5$ and age $=$ 13 Gyr are shown for visual reference.
$\Delta(\mathrm{RV}) \sim 6 \mathrm{~km} \mathrm{~s}^{-1}$, with a dispersion of $12 \mathrm{~km} \mathrm{~s}^{-1}$, relative to our high-resolution spectra (HRS) values.

## 5 CHEMICAL ABUNDANCES

Chemical abundances are determined for each star using the stellar parameters discussed above and a classical model atmospheres analysis. Model atmospheres were generated using the most up-todate models on the MARCS website ${ }^{5}$ (Gustafsson et al. 2008, with additions by B. Plez); the OSMARCS spherical models are used when $\log g<3.5$. Spectral lines of iron were selected from the recent metal-poor stars analyses by Norris et al. (2017) and Monty et al. (2020). Atomic data were adopted from the atomic and molecular line data bases, summarized in linemake. ${ }^{6}$ Chemical abundances are compared to the Sun using the Asplund et al. (2009) solar data.

Elemental abundances are calculated in a three step process: (1) the list of well-known iron lines was examined in each spectrum for an initial iron abundance, and the metallicity of the model atmosphere was updated. This process was run twice with the

[^4]Table 3. Stellar parameters and iron abundances for our GRACES sample. Effective temperatures are from the Mucciarelli \& Bellazzini (2020) calibration and surface gravities are calculated from the Stefan-Boltzmann law (see text). Short ID's are used to identify stars throughout the text and in the figures. Iron abundance errors represent the total combined systematic error due to the stellar parameters and the line-to-line scatter (see Table B2). The number of lines used to calculate the average $[\mathrm{Fe} / \mathrm{H}]$ are given in parentheses. $\Delta \mathrm{Fe}_{\mathrm{NLTE}}$ is the averaged NLTE correction for Fe I lines with known NLTE calculations, in the sense that $\mathrm{Fe}_{\mathrm{ILTE}}=\mathrm{Fe}_{\mathrm{L} T E}+\Delta \mathrm{Fe}_{\mathrm{I}} \mathrm{ItE}$. Slope is the slope of the line fit to $\mathrm{A}(\mathrm{Fe} \mathrm{I})$ versus excitation potential, which can serve as a spectroscopic check of the effective temperature when more than 10 lines are available. The full table is available as online supplementary material.

| ID | Short ID | $T_{\text {eff }}(\mathrm{K})$ | $\log g$ (dex) | [ $\mathrm{Fe}_{\mathrm{I}} / \mathrm{H}$ ] | [ $\mathrm{Fe} \mathrm{II} / \mathrm{H}$ ] | [Fe/H] | $\mathrm{Fe} \mathrm{I}-\mathrm{Fe}$ II | $\Delta \mathrm{Fe}_{\mathrm{INLTE}}$ | Slope |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| P008.5638+28.1855 | P008+28 | $6154 \pm 241$ | $4.61 \pm 0.08$ | $-2.80 \pm 0.23$ (22) | $-2.88 \pm 0.12$ (3) | $-2.82 \pm 0.11$ (25) | 0.08 | 0.07 (13) | -0.06 |
| P016.2907+28.3957 | P016+28 | $5398 \pm 116$ | $2.40 \pm 0.10$ | $-2.95 \pm 0.26$ (50) | $-2.85 \pm 0.28$ (6) | $-2.93 \pm 0.20$ (56) | -0.10 | 0.25 (26) | -0.02 |
| P021.6938+29.0039 | P021+29 | $5878 \pm 137$ | $3.54 \pm 0.10$ | $-3.29 \pm 0.95$ (12) | $-3.14 \pm 0.45$ (4) | $-3.27 \pm 0.41$ (16) | -0.15 | 0.19 (7) | 0.10 |
| P021.9576+32.4131 | P021+32 | $5343 \pm 116$ | $2.02 \pm 0.11$ | $-3.05 \pm 0.13$ (45) | $-3.62 \pm 0.13$ (3) | $-3.21 \pm 0.30$ (48) | 0.57 | 0.34 (23) | $-0.03$ |
| P031.9938 + 27.7363 | P031+27 | $6172 \pm 212$ | $3.79 \pm 0.10$ | $-3.07 \pm 0.78$ (13) | $-3.07 \pm 0.27$ (4) | $-3.07 \pm 0.26$ (17) | 0.00 | 0.18 (8) | 0.01 |



Figure 3. Comparison of $T_{\text {eff }}$ and $\log g$ derived from SDSS photometry, medium-resolution spectroscopy, and our method of using the Mucciarelli \& Bellazzini (2020) calibration with the Stefan-Boltzmann law (see text). The black-dashed lines of fixed $\log g_{\text {FERRE }}=1.0$ and 5.0 (the bounds of the FERRE grid) are shown in the bottom right-hand panel. See Fig. 2 for star labels.
updated metallicities to ensure convergence. (2) A new synthesis of all elements was generated including line abundances and upper limits for all of the clean spectral lines (e.g. see Fig. 5). (3) For the more challenging spectral features (i.e. those that were more severely blended or required hyperfine structure corrections), then a full spectrum synthesis was carried out using linemake to find all features and components within $\pm 10 \AA$ of the feature of interest. When a spectral feature was well fit, then the abundance was measured. If not, a $3 \sigma$ upper limit was calculated. Each synthetic spectrum was broadened in MOOG using a Gaussian smoothing kernel with FWHM $=0.15$, other than two stars (P198+08 and P016+28) that required more broadening $(\mathrm{FWHM}=0.25)$. When there were multiple spectral lines for a given element, then the average of the measured abundances, or the lowest (most constrained) upper limit, was adopted. The number of lines synthesized per element ranged from 1 (Eu II) to 25 (Cr I). Blends, isotopic corrections, and hyperfine structure corrections were taken from linemake and included in the spectrum syntheses for lines of Lii, Oi SciI, Mni, CuI, Zni, Y ii, Zr II, Ba II, La II, and Eu II. A sample line list is available in Appendix A; the full line list is available online.


Figure 4. Comparison of the radial velocities (RVs) derived from our GRACES spectra and those from medium-resolution INT spectra. The MRS radial velocities in the top panel are from Pristine VI (PVI Aguado et al. 2019), and improved measurements with uncertainties are shown in the lower panel from Pristine X (PX Sestito et al. 2020). The GRACES RV errorbars are smaller than the point sizes. The median offset ( $\tilde{m})$ and standard deviation $(\sigma)$, both in $\mathrm{km} \mathrm{s}^{-1}$, are shown in each panel. See Fig. 2 for star labels.

Abundance errors are determined in two ways: (1) the line to line variations that represent measurement errors, e.g. in the continuum placement and/or due to the local SNR (see Tables 3-6), and (2) systematic uncertainties due to the stellar parameters (see Tables 7 and B2). The final abundance uncertainties are calculated by adding the line-to-line scatter ( $\sigma \mathrm{EW}$ ) in quadrature with the uncertainties imposed by the stellar parameter errors ( $\sigma T_{\text {eff }}, \sigma \log g$, and $\sigma[\mathrm{Fe} / \mathrm{H}]$ ). These final uncertainties are used in the abundance plots (i.e. Figs 68).

The EMP standard star HD 122563 has been analysed from an archival very high SNR ( $>200$ ) GRACES spectrum. We determined its stellar parameters using the same methods as for the GRACES targets, and find $T_{\text {eff }}=4750 \pm 89 \mathrm{~K}, \log g=1.12 \pm 0.11$, after adopting an initial metallicity of $[\mathrm{Fe} / \mathrm{H}]=-2.7$. These results are in fair agreement with the literature, e.g. Collet et al. (2018) revisit the analysis of this star with high resolution 3D model atmospheres. They adopt $T_{\text {eff }}=4600 \pm 47 \mathrm{~K}$ based on the IR flux method by Casagrande et al. (2014), and they use the Stefan-Boltzman formula to determine surface gravity $\log g=1.61 \pm 0.07$, based on the available parameters


Figure 5. Synthesized $\mathrm{Fe}_{\mathrm{I}}$ and $\mathrm{Fe}_{\text {II }}$ lines for the three stars with only Fe upper limits. Arranged top to bottom in order of hottest to coolest are P258 $+40\left(T_{\text {eff }}=\right.$ $6554 \mathrm{~K}), \mathrm{P} 237+12\left(T_{\text {eff }}=6148 \mathrm{~K}\right)$, and P246+08 ( $T_{\text {eff }}=6140 \mathrm{~K}$ ). Three Fe lines are shown (Fe II 5169.028 , Fe I 5269.537 , and Fe I $5328.039 \AA$ ), chosen as they provide the tightest constraints on $[\mathrm{Fe} / \mathrm{H}]$ for most stars in our sample. The GRACES spectra (the solid black line) are compared to synthesized spectra (the solid coloured lines that match the colour labels in Fig. 2 per star). The $[\mathrm{Fe} / \mathrm{H}]$ abundances used in the synthetic spectra are noted in each panel. The continuum placement (the black-dashed line) and the $\pm 1 \sigma$ and $-3 \sigma$ noise levels (the grey-dotted lines) are shown.

Table 4. LTE abundances for iron-group and odd-Z elements. Errors represent the total combined systematic error due to the stellar parameters and line-to-line scatter (see Table B2). The number of lines used is given in parentheses. For the elements $\mathrm{K}, \mathrm{Sc}, \mathrm{Mn}, \mathrm{Cu}$, and Zn , we determine upper limits for most stars (see Section B1). The full table is available as online supplementary material.

| ID | $[\mathrm{Na} \mathrm{I} / \mathrm{Fe}]$ | $[\mathrm{K} \mathrm{I} / \mathrm{Fe}]$ | $[\mathrm{Sc} \mathrm{II} / \mathrm{Fe}]$ | $[\mathrm{Cr} \mathrm{I} / \mathrm{Fe}]$ | $[\mathrm{Mn} \mathrm{I} / \mathrm{Fe}]$ | $[\mathrm{Ni} \mathrm{I} / \mathrm{Fe}]$ | $[\mathrm{Cu} \mathrm{I} / \mathrm{Fe}]$ | $[\mathrm{Zn} \mathrm{I} / \mathrm{Fe}]$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P} 008.5638+28.1855$ | $-0.15 \pm 0.17(1)$ | $<0.60$ | $<1.60$ | $-0.20 \pm 0.20(1)$ | $<0.35$ | $<0.05$ | $<1.00$ | $<0.95$ |
| $\mathrm{P} 016.2907+28.3957$ | $0.37 \pm 0.18(2)$ | $<0.55$ | $0.90 \pm 0.53(1)$ | $-0.15 \pm 0.16(4)$ | $<0.15$ | $-0.05 \pm 0.16(1)$ | $<0.50$ | $<0.70$ |
| $\mathrm{P} 021.6938+29.0039$ | $<-0.40$ | $<1.30$ | $<2.20$ | $-0.05 \pm 0.25(1)$ | $<1.05$ | $0.20 \pm 0.27(1)$ | $<1.40$ | $<1.65$ |
| $\mathrm{P} 021.9576+32.4131$ | $0.07 \pm 0.31(2)$ | $0.80 \pm 0.33(1)$ | $<1.10$ | $-0.02 \pm 0.31(3)$ | $<0.40$ | $0.10 \pm 0.32(1)$ | $<0.80$ | $<1.00$ |
| $\mathrm{P} 031.9938+27.7363$ | $-0.10 \pm 0.17(1)$ | $<0.95$ | $<1.90$ | $-0.15 \pm 0.27(1)$ | $<0.80$ | $<0.15$ | $<1.30$ | $<1.30$ |

Table 5. LTE abundances for the $\alpha$-elements. Errors represent the total combined systematic error due to the stellar parameters and line-to-line scatter (Table B2). The number of lines used is given in parentheses. The full table is available as online supplementary material.

| ID | $[\mathrm{O} \mathrm{I/Fe}]$ | $[\mathrm{Mg} \mathrm{I} / \mathrm{Fe}]$ | $[\mathrm{Ca} \mathrm{I} / \mathrm{Fe}]$ | $[\mathrm{Ca} \mathrm{II} / \mathrm{Fe}]$ | $[\mathrm{Ti} \mathrm{I} / \mathrm{Fe}]$ | $[\mathrm{Ti} \mathrm{II} / \mathrm{Fe}]$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| P008.5638+28.1855 | $<1.05$ | $0.47 \pm 0.13(4)$ | $0.08 \pm 0.15(3)$ | $0.78 \pm 0.15(3)$ | $<0.45$ | $<0.55$ |
| $\mathrm{P} 016.2907+28.3957$ | $<1.40$ | $0.55 \pm 0.11(4)$ | $0.29 \pm 0.13(10)$ | $1.17 \pm 0.13(3)$ | $0.48 \pm 0.15(4)$ | $0.61 \pm 0.11(6)$ |
| $\mathrm{P} 021.6938+29.0039$ | $<1.20$ | $0.11 \pm 0.18(2)$ | $0.33 \pm 0.15(4)$ | $0.92 \pm 0.20(3)$ | $<1.10$ | $<0.50$ |
| $\mathrm{P} 021.9576+32.4131$ | $<1.25$ | $0.78 \pm 0.29(3)$ | $0.46 \pm 0.30(7)$ | $0.42 \pm 0.32(3)$ | $<0.20$ | $0.15 \pm 0.34(1)$ |
| $\mathrm{P} 031.9938+27.7363$ | $<1.05$ | $0.50 \pm 0.16(3)$ | $0.38 \pm 0.14(4)$ | $0.95 \pm 0.12(3)$ | $<0.80$ | $<0.65$ |

at that time (e.g. they adopted a larger Hipparcos parallax $\pi^{\prime}=$ $4.22 \pm 0.35$ mas versus the Gaia DR2 value of $\pi^{\prime}=3.444 \pm 0.063$ with zero-point offset of $-0.029 \mathrm{mas})$. Their results are consistent with other photometric, interferometric, and spectroscopic methods, whereas ours are both hotter and brighter based on the new Gaia DR2 parallax measurement. Nevertheless, our abundance results for HD 122563 are similar to those in the literature and to other Galactic standard stars (Figs 7, 8, and B1.)

### 5.1 Iron group

Iron abundances are calculated from the average of the synthetic fits to each spectral feature identified in Table A1. Iron is calculated from $\mathrm{Fe}_{\mathrm{I}}$ and $\mathrm{Fe}_{\mathrm{II}}$ independently, where $[\mathrm{Fe} / \mathrm{H}]$ in Table 3 is the weighted average.

A comparison of the iron abundances between our high-resolution GRACES spectra, the MRS analysis, and the Pristine photometric estimates are shown in Fig. 6. In the top left-hand panel, lines

Table 6. LTE abundances for neutron-capture elements. Errors represent the total combined systematic error due to the stellar parameters and line-to-line scatter (see Table B2). The number of lines used is given in parentheses. We determine upper limits only for most of these elements (see Section B1), other than Ba. The full table is available as online supplementary material.

| ID | $[\mathrm{Y} \mathrm{II} / \mathrm{Fe}]$ | $[\mathrm{Zr} \mathrm{II} / \mathrm{Fe}]$ | $[\mathrm{Ba} \mathrm{II} / \mathrm{Fe}]$ | $[\mathrm{La} \mathrm{II} / \mathrm{Fe}]$ | $[\mathrm{Nd} \mathrm{II} / \mathrm{Fe}]$ | $[\mathrm{Eu} \mathrm{II} / \mathrm{Fe}]$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P} 008.5638+28.1855$ | $<1.15$ | $<2.60$ | $<0.05$ | $<2.25$ | $<2.45$ | $<2.55$ |
| P016.2907+28.3957 | $<0.30$ | $<1.80$ | $2.13 \pm 0.19(2)$ | $1.63 \pm 0.42(1)$ | $1.45 \pm 0.26(1)$ | $<1.75$ |
| P021.6938+29.0039 | $<1.55$ | $<3.15$ | $<0.05$ | $<2.50$ | $<2.05$ | $<1.65$ |
| P021.9576+32.4131 | $<0.55$ | $<2.05$ | $<-0.65$ | $<2.40$ | $<2.60$ | $<2.65$ |
| P031.9938+27.7363 | $<1.30$ | $<2.80$ | $<0.20$ | $<20$ |  |  |

Table 7. LTE lithium abundances from the Li doublet at $6707 \AA$. The $\sigma$ represents the line measurement error due to the continuum placement. $\Delta \mathrm{T}$ and $\Delta \mathrm{g}$ are the systematic errors in the stellar parameters $T_{\text {eff }}$ and $\log g$, while $\Delta \mathrm{Fe}$ is due to the uncertainty in $[\mathrm{Fe} / \mathrm{H}]$ (see Table 3). $\Delta$ is the total combined error of these added in quadrature. The full table is available as online supplementary material.

| ID | $\mathrm{A}(\mathrm{Li})$ | $\sigma$ | $\Delta \mathrm{T}$ | $\Delta \mathrm{g}$ | $\Delta \mathrm{Fe}$ | $\Delta$ |
| :--- | ---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P} 008.5638+28.1855$ | 1.98 | 0.14 | -0.13 | -0.08 | -0.09 | 0.23 |
| $\mathrm{P} 016.2907+28.3957$ | $<0.82$ |  |  |  |  |  |
| $\mathrm{P} 021.6938+29.0039$ | 1.58 | 0.14 | -0.52 | -0.42 | -0.46 | 0.82 |
| $\mathrm{P} 021.9576+32.4131$ | 0.89 | 0.22 | 0.08 | 0.13 | 0.11 | 0.29 |
| $\mathrm{P} 031.9938+27.7363$ | 1.73 | 0.18 | -0.42 | -0.37 | -0.38 | 0.70 |



Figure 6. Comparison of $[\mathrm{Fe} / \mathrm{H}]$ derived from photometry, MRS INT spectra, and our GRACES spectra. The dashed lines of fixed $[\mathrm{Fe} / \mathrm{H}]=-2.5,-3.0$, and -3.5 are shown in the top left-hand panel, which suggest that our Pristine survey photometric metallicities may be limited to $[\mathrm{Fe} / \mathrm{H}] \gtrsim-3$. $Y$-axes are shared between left-hand and right-hand panels. See Fig. 2 for star labels.
of constant metallicity are shown at $[\mathrm{Fe} / \mathrm{H}]=-2.5,-3.0$, and -3.5 . This plot suggests that the precision in the current Pristine photometric metallicities may be limited to $[\mathrm{Fe} / \mathrm{H}] \geq-3$, particularly for the hotter stars that dominate our sample. In the top right-hand panel, our metallicities from the GRACES analyses suggest that the Pristine photometric metallicities near $[\mathrm{Fe} / \mathrm{H}]=-3$ have an intrinsic dispersion of $\Delta[\mathrm{Fe} / \mathrm{H}] \sim \pm 0.5$. This dispersion appears to be even larger for the FERRE results, as seen in the bottom left-hand panel. The latter may also be temperature dependent, in that stars near $T_{\text {eff }}$ $($ FERRE $)=6000 \mathrm{~K}$ result in $[\mathrm{Fe} / \mathrm{H}]_{\text {MRS }}$ (FERRE) metallicities that are too low, as seen in the bottom right-hand panel.

Samples of the spectrum synthesis of three Fe lines (and one Mg line) are shown in Fig. 5 for three stars: P258+40 ( $T_{\text {eff }}=6554 \mathrm{~K}$ ), P237 $+12\left(T_{\text {eff }}=6148 \mathrm{~K}\right)$, and P246+08 $\left(T_{\text {eff }}=6140 \mathrm{~K}\right)$. Note


Figure 7. Comparison of $[\mathrm{Fe} \mathrm{I} / \mathrm{H}]-[\mathrm{Fe} \mathrm{II} / \mathrm{H}]$ versus surface gravity derived from the Stefan-Boltzmann law. Upper panel are 1DLTE abundances, and lower panel includes NLTE corrections (the open circles; see text). [Fe II/H] is lower than $[\mathrm{Fe} / \mathrm{H}]$ for a majority of the stars. The black-dashed line at $\left[\mathrm{Fe}_{\mathrm{I}} / \mathrm{H}\right]-\left[\mathrm{Fe}_{\mathrm{II}} / \mathrm{H}\right]=0$ represents ionization equilibrium - a spectroscopic check for the accuracy of the surface gravity. Reference star HD 122563 is shown as the black diamond.
that P237+12 is the lowest metallicity star in our sample, and we determine an upper limit of $[\mathrm{Fe} / \mathrm{H}] \leq-4.26$, despite a very high SNR spectrum (SNR $\sim 95$ at $6000 \AA$ ). This is partially due to the limited (red) wavelength region available in the GRACES spectra and lack of strong Fe II lines in this wavelength region. Examination of all three spectral lines shown in Fig. 5 provide the mean 1DLTE $3 \sigma$ upper limit for P237+12. A follow-up VLT-UVES spectrum of this star confirms this low metallicity from more and bluer iron features (Lardo et al., in preparation).

Departures from LTE are known to overionize the Fe I atoms due to the impact of the stellar radiation field on the level populations, particularly in hotter stars and metal-poor giants. These non-LTE (NLTE) effects can be significant in our stellar parameter range. To investigate the impact of NLTE corrections on the iron abundances, the $[\mathrm{Fe} \mathrm{I} / \mathrm{H}]-[\mathrm{Fe} \mathrm{II} / \mathrm{H}]$ differences are compared to the surface gravities in Fig. 7. We find that Fe I and Fe II are in excellent agreement for the dwarfs and subgiants ( $\log g \gtrsim 2.5$ ), whereas $\mathrm{Fe}_{\text {II }}$ tends to be lower than $\mathrm{Fe}_{\mathrm{I}}$ for the giants (by $>1 \sigma$ ). This is not the typical signature of neglected NLTE effects. NLTE corrections are examined from two data bases: (1) INSPECT ${ }^{7}$ provides NLTE corrections for some of our Fe I and Fe II lines (Bergemann et al.
${ }^{7}$ INSPECT NLTE corrections are available at http://inspect-stars.net.


Figure 8. Elements with good spectral line detections, and Eu II . $<[\mathrm{Ti} / \mathrm{Fe}]>$ is the average of $[\mathrm{TiI} / \mathrm{Fe}]$ and $[\mathrm{Ti} I \mathrm{I} / \mathrm{Fe}]$ when a detection was made for both species, otherwise it is the highest upper limit between the two species. Our analysis of the GRACES spectrum for HD 122563 is shown as the black diamond. The Galactic reference star abundances are taken from the literature (Venn et al. 2004; Aoki et al. 2013; Yong et al. 2013a; Roederer et al. 2014; Frebel, Simon \& Kirby 2014).

2012; Lind, Bergemann \& Asplund 2012) and (2) the MPIA NLTE grid $^{8}$ that provides NLTE correction for several additional lines (Bergemann et al. 2012; Kovalev et al. 2019). The NLTE corrections for our Fe II lines are negligible throughout. However, when the Fe I NLTE corrections are applied (bottom panel), the differences increase such that the giants show $<[\mathrm{Fe} \mathrm{I} / \mathrm{H}]_{\mathrm{NLTE}}-\left[\mathrm{Fe}_{\mathrm{II}} / \mathrm{H}\right]>\sim+0.5$. The average NLTE corrections per star are summarized in Table 3.

Offsets in stellar parameters due to enhancements of certain chemical elements have been predicted to affect the isochrones for old, metal-poor stars (VandenBerg et al. 2012). Specifically, enhanced $[\mathrm{Mg} / \mathrm{Fe}]$ or $[\mathrm{Si} / \mathrm{Fe}]$ by +0.4 relative to scaled-solar has been predicted to move a 12 Gyr isochrones with $[\mathrm{Fe} / \mathrm{H}]=-2$ to lower temperatures and higher gravities. These changes in $T_{\text {eff }}$ and $\log g$ would impact the $\mathrm{Fe}_{\mathrm{I}}$ and $\mathrm{Fe}_{\text {II }}$ line abundances, and move $\mathrm{Fe}_{\mathrm{I}}$ closer to Fe II, providing a possible resolution to our results. It is not clear how/if this effect is incorporated into the MB2020 calibrations, but regardless, this chemical effect will make any calibrations of the stellar parameters of old, metal-poor upper RGB stars subject to larger uncertainties. We note that our upper RGB stars do show a significant range in $[\mathrm{Mg} / \mathrm{Fe}]_{\mathrm{RGB}}=+0.1$ to +0.8 , with $\sigma[\mathrm{Mg} / \mathrm{Fe}]=$ 0.1 to 0.4 (see below). We also notice that the offsets from $\mathrm{Fe} \mathrm{I}=\mathrm{Fe}$ II are small for our stars on the lower RGB and seem to rise on the upper RGB, consistent with the predictions from the chemically dependent isochrone analysis. Regardless of these observations, we do not attempt a purely spectroscopic analysis of the stellar parameters for our RGB stars since we have very few Fe II lines ( $<5$ ) in these GRACES spectra.

The other iron-group elements Cr and Ni were also synthesized, but only 1-4 spectral lines of each element are available in our GRACES spectra.

These abundances are provided in Table 4 and shown in Fig. 8. When Cr or Ni are calculated, their 1DLTE abundances are in excellent agreement with Fe , which is similar to other metal-poor stars in the Galaxy. Examination of the NLTE corrections suggests that $[\mathrm{Cr} / \mathrm{Fe}]$ may be increase by up to $\sim 0.4$. This would be important for the detailed interpretation of the chemistry of each star; however, we do not include the NLTE effects in Fig. 8 since the Galactic comparison stars are not also corrected.

### 5.2 Carbon

As the GRACES spectra are restricted to redder wavelengths, we do not have any carbon features to analyse. However, [C/Fe] is determined in the FERRE analysis of our MRS from the G-band and features below 4300 A. In Table 2, we identify our targets that were reported to have C-enhancements by Aguado et al. (2019). A total of eight of the 30 stars in our sample were identified by FERRE to have $[\mathrm{C} / \mathrm{Fe}]>+1.0(\mathrm{P} 016+28, \mathrm{P} 021+29, \mathrm{P} 113+45, \mathrm{P} 133+28$, P184+01, P188+00, P224+02, P339.1+25.5). Unfortunately, the FERRE pipeline struggles to determine C when the SNR of the MRS is low ( $\$ 25$ ) in the temperature range of our targets. Closer inspection of the MRS shows that five of these are likely upper limits to non-existent G-bands.

Only three stars appear to have noticeable G bands in the MRS spectra, and in each of these cases the FERRE analysis found them to be very carbon-rich, with $[\mathrm{C} / \mathrm{Fe}]>+2(\mathrm{P} 016+28, \mathrm{P} 184+01$, $\mathrm{P} 224+02$ ). Only $\mathrm{P} 016+28$ is flagged to have a reliable carbon abundance. The other two do appear to be C-enhanced, but their specific $[\mathrm{C} / \mathrm{Fe}]$ values are quite uncertain. The slight changes in our

[^5]stellar parameters from the MB2020 calibrations/SB law are also likely to affect the final C abundances.

In summary, we find the C abundances for most of our targets are not sufficiently reliable from the MRS analysis; nevertheless, one star is clearly C-rich ( $\mathrm{P} 016+28$ ), and two others are very likely C-enhanced (P184+01, P224+02).

### 5.3 Alpha elements

Alpha elements in EMP stars form primarily though He-capture during various stages in the evolution of massive stars, and dispersed through SNe II events. Thus, the $[\alpha / \mathrm{Fe}]$ ratio is a key tracer of the relative contributions of SN II to SN Ia products in a star-forming region. In this paper, the $\alpha$-elements include $\mathrm{Na}, \mathrm{Mg}, \mathrm{Ca}$, and Ti . We have included Na because it typically scales linearly with Mg in metal-poor stars in the Galaxy (e.g. Pilachowski, Sneden \& Kraft 1996; Venn et al. 2004; Norris et al. 2013). We have also included Ti since it too scales with other $\alpha$-elements even though the dominant isotope ${ }^{48} \mathrm{Ti}$ forms primarily through Si-burning in massive stars (e.g. Woosley, Heger \& Weaver 2002).

Na abundances or upper limits are from the two strong Na D lines. These lines are clear and present in most of the stars in our sample, and easily separated from any interstellar lines. NLTE effects can be significant for these resonance lines, however, corrections in this analysis are small (ranging from $\Delta(\mathrm{Na})=-0.1$ to -0.2 for most stars), as shown in Table B1. Mg is from 2 to 4 lines of MgI in all stars, even P237+12 that has only an iron upper limit. NLTE corrections are small (typically $\Delta \mathrm{Mg} \leq+0.2$ ). Ca is from 1 to 10 lines of CaI in most stars, or the CaI 6122.217 and CaI 6162.173 lines are used to estimate an upper limit (e.g. see Fig. 9). NLTE corrections are moderate (typically $\Delta \mathrm{Ca} \leq+0.3$ ). The Ca II triplet is also examined, however, we do not use those results in our analysis (especially without NLTE corrections). Ti is from 1-4 lines of TiI and $1-6$ lines of Ti II. For many stars, upper limits only were available and estimated from Ti i lines. The average NLTE corrections for Ti i can be large ( $\Delta \mathrm{Ti} \leq+0.6$ ), however, the NLTE corrections to Ti II are negligible. Again, we do not include the NLTE corrections in Fig. 8 since abundances for the Galactic comparison stars are not also corrected.

The majority of these newly discovered EMP stars show 1DLTE abundances that are within $1 \sigma$ uncertainties of the Galactic comparison stars, especially given our results for the EMP standard star, HD 122563 (the black point in each abundance plot). Only a handful of stars have $\alpha$-element abundances that are statistically lower than the Galactic comparison stars. These include the following:
(i) Two stars with $[\mathrm{Fe} / \mathrm{H}]<-3$ ( $\mathrm{P} 184+43$ and $\mathrm{P} 207+14$ ), and a third star near $[\mathrm{Fe} / \mathrm{H}]=-2.6(\mathrm{P} 198+08)$, show sub-solar $[\mathrm{Ca} / \mathrm{Fe}]$. This is an unusual abundance signature when compared with the Galactic halo sample, especially as all three are enriched in $[\mathrm{Mg} / \mathrm{Fe}]$ ( $>+0.5$ ). Sample spectra and our 1DLTE synthesis for lines of Mg I, NaI, and CaI are shown in Fig. 9. NLTE corrections are small and do not affect these trends (see Table B1). This abundance pattern has been seen in only a few EMP stars (see Sitnova et al. 2019), and is discussed further below.
(ii) One star near $[\mathrm{Fe} / \mathrm{H}]=-3(\mathrm{P} 182+09)$ shows a low, solarlike $[\mathrm{Mg} / \mathrm{Fe}]$ value, yet high values of $[\mathrm{Ca} / \mathrm{Fe}] \sim+0.8$. This pattern has been seen for stars in dwarf galaxies, and is typically attributed to an effectively truncated upper IMF, loss of gas from high mass supernova events, and/or inhomogeneous mixing of supernova yields in the dwarf galaxy's interstellar medium (e.g. Tolstoy et al. 2009;


Figure 9. Spectrum syntheses for two stars near $[\mathrm{Fe} / \mathrm{H}]=-3$ that are notably Mg-rich, but Ca-poor. Syntheses of the Mg I $5172.68 \AA$ and Na I $5889.95 \AA$ (top panels), and two CaI lines ( $6122.21 \AA, 6162.17 \AA$; bottom panels) are shown, for P207+14 (brown, top) and P184+43 (blue, bottom). These absorption lines provide the best abundances or the tightest constraints for these two stars. The GRACES spectra are the solid black lines, and the synthesized spectra are the solid coloured lines with the [X/H] measurements in the legend. Spectra are offset for clarity. The grey-dashed lines represent the $\pm 1 \sigma$ synthesis black-dashed line represents the continuum placement and the grey-dotted lines are $\pm 1 \sigma$ and $-3 \sigma$, where $\sigma$ is defined as the measured scatter in the continuum.

McWilliam et al. 2013; Kobayashi, Nomoto \& Hachisu 2015; Frebel \& Norris 2015).
(iii) One star near $[\mathrm{Fe} / \mathrm{H}]=-3.5(\mathrm{P} 184+01)$ shows an enrichment in $[\mathrm{Na} / \mathrm{Fe}]$. This star will be discussed further below (see Section 6.1).

Oxygen is examined from the OI $7770 \AA$ triplet feature, however, this resulted in upper limit abundances for most of our stars (see Appendix A. Oxygen could be measured in only six stars, and NLTE corrections were applied (see Table B1). Three stars (P116+33, $\mathrm{P} 198+08$, and $\mathrm{P} 339.1+25.5$ ), showing $[\mathrm{O} / \mathrm{Fe}] \sim+0.5$, consistent with $[\mathrm{Mg} / \mathrm{Fe}]$ after oxygen NLTE corrections are applied. Three other stars ( $\mathrm{P} 184+01, \mathrm{P} 207+14$, and $\mathrm{P} 224+02$ ) show $[\mathrm{O} / \mathrm{Fe}]>+1.5$, which is much higher than the other $\alpha$-elements in those stars. We note that two of these stars are carbon-enhanced metal-poor (CEMP; Section 5.2) and the third is one of our high $[\mathrm{Mg} / \mathrm{Ca}]$ stars. The other CEMP and high $[\mathrm{Mg} / \mathrm{Ca}]$ stars in our sample have high [ $\mathrm{O} / \mathrm{Fe}$ ] upper limits only that do not constrain oxygen. These oxygen abundances support our identifications above that these are stars of special interest.

### 5.4 Neutron-capture elements

Elemental abundances or upper limits are determined for six neutron capture elements: $\mathrm{Y}, \mathrm{Zr}, \mathrm{La}, \mathrm{Nd}, \mathrm{Ba}$, and Eu. These formed in massive stars and core collapse supernovae through rapid neutron capture


Figure 10. Spectrum syntheses for one Ba-rich star (P184+01, blue) and one Ba-poor star (P192+13, red). Our spectrum syntheses for the two Ba II lines $(6141.73 \AA, 6496.91 \AA)$ are shown (bottom panels), and our best-fitting syntheses for Mg I 5172.68 $\AA$ and Na I $5889.95 \AA$ (top panels) for comparison. See Fig. 9 for additional label information.
reactions, and those other than Eu also form via slow neutron captures during the thermal pulsing asymptotic giant branch (AGB) phase in intermediate-mass stars. The specific details and yields from these nucleosynthetic processes is a dynamic field of current research. For the core-collapse SNe , new models, and calculations of their yields include details of the SN explosion energies, explosion symmetries, early rotation rates, and metallicity distributions (e.g. Kratz et al. 2007; Nishimura, Takiwaki \& Thielemann 2015; Tsujimoto \& Nishimura 2015; Kobayashi et al. 2020), as well as exploration of contributions from compact binary mergers as a (or as the most) significant site for the r-process (e.g. Fryer et al. 2012; Korobkin et al. 2012; Côté et al. 2016; Emerick et al. 2018). Similarly, predictive yields from AGB stars by mass, age, metallicity distributions, and details of convective-reactive mixing are also an active field of research (e.g. Lugaro et al. 2012; Cristallo et al. 2015; Pignatari et al. 2016).

Only Ba and Eu are discussed in this section. For all stars, we have $1-2$ Ba II lines ( $6141.73 \AA, 6496.91 \AA$ ). Hyperfine structure and isotopic splitting are taken into account using the atomic data in linemake. For Eu, the GRACES spectra only permit studies of the Eu II $6645 \AA$ line, which is too weak to be observed in any of our spectra. The upper limits for Eu from this line are also too high to be scientifically useful in testing for pure r-process enrichment in these stars. It would be important to examine the much stronger Eu II $4129 \AA$ line to constrain the pure r-process contributions in these stars.

Two stars appear to be Ba-rich (P184+01 and P016+28); as seen in Fig. 8, both appear to have $[\mathrm{Ba} / \mathrm{Fe}] \sim+1$ with $[\mathrm{Fe} / \mathrm{H}]$ $\Sigma-3$. The spectrum synthesis of the two BaII lines in P184+01 is shown in Fig. 10, where these lines are clear, strong, and well


Figure 11. Lithium abundances from Li I $6707 \AA$. Stellar labels are the same as in Fig. 8. The Spite plateau (Spite \& Spite 1982; Sbordone et al. 2010) is shown as the grey-dashed line.
measured. NLTE corrections were calculated for the two Ba-rich stars following the methods in Mashonkina, Gehren \& Bikmaev (1999) and Mashonkina \& Belyaev (2019), using models representing their specific stellar atmospheres and high LTE Ba abundances. The NLTE corrections for $\mathrm{P} 184+01$ increase $[\mathrm{Ba} / \mathrm{Fe}]$ by 0.09 dex, when averaged between the individual corrections for each of the two lines ( 6141 and $6496 \AA$ ). Alternatively, $[\mathrm{Ba} / \mathrm{Fe}]$ decreases by 0.44 dex when NLTE corrections are calculated for P016+28. Including these corrections, the NLTE Ba abundances are still significantly higher than the 1DLTE results in similar EMP stars in the Galaxy.

Six of our stars appear to be Ba-poor (Fig. 8). The spectrum synthesis for $\mathrm{P} 192+13$ shows that the Ba II 6141 and $6497 \AA$ lines are not present (Fig. 10. Using the $3 \sigma$ line depth, we find upper limits of $[\mathrm{Ba} / \mathrm{Fe}]<-0.4$ near $[\mathrm{Fe} / \mathrm{H}]=-2.6$. For our six Ba-poor stars, the $[\mathrm{Ba} / \mathrm{Fe}]$ abundances and upper limits are within the lower envelope of Ba abundances for stars in the Galaxy.

The other neutron capture elements with spectral features in the GRACES wavelength regions are examined in Appendix B1. Only upper limits could be determined, and they did not provide useful scientific constraints.

### 5.5 Lithium

The Li i 6707 spectral line is present in the spectra of over half of our targets. Our spectrum syntheses for Li included hyperfine structure and isotopic splitting, with atomic data taken from linemake. The study of lithium in EMP stars is an active topic of discussion due to the links between EMP stars and the chemistry of the early Universe. The cosmological lithium problem refers to the discrepancy between the amount of Li predicted from big bang nucleosynthesis $[\mathrm{A}(\mathrm{Li})=$ 2.67 to 2.74; Cyburt et al. 2016; Coc \& Vangioni 2017] and the highest Li abundances measured in the atmospheres of unevolved metal-poor stars [A(Li) ~ 2.2, the Spite Plateau; Spite \& Spite 1982; Bonifacio et al. 2007; González Hernández et al. 2008; Aoki et al. 2009; Sbordone et al. 2010]. Finding unevolved EMP stars with detectable Li provides strong constraints on the lithium problem.

A majority of our sample shows expected trends between $\mathrm{A}(\mathrm{Li})$, $T_{\text {eff }}$, and metallicity (Fig. 11). Most of the hotter and higher metallicity stars are found near the Spite plateau. As metallicity decreases, a higher degree of scatter in $\mathrm{A}(\mathrm{Li})$ is observed, consistent with the meltdown of the Spite plateau observed by Sbordone et al. (2010) and Bonifacio et al. (2012). The RGB stars in our sample show lower lithium abundances (or upper limits), as expected since Li is destroyed through surface convection in cooler stars (Spite \& Spite 1982). Five stars, however, are notable: P191+12, P224+10, $\mathrm{P} 237+12, \mathrm{P} 246+08, \mathrm{P} 258+40 . \mathrm{P} 191+12$, and P224+10 have metal-
licities of $[\mathrm{Fe} / \mathrm{H}]=-3.85$ and -3.68 , respectively, and the other three stars only have metallicity upper limits with $[\mathrm{Fe} / \mathrm{H}]<-3.5$, but all four have detectable Li at the $3 \sigma$ level. Their measured $\mathrm{A}(\mathrm{Li})$ places them at the Spite plateau (see Table 7). Similar in $T_{\text {eff }}, \log g$, metallicity, and $\mathrm{A}(\mathrm{Li})$ to the primary star of the spectroscopic binary CS22876-032 (González Hernández et al. 2008, 2019), these mainsequence and turn-off stars are excellent candidates for follow-up studies related to the cosmological lithium problem.

## 6 DISCUSSION

Using the chemical abundances determined in this paper, we discuss our EMP stars in terms of the accretion history and chemical evolution of the Galaxy.

### 6.1 New CEMP candidates

In this paper, we have analysed three stars with slight to large carbon enhancements.

As their precise $[\mathrm{C} / \mathrm{Fe}]$ results are quite uncertain, we regard these stars simply as CEMP candidates, rather than confirmed CEMP stars. At the lowest metallicities, stars are often found to be enhanced in carbon (Beers et al. 1992; Norris, Ryan \& Beers 1997), typically comprising 40 per cent of the EMP stars (see Yong et al. 2013b; Lee et al. 2013; Placco et al. 2014), though recently those percentages have been lowered through considerations of the carbon 3DNLTE corrections (Norris \& Yong 2019).

Different types of CEMP stars have been identified and defined by Beers \& Christlieb (2005), where the two main classes are the CEMPs stars, which show additional enhancement in s-process elements (such that $[\mathrm{C} / \mathrm{Fe}]>+0.7$ and $[\mathrm{Ba} / \mathrm{Fe}]>+1.0$ ), and the CEMP-no stars, which do not show any s-process enhancements. These initial definitions have been further refined by Yoon et al. (2016), based on the trends observed between $[\mathrm{Fe} / \mathrm{H}]$ and $[\mathrm{C} / \mathrm{Fe}]$. The C excess in CEMP-no stars is generally attributed to nucleosynthetic pathways associated with the very first stars to be born in the universe (Iwamoto et al. 2005; Meynet, Ekström \& Maeder 2006).

Of our three new CEMP candidates, we find that two (P016+28 and $\mathrm{P} 184+01$ ) are enriched in barium, with $[\mathrm{Ba} / \mathrm{Fe}]>+1$ (to within their $1 \sigma$ uncertainties), which suggests that they may belong to the CEMP-s sub-class. Examining P016+28 further, the carbon abundance from FERRE is $[\mathrm{C} / \mathrm{Fe}]=+2.42$, for an absolute carbon abundance of $\mathrm{A}(\mathrm{C})=7.76$. If this carbon abundance is accurate, this star would be amongst the high-C/Group I population in Yoon et al. $[2016, \mathrm{~A}(\mathrm{C})=7.96 \pm 0.42]$. Meanwhile, $\mathrm{P} 184+01$ has $[\mathrm{Fe} / \mathrm{H}]=$ -3.49 and a very uncertain carbon abundance of $\mathrm{A}(\mathrm{C})=7.26$, which places it between Groups I, II, and III. Another way to test the CEMP-s hypothesis for these two stars is through radial velocity monitoring, as most CEMP-s stars are found in a binary systems (e.g. Lucatello et al. 2005; Hansen et al. 2016; Starkenburg et al. 2014, and references therein). This property has contributed to the theory that CEMP-s stars have received their carbon and s-process enhancements through mass-transfer with an AGB star in a binary system (Abate et al. 2013). We do not search for radial velocity variations in our data though, since the GRACES spectra were rarely taken over several epochs, and the medium-resolution INT spectra do not have sufficient precision.

The remaining CEMP-no candidate, P224+02, has a low barium upper limit. As this star has $[\mathrm{Fe} / \mathrm{H}]=-3.68$ [and a tentative $\mathrm{A}(\mathrm{C})=$ 7.29], it falls between the $\mathrm{A}(\mathrm{C})$-metallicity groups in Yoon et al. (2016). Groups II and III are dominated by CEMP-no stars, but recent analysis of Group I CEMP stars has shown that 14 per cent are

CEMP-no (Norris \& Yong 2019). While generally low in s-process elements, the Group I CEMP-no stars also show higher [Sr/Ba] abundances than the majority of Group I CEMP-s/rs stars. To explain the [Sr/Ba] ratios, Norris \& Yong (2019) speculated that Group I CEMP-no stars may experience some mass exchange with massive AGB stars or rapidly rotating 'spinstars' in binary systems (both produce less s-process material). Unfortunately, we do not determine [ $\mathrm{Sr} / \mathrm{Fe}$ ] as the Sr II lines are at blue wavelengths, not reached by our GRACES spectra. Alternatively, we examine the $\alpha$-elements ( $\mathrm{Na}, \mathrm{Mg}, \mathrm{Ca}$ ) since some CEMP-no stars can show enrichments in these elements; P224+02 shows normal halo abundances for these elements. As discussed by Maeder \& Meynet (2015), the predictions for these elements depend on mixing in massive stars though, and the predictions can vary widely. Frebel \& Norris (2015) showed that enhanced alpha-elements only occur in about half of their CEMP-no sample, and even less when $[\mathrm{Fe} / \mathrm{H}] \lesssim-3$.

The exact origin(s) of the CEMP-no stars is not yet clear, however it has also been proposed that CEMP-no stars may form in dwarf galaxies, and thereby may be associated with accreted systems (Yuan et al. 2020; Limberg et al. 2020). To examine this further, we compute the orbits of our 30 GRACES stars below.

### 6.2 Other stars with interesting chemistries

Highlighted in Section 5.3, three stars (P184+43, P198+08, and $\mathrm{P} 207+14)$ show very low $[\mathrm{Ca} / \mathrm{Fe}](\leq-0.3)$ and large $[\mathrm{Mg} / \mathrm{Fe}]$ ( $>+0.5$ ). This results in $[\mathrm{Mg} / \mathrm{Ca}] \gtrsim+0.8$. This rare abundance pattern had been seen in only a few EMP stars, e.g. one star (HE1424$0241)$ at $[\mathrm{Fe} / \mathrm{H}]=-4$ was highlighted by Cohen et al. (2007) for its high $[\mathrm{Mg} / \mathrm{Ca}]=+0.83$, mostly driven by its low Ca . This abundance pattern cannot be explained by uncertainties in the stellar parameters (including any possible systematic errors in the surface gravity, e.g. if these were on the horizontal branch); instead, it is interpreted as contributions to stellar Mg and Ca abundances from only a small number of SN II explosions, i.e. where the nucleosynthetic yield for explosive alpha-burning nuclei like Ca was very low compared to that for the hydrostatic alpha-burning element Mg (see Sitnova et al. 2019). These results are further supported by our high [O/Fe]_NLTE values (see Appendix B3).

Two similar stars in the Hercules dwarf galaxy with $[\mathrm{Mg} / \mathrm{Ca}]=$ +0.58 and +0.94 dex were studied by Koch et al. (2008). Koch et al. (2008) argued that such high ratios can be attributed to enrichment from high mass ( $\sim 35 \mathrm{M}_{\odot}$ ) Type II SNe, based on yields from Woosley \& Weaver (1995). Furthermore, their chemical evolution models for Hercules-like dwarf galaxies indicate that the observed [ $\mathrm{Mg} / \mathrm{Ca}$ ] ratios can only be reproduced in 10 per cent of the systems that are enriched by only a few ( $1-3$ ) Type II events. Clearly, these are chemically unique objects that reflect the chemical evolution of rare environments. Sitnova et al. (2019) also note that these exceptional stars comprise $<10$ per cent of stars with $[\mathrm{Fe} / \mathrm{H}]<-3$ and do not typically reveal carbon enhancement, consistent with our results.

### 6.3 Orbit calculations

Gaia DR2 proper motions and astrometry have dramatically accelerated the fields of Galactic Archaeology and near-field cosmology by providing the data needed to calculate the detailed orbits of nearby stars. The stars in this study were also selected to have small parallax errors, and therefore precise distances. When combined with the precision radial velocities from our high-resolution GRACES spectra, then we are able to estimate the orbits for these stars to within the accuracy of our assumptions on the MW potential.


Figure 12. Orbital elements for stars from 2018A-2019B data sets. The star symbols represent stars in planar disc orbits, and the squares are stars that reach the outer Galactic halo.

Orbital parameters for the stars in this paper are calculated with Galpy (Bovy 2015), using the parallax distances, our RVs from the GRACES spectra, and the Gaia DR2 proper motions. The MWPotential $14^{9}$ was adopted, though a more massive halo of $1.2 \times$ $10^{12} \mathrm{M}_{\odot}$ was chosen following Sestito et al. (2019). Errors have been propagated from the uncertainties in the proper motions, RVs, and distances via Monte Carlo sampling of the Gaussian distributions of the input quantities.

The apocentric and pericentric distances ( $\mathrm{R}_{\text {apo }}$ and $\mathrm{R}_{\text {peri }}$ ), perpendicular distance from the Galactic plane ( $\mathrm{Z}_{\max }$ ), and eccentricity (e) of the calculated orbits for our stars are shown in Fig. 12. Following Sestito et al. (2019), stars with $\mathrm{R}_{\text {apo }}<15 \mathrm{kpc}$ and $|\mathrm{Z}|_{\max }<3 \mathrm{kpc}$ are considered to be confined to the Galactic plane, while stars with $\mathrm{R}_{\text {apo }}>30 \mathrm{kpc}$ are considered to be members of the outer halo. The orbital energy ( E ) and action parameters (vertical $\mathrm{J}_{z}$, azimuthal $\mathrm{J}_{\phi}$ ) for the sample are also calculated with Galpy, and shown in Fig. 13. All targets appear to be bound to the MW, to within their uncertainties.

### 6.4 Stars with interesting orbits

Five of our new EMP stars (P184+43, P191+12, P237+12, $\mathrm{P} 244+10$, and P339.1+25.5) have distinctly planar-like orbits $\left(|\mathrm{Z}|_{\max }<3 \mathrm{kpc}\right)$. All five have $[\mathrm{Fe} / \mathrm{H}]<-3$ and somewhat elliptical orbits ( $e=0.3$ to 0.7 ). P237+12 is the most metal-poor star in the GRACES sample with a 1DLTE metallicity upper limit of $[\mathrm{Fe} / \mathrm{H}]<-4.26$. This star has Mg below the canonical MW halo plateau values, though the abundances, when available, are generally within the regime of normal Galactic halo stars. The implications of finding planar-like EMP stars, in the context of Galactic evolution, is discussed further in the following section. P339.1+25.5 stands

[^6]

Figure 13. Action vectors and energies for stars from 2018A-2019B data sets. Same symbols as in Fig. 12. The grey-dotted box in the right-hand panel is the dynamical cut for Gaia-Sequoia from Myeong et al. (2019; $e \sim 0.6$ with $J_{\phi} / J_{\text {tot }}<-0.5$ and $\left.\left(J_{z}-J_{R}\right) / J_{\text {tot }}<0.1\right)$ and the grey-dashed ellipse represents the mean dynamical properties of the associated Gaia-Seqouia stars from Limberg et al. (2020).
out dynamically as it has the lowest $|\mathrm{Z}|_{\text {max }}(<1 \mathrm{kpc})$ of the stars in this sample, suggesting it may be coincident with the prograde Galactic thin disc. However, its somewhat elliptical orbit ( $e \sim 0.7$ ) is uncharacteristic of typical thin disc stars.

The star P184+43 with a prograde, planar orbit also has an unusual chemistry, as it is enriched in magnesium, $[\mathrm{Mg} / \mathrm{Fe}]=+0.6$, and yet has a very low upper limit on calcium, $[\mathrm{Ca} / \mathrm{Fe}]<-0.2$. In Section 6.2, we speculated that this peculiar abundance pattern may suggest a lack of contributions from lower mass stars and SN Ia. If so, then this star could have formed in a dwarf galaxy that was accreted by the MW at early times, before SN Ia could enrich it. This speculation is discussed further below (Section 6.5).

Five high-energy, highly retrograde stars (P016+28, P021+32, P031+27, P133+28, and P182+09) appear to be dynamically related to the 'Gaia-Sequoia' accretion event (Myeong et al. 2019). Sequoia is the population of high energy retrograde halo stars that are presumed to be associated with an ancient accretion event of a counter-rotating progenitor dwarf galaxy (Matsuno, Aoki \& Suda 2019; Myeong et al. 2019; Limberg et al. 2020; Monty et al. 2020; Yuan et al. 2020; Cordoni et al. 2021). Myeong et al. (2019) identifies stars with $e \sim 0.6, J_{\phi} / J_{\text {tot }}<-0.5$, and $\left(J_{z}-J_{R}\right) / J_{\text {tot }}<0.1$ to be linked to Gaia-Sequoia. These five stars also meet the more recent and stricter membership criteria by Limberg et al. (2020, see Fig. 13), to within their errors. We acknowledge that these simple action vector cuts do not account for background stars that are non-coincidental with Sequoia. Limberg et al. (2020) explored the effect of background contamination via a membership clustering algorithm and found that up to $\sim 50$ per cent of their Sequoia sample may indeed be contamination. Due to the small size of our sample, we do not explore
this further and only offer these stars as Gaia-Sequoia candidates to be confirmed/rejected in later studies. We note that all five have $[\mathrm{Fe} / \mathrm{H}] \sim-3$, and normal halo $[\alpha / \mathrm{Fe}]$ ratios. These add to the few EMP stars now found associated with Gaia-Sequoia (see also also Monty et al. 2020; Limberg et al. 2020; Cordoni et al. 2021).

The action vectors computed for the orbit of P244+10 suggest that it may also be associated with Gaia-Sequoia; however, its low-energy planar-like orbit is uncharacteristic of other Sequoia members. P244+10 is more dynamically similar to stars associated with the Thamnos event (Helmi et al. 2017; Koppelman, Helmi \& Veljanoski 2018; Limberg et al. 2020). Thamnos is also believed to be a lower metallicity - higher $\alpha$-abundance population than GaiaSeqouia (Koppelman et al. 2018; Limberg et al. 2020; Monty et al. 2020), and our chemical abundance study would support that. We find $\mathrm{P} 244+10$ has $[\mathrm{Fe} / \mathrm{H}]=-3.5 \pm 0.3$, compared to the five GaiaSequoia targets (above) with $<[\mathrm{Fe} / \mathrm{H}]>=-3.0 \pm 0.2$, and highlight that P244+10 is an interesting star for follow-up investigations.

### 6.5 Formation and early chemical evolution of the galaxy

This work is consistent with the results by Sestito et al. (2019) who found that a large number of ultra metal-poor stars in the literature are on planar orbits in the Galaxy. We have found five new EMP stars on planar-like orbits (or 16 per cent of our sample). Four are on prograde orbits and one ( $\mathrm{P} 244+10$ ) is on a retrograde orbit. These ratios are comparable to our earlier results from an analysis of CFHT spectra for 115 metal-poor candidates which resulted in 16 very metal-poor stars $([\mathrm{Fe} / \mathrm{H}]<-2.5)$ confined to the Galactic plane ( $\mathrm{R}_{\text {apo }}<15 \mathrm{kpc}$, $\mathrm{Z}_{\text {max }}<3 \mathrm{kpc}$ ), including one on an extremely retrograde orbit (Venn
et al. 2020). In comparison with the larger Pristine data base of medium-resolution INT spectra, Sestito et al. (2020) found that the ratio of metal-poor stars $([\mathrm{Fe} / \mathrm{H}]<-2.5)$ with prograde versus retrograde orbits is 1.28 , based on 358 stars. We find a similar ratio of 1.23 , for our sample of 29 stars with $[\mathrm{Fe} / \mathrm{H}]<-2.5$. When compared to the Numerical Investigation of a Hundred Astronomical Objects (NIHAO; Wang et al. 2015) hydrodynamic simulations of galaxy formation, specifically the NIHAO-UHD simulations (Buck 2020), these simulations show that such a population of stars is ubiquitous among these MW-like galaxies as investigated by Sestito et al. (2021).

In Section 6.2, we speculated that P184+43, with its planar orbit and unusual chemistry $([\mathrm{Mg} / \mathrm{Ca}]>+0.8)$, may have formed in a dwarf galaxy that was accreted at early times. The age estimate is based on its low metallicity $[\mathrm{Fe} / \mathrm{H}]=-3.3 \pm 0.3$ and chemical pattern, which suggests a lack of contributions from lower mass stars and SN Ia. It is possible that this star and its host dwarf galaxy were amongst the original building blocks that formed the proto Milky Way, as suggested from an analysis of NIHAO hydrodynamic simulations by Sestito et al. (2021).

The chemistry of the Gaia-Sequoia candidates P016+28, $\mathrm{P} 021+32$, and P031+27 are largely consistent with previous studies, which show typical $\alpha$-enhancement at low metallicities (Matsuno et al. 2019; Limberg et al. 2020; Monty et al. 2020; Yuan et al. 2020). Cordoni et al. (2021) find that this $\alpha$-abundances pattern span a metallicity range from $-3.6<[\mathrm{Fe} / \mathrm{H}]<-2.4$. However, amongst our two other Gaia-Sequoia candidate stars, P133+28 and $\mathrm{P} 182+09$, the former shows low $[\mathrm{Mg} / \mathrm{Fe}]$ and $[\mathrm{Ca} / \mathrm{Fe}]$, whereas the latter has solar-like $[\mathrm{Mg} / \mathrm{Fe}]$ and enriched $[\mathrm{Ca} / \mathrm{Fe}]$, such that $\mathrm{P} 182+09$ has $[\mathrm{Mg} / \mathrm{Ca}]=-0.8$. Monty et al. (2020) also found one Gaia-Sequoia candidate (G184-007) with low $[\mathrm{Mg} / \mathrm{Fe}]$ and $[\mathrm{Ca} / \mathrm{Fe}]$ though at a much higher metallicity $([\mathrm{Fe} / \mathrm{H}]=-1.67$ for G184007 versus $[\mathrm{Fe} / \mathrm{H}]=-2.84$ and -2.93 for $\mathrm{P} 133+28$ and $\mathrm{P} 182+09$, respectively). If the location of the 'knee' in the $[\mathrm{Mg} / \mathrm{Fe}]$ versus $[\mathrm{Fe} / \mathrm{H}]$ plane, as identified by Monty et al. (2020) at $[\mathrm{Fe} / \mathrm{H}]=-1.6$ or -2.3 , is an accurate reflection of the chemical evolution of GaiaSequoia, then our low $[\mathrm{Mg} / \mathrm{Fe}]$ ratios in $\mathrm{P} 133+28$ and $\mathrm{P} 182+09$ would be difficult to reconcile. Either they are not Gaia-Sequoia members, or alternatively, if Gaia-Sequoia had episodes of star formation that stochastically enriched its interstellar medium, there could be a range in elements like Mg. Similar abundance patterns have been seen in EMP stars in dwarf galaxies, such as Carina and Sextans (De Boer et al. 2014; Norris et al. 2017; Lucchesi et al. 2020; Theler et al. 2020).

Furthermore, two of our Gaia-Sequoia candidates (P021+32 and $\mathrm{P} 133+28$ ) may be enriched in potassium (see Fig. B1). An anticorrelation of stars that are Mg-poor but K-rich was discovered in the outer globular cluster NGC 2419 (Cohen, Huang \& Kirby 2011; Cohen \& Kirby 2012). This describes P133+28 well, though our Mg abundance for $\mathrm{P} 021+32$ is quite high and would not fit this pattern well. Other elements ( Sc , and to a lesser extent Si and Ca ) also showed variations, such that a more detailed analysis of these two Gaia-Sequoia candidates, especially with broader spectra that can reach more elements, would be interesting.

Finally, one of our new CEMP candidates, P016+28, appears to be dynamically associated with the Gaia-Sequoia event. We note that Yuan et al. 2020 identify one CEMP-no candidate with GaiaSequoia (CS29514-007, from Roederer et al. 2014). CS29514-007 $([\mathrm{Fe} / \mathrm{H}]=-2.8)$ has a similar metallicity to P016+28 $([\mathrm{Fe} / \mathrm{H}]=$ $-2.93 \pm 0.20$ ), but significantly different barium (CS29514-007 has $[\mathrm{Ba} / \mathrm{Fe}] \sim 0$, whereas we find $\mathrm{P} 016+28$ is rich in neutroncapture elements ( $\mathrm{Ba}, \mathrm{La}, \mathrm{Nd}$ ) by $\geq+1.5$; see Appendix B1). It
would be interesting if these two stars probe the most metal-poor regime of their (former) host and could constrain its early chemical evolution.

## 7 CONCLUSIONS

We present detailed spectral analyses for 30 new metal-poor stars found within the Pristine survey and followed up with Gemini GRACES high-resolution spectroscopy. All of these stars were previously observed with INT MRS.
(i) We confirm that 19 of our targets are EMP with $[\mathrm{Fe} / \mathrm{H}]<-3.0$ ( 63 per cent), three of which only have iron upper limits. If we consider their $1 \sigma(\mathrm{Fe})$ errors, then we confirm 24 are EMP stars ( 80 per cent). The most metal-poor star in the sample is $\mathrm{P} 237+12$, with $[\mathrm{Fe} / \mathrm{H}]<-4.26$.
(ii) The INT MRS showed that three of our targets may be carbon enhanced. We find that one is a CEMP-no candidate based on low $[\mathrm{Ba} / \mathrm{Fe}]$ upper limits, while the other two appear to be CEMP-s candidates.
(iii) Three stars ( $\mathrm{P} 184+43, \mathrm{P} 198+08$, and $\mathrm{P} 207+14$ ) are found to be deficient in Ca , yet Mg enriched, yielding $[\mathrm{Mg} / \mathrm{Ca}] \gtrsim+0.8$. This is a rare abundance signature, interpreted as the yields from a small number of SN II that underproduce Ca in explosive alpha-element production compared to Mg from hydrostatic nucleosynthesis.
(iv) Five stars (P184+43, P191+12, P237+12, P244+10, and P339.1+25.5) orbit in the Galactic plane, including the most metalpoor star in our sample ( $\mathrm{P} 237+12$ ). We suggest they were brought in with one or more dwarf galaxies that were building blocks that formed the Galactic plane. As additional support one of these stars (P244+10) has a retrograde planar orbit. This star overlaps in eccentricity and action with the Gaia-Sequoia accreted dwarf galaxy; however, its low energy and low metallicity $([\mathrm{Fe} / \mathrm{H}]=-3.5 \pm 0.3)$ are in better agreement with the Thamnos event.
(v) Five stars are new candidates for the accreted stellar population from Gaia-Sequoia, based on their positions in the eccentricity-action-energy phase space ( $\mathrm{P} 016+28, \mathrm{P} 021+32$, $\mathrm{P} 031+27, \mathrm{P} 133+28$, and $\mathrm{P} 182+09$ ). We find that $\mathrm{P} 016+28$, $\mathrm{P} 021+32, \mathrm{P} 031+27$ are enhanced in Mg and Ca , consistent with previous chemical studies of the Sequoia population; however, $\mathrm{P} 133+28$ and $\mathrm{P} 182+09$ both show low $[\mathrm{Mg} / \mathrm{Fe}]$. This could imply these stars are non-members; however, it is also possible that GaiaSequoia had episodes of star formation that stochastically enriched its interstellar medium. These two stars show different $[\mathrm{Ca} / \mathrm{Fe}]$ from the rest of the population (one is Ca-poor and the other Ca-rich), and two Gaia-Sequoia members P133+28 and P021+32) are enriched in K. Also, we have found that P016+28 is a CEMP-s candidate, showing enhancements of $\mathrm{C}, \mathrm{Ba}, \mathrm{La}$, and Nd .

This work shows that the Pristine survey has been highly successful in finding new and interesting metal-poor stars, especially when combined with Gaia DR2 parallaxes and proper motions for testing stellar population and galaxy formation models. We look forward to the upcoming large spectroscopic surveys that will be able to tackle statistically large samples of these metal-poor stars for a detailed chemo-dynamical evaluation of the metal-poor components of our Galaxy.

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## DATA AVAILABILITY

The data underlying this article and online supplementary material will be shared on reasonable requests to the corresponding author.

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## SUPPORTING INFORMATION

Supplementary data are available at MNRAS online.
Table 1. Stellar identifications, positions, and CaHK and SDSS dereddened magnitudes for our GRACES targets, selected from the Pristine survey (Starkenburg et al. 2017a; Aguado et al. 2019).
Table 2. Stellar parameters from the Pristine photometric survey (PRIS, Starkenburg et al. 2017b) and follow-up medium resolution spectroscopy (MRS) analysed with FERRE Aguado et al. (2019) are shown.
Table 3. Stellar parameters and iron abundances for our GRACES sample.
Table 4. LTE abundances for iron-group and odd-Z elements.
Table 5. LTE abundances for the $\alpha$-elements. Errors represent the total combined systematic error due to the stellar parameters and line-to-line scatter (Table B2).
Table 6. LTE abundances for neutron-capture elements.
Table 7. LTE lithium abundances from the Li doublet at 6707 Å.
Table A1. Sample of the line list and atomic data used in this paper.
Table B1. NLTE Corrections. NLTE deviations were calculated on a line-by-line basis for each star given its line list and stellar parameters; the averaged NLTE correction is given below.
Table B2. Systematic errors for Fe and Mg .
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## APPENDIX A: SPECTRA AND LINE DATA

## A1 The 1D spectra

The reduced 1D spectra for a subset of the stars in this paper (in $T_{\text {eff }}$ and $[\mathrm{Fe} / \mathrm{H}]$ ) are shown in Fig. A1. Only the wavelength region used in this paper for the chemical analysis is shown; a zoomed in region from 470 to 680 nm . Each star and its metallicity are labelled, and the objects are sorted by effective temperature. The Balmer lines ( $\mathrm{H} \alpha$ and $\mathrm{H} \beta$ are clear, as well as the Mgb lines. The atmospheric bands near 5850 and 6300 are clear in most stars, as well as some sky emission lines from an imperfect sky subtraction. These stars were not telluric cleaned due to inconsistent observations of telluric standards.

## A2 Line list

A sample line list is provided in Table A1, including the element, wavelength, excitation potential ( $\chi$ in eV ), and oscillator strengths ( $\log g f)$. The majority of the analysis of our GRACES data was carried out using spectrum syntheses, thus the line abundance from each spectral feature is listed (rather than an equivalent width). These line abundances have been averaged together for the final abundance, per element, per star.


Figure A1. Portion of the 1D spectra for our GRACES data, sorted by temperature. This region was selected for our detailed analyses as it has the highest SNR, is mostly free of telluric and sky lines, and contains spectral lines for many elements of interest.

Table A1. Sample of the line list and atomic data used in this paper. The best 1DLTE synthetic fit abundance per line in each star is listed as $A(X)=$ $\log [N(X) / N(H)]+12$. Shortened target names are used (see Table 2). The full table is available as online supplementary material.

| Elem | $\lambda$ <br> $(\AA)$ | $\chi$ <br> $(\mathrm{eV})$ | $\log (g f)$ | P 016 <br> +28 | P237 <br> +12 | P 247 <br> +06 |
| :--- | :--- | :--- | :--- | ---: | ---: | ---: |
| Fe I | 5328.039 | 0.914 | -1.47 | 4.70 | $<3.37$ | 4.00 |
| Fe II | 5169.028 | 2.891 | -0.87 | 4.75 | $<3.27$ | 4.20 |
| Na I | 5889.951 | 0.0 | 0.12 | 3.71 | $<1.98$ | 2.94 |
| Mg I | 5172.684 | 2.71 | -0.4 | 5.22 | 3.39 | 4.70 |
| Ba II | 6496.91 | 0.604 | -0.38 | 1.40 | $<-0.68$ | -1.92 |
| Eu II | 6645.072 | 1.379 | -0.517 | $<-0.66$ | $<0.01$ | $<-1.33$ |

## APPENDIX B: SYSTEMATICS AND UPPER LIMITS

## B1 The world of (mostly) upper limits.

In higher metallicity stars, several spectral lines of additional elements exist in the GRACES wavelength region. We examine those regions, to provide additional abundances, but mostly upper limits only. The upper limits in this section do not provide useful constrains for nucleosynthetic interpretations, thus they are collected here in an Appendix, for completeness. These elements include the oddelements ( $\mathrm{K}, \mathrm{Sc}, \mathrm{Mn}, \mathrm{Cu}$ ), also Zn , and the neutron capture elements (Y, Zr, La, Nd); see Fig. B1. As the analyses of these lines has been carried out with spectrum syntheses, then isotopic splitting and/or hyperfine structure has been taken into account using the atomic data in linemake (see main text). The upper limits on $\mathrm{Zn}, \mathrm{Y}, \mathrm{Nd}$, and La are in good agreement with the distribution of $[\mathrm{X} / \mathrm{Fe}]$ in metal-poor stars in the Galaxy. One r-process rich star (P016+28; CEMP-s, discussed in the main text) also has enriched (and therefore measurable) La and Nd abundances.

Sc and K abundances were measured in 1 and 5 targets, respectively. It is unclear if the increase in K with decreasing metallicity is astrophysically significant, as the majority of our targets can only provide upper limits and the uncertainties for the few stars where we could make measurements are large.

Oxygen is included here in the appendix since we could analyse the strong $\lambda 7770$ triplet (see Fig. B2); however, these lines are known to form over many layers in a stellar atmosphere, being very sensitive to small uncertainties in stellar parameters, and especially NLTE corrections. They are also in a region with some telluric contamination. The O abundances for six stars where we could measure the OI triplet are shown in Fig. B3.

## B2 NLTE corrections

NLTE corrections to our 1DLTE abundances for some elements have been determined from the MPIA data base (see main text). The averaged NLTE correction per element per star is shown in Table B1.

## B3 Systematic error tables

Systematic errors have been calculated for all elements with abundance determinations (i.e. not those with only upper limits). These include uncertainties due to errors in the temperature, gravity, and metallicity estimates (see Table 3). An example is shown in Table B2. $\Delta \mathrm{T}, \Delta \mathrm{g}$, and $\Delta \mathrm{Fe}$ are the corresponding systematic errors in the element abundances due to the stellar parameters, while $\sigma$ is the line-to-line scatter for a given element. When the number of lines $N_{X}>5$ for species X , then $\sigma$ is reduced by $1 / \sqrt{N_{X}}$. These errors are combined in quadrature for a conservative total error, $\Delta$, which is then adopted for our plots and chemical abundance discussions.


Figure B1. Elemental abundances for the chemical elements with mainly upper limit in our analysis. See Fig. 8 for more information on the labels and Galactic comparison stars.


Figure B2. Synthesized O I lines for P207+14 (brown, bottom), P184+43 (blue, middle), and P192+13 (red, top). Labels the same as in Fig. 8.

$[\mathrm{Fe} / \mathrm{H}]_{\text {NLTE }}$

Figure B3. NLTE abundances for oxygen and iron, $[\mathrm{O} / / \mathrm{Fe}]$ versus $[\mathrm{Fe} / \mathrm{H}]$. Labels the same as in Fig. 8.
Table B1. NLTE Corrections. NLTE deviations were calculated on a line-by-line basis for each star given its line list and stellar parameters; the averaged NLTE correction is given below. Corrections in oxygen are from Sitnova, Mashonkina \& Ryabchikova (2013), Na from Lind et al. (2011), Mg from Bergemann et al. (2017), Ca from Mashonkina, Korn \& Przybilla (2007), Ti from Bergemann (2011), and Cr from Bergemann \& Cescutti (2010). The full table is available as online supplementary material.

| ID | $\Delta[\mathrm{O} \mathrm{I} / \mathrm{H}]$ | $\Delta[\mathrm{Na} \mathrm{I} / \mathrm{H}]$ | $\Delta[\mathrm{Mg} \mathrm{I} / \mathrm{H}]$ | $\Delta[\mathrm{Ca} \mathrm{I} / \mathrm{H}]$ | $\Delta[\mathrm{Ti} \mathrm{I} / \mathrm{H}]$ | $\Delta[\mathrm{Ti} \mathrm{II} / \mathrm{H}]$ | $\Delta[\mathrm{Cr} \mathrm{I} / \mathrm{H}]$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P} 008.5638+28.1855$ |  | $-0.17(1)$ | $0.05(4)$ | $0.13(3)$ | $0.35(2)$ | $0.04(2)$ | $0.45(1)$ |
| $\mathrm{P} 016.2907+28.3957$ |  | $-0.40(2)$ | $0.16(4)$ | $0.26(6)$ | $0.62(3)$ | $0.04(6)$ | $0.62(4)$ |
| P021.6938+29.0039 |  | $-0.06(2)$ | $0.14(2)$ | $0.21(3)$ |  | $0.04(2)$ | $0.61(1)$ |
| P021.9576+32.4131 |  | $-0.18(2)$ | $0.20(3)$ | $0.31(6)$ | $0.59(2)$ | $0.06(1)$ | $0.69(3)$ |
| P031.9938+27.7363 |  | $-0.13(1)$ | $0.12(3)$ | $0.25(3)$ |  | $0.05(2)$ | $0.57(1)$ |

Table B2. Systematic errors for Fe and Mg . The $\sigma$ represents the line-to-line scatter for a given element, added in quadrature with errors imposed by the continuum placement for each line used. When the number of lines $N_{X}>5$ for species X , then $\sigma$ is reduced by $1 / \sqrt{N_{X}}$. $\Delta \mathrm{T}$ and $\Delta \mathrm{g}$ are the systematic errors in the stellar parameters $T_{\text {eff }}$ and $\log g$, while $\Delta \mathrm{Fe}$ is due to the uncertainty in $[\mathrm{Fe} / \mathrm{H}]$ (see Table 3). $\Delta$ is the total combined error of these added in quadrature. Additional tables for all other elements in this paper are available as online supplementary material.

| ID | [ $\mathrm{Fe} \mathrm{I/H]}$ |  |  |  |  | [ Fe II/H] |  |  |  |  | [ $\mathrm{Mg} \mathrm{I} / \mathrm{H}$ ] |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\sigma$ | $\Delta \mathrm{T}$ | $\Delta \mathrm{g}$ | $\Delta \mathrm{Fe}$ | $\Delta$ | $\sigma$ | $\Delta \mathrm{T}$ | $\Delta \mathrm{g}$ | $\Delta \mathrm{Fe}$ | $\Delta$ | $\sigma$ | $\Delta \mathrm{T}$ | $\Delta \mathrm{g}$ | $\Delta \mathrm{Fe}$ | $\Delta$ |
| P008.5638+28.1855 | 0.05 | $-0.15$ | $-0.12$ | $-0.11$ | 0.23 | 0.12 | 0.01 | 0.01 | 0.02 | 0.12 | 0.05 | $-0.06$ | $-0.03$ | -0.04 | 0.09 |
| P016.2907+28.3957 | 0.04 | 0.13 | 0.16 | 0.16 | 0.26 | 0.09 | 0.16 | 0.13 | 0.16 | 0.28 | 0.07 | 0.28 | 0.31 | 0.29 | 0.51 |
| P021.6938 + 29.0039 | 0.06 | -0.62 | -0.51 | $-0.50$ | 0.95 | 0.17 | -0.23 | $-0.28$ | $-0.20$ | 0.45 | 0.13 | -0.27 | -0.22 | -0.21 | 0.42 |
| P021.9576+32.4131 | 0.05 | 0.05 | 0.07 | 0.07 | 0.13 | 0.07 | -0.06 | -0.07 | -0.04 | 0.13 | 0.07 | 0.12 | 0.12 | 0.08 | 0.19 |
| P031.9938 + 27.7363 | 0.06 | $-0.48$ | $-0.43$ | $-0.42$ | 0.78 | 0.09 | $-0.15$ | $-0.15$ | $-0.13$ | 0.27 | 0.10 | $-0.11$ | $-0.10$ | $-0.09$ | 0.20 |

## APPENDIX C: ORBITAL PARAMETERS TABLE

Gaia DR2 proper motions and parallax distances have been used with our GRACES radial velocities to determine the orbital parameters
and action vectors for stars in this paper (see the main text). Results are shown here in Table C1, where actions and energies have been normalized to the Sun for brevity ( $J_{\phi \odot}=2009.92 \mathrm{kpc} \mathrm{km} \mathrm{s}^{-1}, J_{z \odot}=$ $0.35 \mathrm{kpc} \mathrm{km} \mathrm{s}^{-1}, E_{\odot}=-64943.61 \mathrm{~km}^{2} \mathrm{~s}^{-2}$; Sestito et al. 2019).
Table C1. Gaia DR2 proper motions, parallaxes, orbital parameters, and action vectors for stars in this paper, based on orbits calculated using the $1 / \sigma$ distances. Actions and energies have been normalized to the Sun for brevity ( $J_{\phi \odot}=2009.92 \mathrm{kpc} \mathrm{km} \mathrm{s}^{-1}, J_{z \odot}=0.35 \mathrm{kpc} \mathrm{km} \mathrm{s}^{-1}, E_{\odot}=-64943.61 \mathrm{~km}^{2} \mathrm{~s}^{-2}$; Sestito et al. 2019).

| ID | $\begin{gathered} \mu_{\alpha} \\ \left(\mu \mathrm{as}_{\mathrm{yr}}{ }^{-1}\right) \end{gathered}$ | $\begin{gathered} \mu_{\delta} \\ \left(\mu \mathrm{as}_{\mathrm{yr}}{ }^{-1}\right) \end{gathered}$ | $\begin{gathered} \sigma \\ (\mu \mathrm{as}) \end{gathered}$ | $\begin{gathered} r_{\text {peri }} \\ (\mathrm{kpc}) \end{gathered}$ | $\begin{gathered} r_{\mathrm{apo}} \\ (\mathrm{kpc}) \end{gathered}$ | Eccentricity | $\begin{gathered} \|\mathrm{Z}\|_{\max } \\ (\mathrm{kpc}) \end{gathered}$ | $J_{\phi} / J_{\phi \odot}$ | $J_{z} / J_{z \odot}$ | $E / E_{\odot}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| P008.5638+28.1855 | $44.54 \pm 0.07$ | $12.19 \pm 0.07$ | $0.8800 \pm 0.0436$ | $6.0 \pm 0.1$ | $11.7 \pm 0.7$ | $0.32 \pm 0.02$ | $10.9 \pm 0.6$ | $-0.27 \pm 0.02$ | $3113.98 \pm 11.60$ | $0.803 \pm-0.028$ |
| P016.2907+28.3957 | $3.66 \pm 0.06$ | $-1.95 \pm 0.05$ | $0.0840 \pm 0.0365$ | $5.7 \pm 2.1$ | $29.3 \pm 7.0$ | $0.68 \pm 0.03$ | $20.3 \pm 1.4$ | $-0.70 \pm 0.40$ | $2061.04 \pm 572.95$ | $0.391 \pm-0.117$ |
| P021.6938+29.0039 | $13.42 \pm 0.09$ | $4.54 \pm 0.07$ | $0.3643 \pm 0.0452$ | $4.8 \pm 0.1$ | $11.6 \pm 0.9$ | $0.42 \pm 0.03$ | $8.4 \pm 1.6$ | $0.45 \pm 0.05$ | $1532.21 \pm 403.68$ | $0.849 \pm-0.038$ |
| P021.9576+32.4131 | $6.83 \pm 0.09$ | $-4.16 \pm 0.08$ | $0.1301 \pm 0.0519$ | $3.3 \pm 3.3$ | $13.2 \pm 3.1$ | $0.67 \pm 0.21$ | $4.0 \pm 1.2$ | $-0.39 \pm 0.48$ | $254.75 \pm 112.52$ | $0.860 \pm-0.159$ |
| P031.9938+27.7363 | $12.91 \pm 0.09$ | $-26.81 \pm 0.10$ | $0.4654 \pm 0.0553$ | $2.5 \pm 1.1$ | $11.8 \pm 0.6$ | $0.66 \pm 0.11$ | $3.5 \pm 1.4$ | $-0.42 \pm 0.12$ | $307.35 \pm 178.99$ | $0.922 \pm-0.062$ |
| P113.8240+45.1863 | $-33.61 \pm 0.07$ | $-23.27 \pm 0.05$ | $0.7620 \pm 0.0506$ | $9.0 \pm 0.1$ | $20.9 \pm 2.1$ | $0.40 \pm 0.04$ | $17.9 \pm 2.3$ | $0.64 \pm 0.02$ | $3755.69 \pm 437.76$ | $0.496 \pm-0.046$ |
| P116.9657+33.5337 | $0.94 \pm 0.07$ | $-11.58 \pm 0.04$ | $0.1269 \pm 0.0452$ | $5.7 \pm 3.9$ | $45.4 \pm 80.6$ | $0.76 \pm 0.09$ | $24.0 \pm 30.6$ | $-0.77 \pm 0.79$ | $1440.86 \pm 297.30$ | $0.325 \pm-0.292$ |
| P133.0683+28.7219 | $-0.73 \pm 0.08$ | $-11.92 \pm 0.05$ | $0.1443 \pm 0.0514$ | $5.7 \pm 4.9$ | $16.4 \pm 14.8$ | $0.55 \pm 0.25$ | $6.9 \pm 7.0$ | $-0.61 \pm 0.66$ | $635.43 \pm 383.09$ | $0.748 \pm-0.252$ |
| P180.3206+02.5788 | $-0.05 \pm 0.10$ | $-11.36 \pm 0.06$ | $0.1616 \pm 0.0608$ | $4.4 \pm 1.1$ | $59.9 \pm 78.7$ | $0.82 \pm 0.10$ | $51.2 \pm 58.1$ | $0.25 \pm 0.37$ | $3365.47 \pm 795.44$ | $0.136 \pm-0.228$ |
| P182.5866+09.8940 | $-76.32 \pm 0.09$ | $-46.52 \pm 0.06$ | $0.7807 \pm 0.0476$ | $4.5 \pm 0.4$ | $34.2 \pm 12.0$ | $0.75 \pm 0.05$ | $10.5 \pm 4.6$ | $-0.87 \pm 0.10$ | $372.56 \pm 89.22$ | $0.339 \pm-0.162$ |
| P184.1783+01.0664 | $-1.92 \pm 0.12$ | $-6.88 \pm 0.07$ | $0.2203 \pm 0.0587$ | $8.3 \pm 0.1$ | $27.3 \pm 0.8$ | $0.53 \pm 0.01$ | $26.2 \pm 0.8$ | $-0.30 \pm 0.12$ | $5894.07 \pm 637.49$ | $0.383 \pm-0.014$ |
| P184.2997+43.4721 | $-19.30 \pm 0.05$ | $-37.97 \pm 0.06$ | $1.4142 \pm 0.0506$ | $1.8 \pm 0.1$ | $8.5 \pm 0.0$ | $0.64 \pm 0.02$ | $2.5 \pm 0.2$ | $0.31 \pm 0.02$ | $245.74 \pm 4.87$ | $1.140 \pm-0.005$ |
| P188.0262+00.2055 | $25.18 \pm 0.10$ | $-35.02 \pm 0.07$ | $0.7269 \pm 0.0441$ | $1.6 \pm 0.2$ | $21.4 \pm 1.9$ | $0.86 \pm 0.02$ | $4.1 \pm 0.4$ | $0.34 \pm 0.03$ | $145.12 \pm 5.97$ | $0.600 \pm-0.051$ |
| P191.8535+12.0508 | $-11.78 \pm 0.08$ | $-0.00 \pm 0.05$ | $0.4436 \pm 0.0362$ | $4.7 \pm 0.2$ | $9.5 \pm 0.2$ | $0.34 \pm 0.03$ | $2.5 \pm 0.2$ | $0.64 \pm 0.02$ | $233.92 \pm 21.55$ | $0.958 \pm-0.003$ |
| P192.3242+13.3956 | $-12.93 \pm 0.09$ | $-1.36 \pm 0.06$ | $0.2900 \pm 0.0435$ | $2.6 \pm 0.4$ | $11.1 \pm 0.8$ | $0.62 \pm 0.07$ | $4.2 \pm 0.7$ | $0.42 \pm 0.05$ | $392.90 \pm 52.80$ | $0.946 \pm-0.031$ |
| P194.9935+12.0585 | $-32.89 \pm 0.07$ | $-27.50 \pm 0.05$ | $0.8620 \pm 0.0335$ | $0.6 \pm 0.2$ | $8.2 \pm 0.4$ | $0.86 \pm 0.04$ | $3.8 \pm 0.4$ | $0.10 \pm 0.03$ | $349.95 \pm 37.17$ | $1.183 \pm-0.004$ |
| P198.0851+8.9428 | $-0.22 \pm 0.10$ | $-0.72 \pm 0.07$ | $-0.0585 \pm 0.0555$ | $23.9 \pm 28.5$ | $86.0 \pm 247.6$ | $0.33 \pm 0.20$ | $55.6 \pm 85.7$ | $-0.06 \pm 0.56$ | $15444.69 \pm 23639.44$ | $0.204 \pm-0.445$ |
| P207.3454+14.1268 | $-6.03 \pm 0.14$ | $-16.95 \pm 0.10$ | $0.5402 \pm 0.0814$ | $2.6 \pm 0.6$ | $8.0 \pm 0.1$ | $0.52 \pm 0.09$ | $3.6 \pm 0.4$ | $0.35 \pm 0.08$ | $485.66 \pm 64.42$ | $1.124 \pm-0.021$ |
| P207.9290+03.2767 | $-27.35 \pm 0.07$ | $-9.93 \pm 0.05$ | $0.4321 \pm 0.0411$ | $0.9 \pm 0.4$ | $11.6 \pm 65.9$ | $0.83 \pm 0.07$ | $8.4 \pm 59.7$ | $-0.12 \pm 0.07$ | $813.71 \pm 58.63$ | $1.065 \pm-0.043$ |
| P209.0986+9.8244 | $-20.90 \pm 0.08$ | $-1.71 \pm 0.06$ | $0.3218 \pm 0.0435$ | $1.5 \pm 0.4$ | $14.1 \pm 2.0$ | $0.80 \pm 0.07$ | $10.4 \pm 3.3$ | $0.19 \pm 0.08$ | $1086.27 \pm 316.95$ | $0.825 \pm-0.073$ |
| P224.8444+02.3043 | $-2.31 \pm 0.06$ | $-0.10 \pm 0.06$ | $0.0194 \pm 0.0397$ | $13.4 \pm 13.6$ | $331.6 \pm 662.9$ | $0.76 \pm 0.15$ | $239.9 \pm 476.0$ | $0.57 \pm 1.10$ | $11107.29 \pm 13163.12$ | $-0.105 \pm-0.728$ |
| P236.9604+11.6155 | $-0.86 \pm 0.09$ | $-3.12 \pm 0.14$ | $0.1705 \pm 0.0599$ | $4.1 \pm 0.6$ | $6.3 \pm 0.3$ | $0.21 \pm 0.06$ | $3.9 \pm 1.0$ | $0.38 \pm 0.11$ | $883.84 \pm 371.10$ | $1.147 \pm-0.035$ |
| P237.8589+12.5660 | $-5.94 \pm 0.06$ | $-7.86 \pm 0.05$ | $0.2971 \pm 0.0410$ | $2.1 \pm 0.4$ | $6.6 \pm 0.1$ | $0.52 \pm 0.07$ | $2.5 \pm 0.4$ | $0.30 \pm 0.06$ | $328.14 \pm 71.82$ | $1.268 \pm-0.026$ |
| P244.8986+10.9310 | $-16.05 \pm 0.06$ | $-12.30 \pm 0.04$ | $0.3805 \pm 0.0588$ | $1.1 \pm 0.6$ | $7.9 \pm 14.5$ | $0.74 \pm 0.14$ | $2.3 \pm 6.0$ | $-0.17 \pm 0.09$ | $209.31 \pm 17.05$ | $1.291 \pm-0.013$ |
| P246.9682+08.5360 | $-6.41 \pm 0.05$ | $12.37 \pm 0.04$ | $0.2747 \pm 0.0392$ | $3.7 \pm 0.4$ | $28.7 \pm 6.8$ | $0.76 \pm 0.07$ | $9.5 \pm 3.5$ | $0.69 \pm 0.04$ | $398.12 \pm 84.91$ | $0.424 \pm-0.118$ |
| P247.2115+06.6348 | $-1.27 \pm 0.06$ | $-2.96 \pm 0.03$ | $0.0830 \pm 0.0410$ | $2.6 \pm 0.9$ | $7.9 \pm 2.6$ | $0.47 \pm 0.21$ | $7.2 \pm 1.9$ | $-0.02 \pm 0.15$ | $1900.73 \pm 456.17$ | $1.101 \pm-0.116$ |
| P257.3131+12.8939 | $2.14 \pm 0.07$ | $-1.62 \pm 0.06$ | $0.0565 \pm 0.0370$ | $8.4 \pm 3.5$ | $23.5 \pm 32.4$ | $0.37 \pm 0.12$ | $22.7 \pm 32.3$ | $-0.06 \pm 0.26$ | $5781.40 \pm 3366.22$ | $0.610 \pm-0.363$ |
| P258.1048+40.5405 | $0.83 \pm 0.06$ | $1.07 \pm 0.08$ | $0.3890 \pm 0.0364$ | $3.0 \pm 0.0$ | $8.3 \pm 0.0$ | $0.47 \pm 0.00$ | $4.7 \pm 0.2$ | $0.37 \pm 0.01$ | $736.29 \pm 55.41$ | $1.076 \pm-0.005$ |
| P339.1417+25.5503 | $33.41 \pm 0.06$ | $11.41 \pm 0.05$ | $0.9142 \pm 0.0342$ | $2.6 \pm 0.1$ | $12.8 \pm 0.4$ | $0.66 \pm 0.02$ | $0.8 \pm 0.0$ | $0.50 \pm 0.01$ | $22.68 \pm 0.72$ | $0.883 \pm-0.014$ |
| P339.3203+25.8764 | $20.30 \pm 0.08$ | $2.16 \pm 0.06$ | $0.2368 \pm 0.0438$ | $2.0 \pm 1.1$ | $46.0 \pm 76.7$ | $0.90 \pm 0.02$ | $9.4 \pm 19.7$ | $-0.45 \pm 0.22$ | $157.15 \pm 57.13$ | $0.337 \pm-0.308$ |


[^0]:    * E-mail: clkielty@uvic.ca

[^1]:    ${ }^{1}$ We adopt the square bracket notation for chemical abundances relative to the Sun, such that $[\mathrm{X} / \mathrm{Y}]=\log (\mathrm{X} / \mathrm{Y})_{\odot}-\log (\mathrm{X} / \mathrm{Y})_{*}$, where X and Y are column densities for two given elements.

[^2]:    ${ }^{2}$ We note that the Pristine survey has more than doubled its survey area since its initial footprint.

[^3]:    ${ }^{3}$ Gaia DR2 extinction values (v 3.4) at http://stev.oapd.inaf.it/cgi-bin/cmd.
    ${ }^{4}$ IAU 2015 Resolution B2 on the bolometric magnitude scale available at https://www.iau.org/static/resolutions/IAU2015_English.pdf.

[^4]:    ${ }^{5}$ MARCS model atmospheres at https://marcs.astro.uu.se/.
    ${ }^{6}$ linemake contains laboratory atomic data (transition probabilities, hyperfine and isotopic substructures) published by the Wisconsin Atomic Physics and the Old Dominion Molecular Physics groups. These lists and accompanying line list assembly software have been developed by C. Sneden and are curated by V. Placco at https://github.com/vmplacco/linemake.

[^5]:    ${ }^{8}$ MPIA NLTE corrections are available at http://nlte.mpia.de.

[^6]:    ${ }^{9}$ This potential is three-component model composed of a power law, exponentially cut-off bulge, Miyamoto Nagai Potential disc, and Navarro, Frenk, \& White (1997) dark matter halo.

[^7]:    ${ }^{10} \mathrm{http}: / /$ www.astropy.org

