Correlation between technetium and lithium in a sample of oxygen-rich AGB variables

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ABSTRACT

Context. The elements technetium and lithium are two important indicators of internal nucleosynthesis and mixing in late-type stars. Studying their occurrence and abundance can give deep insight into the structure and evolution in the late phases of the stellar life cycle.

Aims. The aims of this paper are: 1) to revisit the Tc content of a sample of oxygen-rich (M-type) asymptotic giant branch (AGB) variables and 2) to increase the number of such stars for which the Li abundance has been measured to provide constraints on the theoretical models of extra-mixing processes.

Methods. To this end, we analysed high-resolution spectra of 18 sample stars for the presence of absorption lines of Tc and Li. The abundance of the latter was determined by comparing the observed spectra to hydrostatic MARCS model spectra. Bolometric magnitudes were established from near-IR photometry and pulsation periods.

Results. We correct the classification with respect to the presence of Tc for a number of stars. We reclassify the star V441 Cyg as Tc-rich, and the unusual Mira star R Hya, as well as W Eri, as Tc-poor. The abundance of Li, or an upper limit to it, was determined for all of the sample stars. In all stars with Tc we also detected Li. Most of them have a Li content slightly below the solar photospheric value, except for V441 Cyg, which is super-Li rich with ~1000 times the solar abundance. We also found that, similar to Tc, a lower luminosity limit seems to exist for the presence of Li.

Conclusions. We conclude that the higher Li abundance found in the cooler and higher luminosity objects could stem from a Li production mechanism operating on the thermally pulsing AGB. The stellar mass might have a crucial influence on this (extra mixing) production mechanism. Our findings for R Hya and V441 Cyg have some important consequences for these intriguing objects. It was speculated that the declining pulsation period of R Hya is caused by a recent thermal pulse (TP). While not detecting Tc does not rule out a TP, it indicates that the TPs are not strong enough to drive 3DUP in R Hya. The pieces of evidence concerning the mass of V441 Cyg are not entirely conclusive. It could either be a low-mass, intrinsic S-star that produced its large amount of Li by extra-mixing processes, or an intermediate-mass star (M ≳ 4 M⊙) undergoing Li production via hot bottom burning.

Key words. stars: AGB and post-AGB – stars: abundances – stars: evolution – stars: interiors – stars: individual: R Hya – stars: individual: V441 Cyg

1. Introduction

The asymptotic giant branch (AGB) phase is the last stage of evolution with nuclear burning for stars of low and intermediate mass (1–8 M⊙). In the most luminous part of the AGB, the behaviour of an AGB star is characterised by the so-called thermal pulses (TP), thermal instabilities of the He shell accompanied by changes in luminosity, temperature, pulsation period, and internal structure (see e.g. Busso et al. 1999; Herwig 2005, for reviews). Between the repeated events of explosive He-burning, heavy elements can be produced via the “slow neutron capture process” (s-process, see e.g. Wallerstein et al. 1997) in the region between the hydrogen- and the helium-burning shells. The processed material may then be brought to the stellar surface by the convective envelope that temporarily extends to these very deep layers. This mixing event is called the third dredge-up (3DUP) and is the cause of the eventual metamorphosis of an oxygen-rich M-star into a carbon-rich C-star.

The element technetium (Tc, Z = 43) is a well-established diagnostic tool in the study of the thermally pulsing AGB (TP-AGB) phase. Because of the short half life time of the longest lived Tc isotope produced in the s-process (99Tc, \( \tau_{1/2} = 2.1 \times 10^5 \) yr), any Tc that is detected in the star’s atmosphere must have been produced in-situ. This requirement has been used to study the evolution of AGB stars ever since the pioneering discovery of Tc absorption lines in the spectra of late type giants by Merrill (1952b). Several classes of objects have been investigated for the presence of Tc in the past (e.g. Dominy & Wallerstein 1986; Little et al. 1987; Van Eck & Jorissen 1999).

A key question in this research is if and when in the evolution on the AGB, in terms of luminosity, the 3DUP sets in. This question was addressed by Lebzelter & Hron (1999, 2003) for a sample of solar-neighborhood semi-regular pulsating AGB stars and for a larger sample of Galactic disk AGB stars, including several Mira variables. Recently, Uttenthaler et al. (2007a) has investigated a sample of Galactic bulge AGB variables, for which...
the distance and hence luminosity is more precisely known than for their Galactic disk counterparts. The general conclusion of these works is that the lower luminosity limit for 3DUP to set in, as predicted by theoretical evolutionary models of the AGB, is consistent with the lowest luminosity Tc-rich stars. However, being above this limit is not sufficient for a star to have Tc in its atmosphere (Lebzelter & Hron 2003; Uttenthaler et al. 2007a).

In the present paper we revisit the Tc content of a sample of oxygen-rich AGB stars, with important consequences for a few individual stars.

The element lithium (Li, $Z = 3$) is very fragile and temperature-sensitive. Once it is mixed into stellar layers with temperatures exceeding $3 \times 10^6$ K, it is destroyed via proton captures to form helium. Its fragility makes Li an important diagnostic tool for stellar evolution (Rebolo 1991), and also has a high significance in the determination of cosmological parameters (Spite & Spite 1982; Korn et al. 2006). The standard model (e.g. Michaud & Charbonneau 1991) predicts a strong reduction in the Li surface abundance below the first dredge up to values $\log \epsilon (\text{Li}) < 1.5$, or even less if depletion effects on the main sequence are considered. Most giants for which a Li abundance has been determined (see a summary by Michaud & Charbonneau 1991) agree with this result.

Despite its fragility, Li can be produced rather than destroyed under certain condition in stars via the so-called Cameron-Fowler or $^7$Be-transport mechanism ($^4\text{He}(\alpha, \gamma)^7\text{Be}(e^-, \gamma)^7\text{Li}$; Cameron & Fowler 1971). The production of Li is always connected to mixing mechanisms at or below the bottom of the convective envelope, and requires $^3$He to be present in the stellar atmosphere. One stage in stellar evolution where Li production occurs is the luminosity bump of the red giant branch (RGB) when the H-burning shell erases the molecular weight discontinuity left behind by the first dredge up. A small fraction of giants in this phase are known to be very Li-rich (de la Reza et al. 1997; Charbonnel & Balachandran 2000). The mixing process below the convective envelope has been named extra-mixing or cool bottom processing (CBP; Wasserburg et al. 1995). Its effects are also reflected in the carbon isotopic ratio measured from the spectra of giant stars (Gilroy & Brown 1991), as well as in other isotopic ratios measured in meteoritic pre-solar grains of RGB or AGB origin (Nollet et al. 2003).

The physical cause of the extra-mixing below the convective envelope is hitherto unknown. Eggleton et al. (2006), on the basis of a 3D simulation, find that Rayleigh-Taylor instabilities below the convective envelope can develop from the inversion of the mean molecular weight gradient induced by $^3$He burning. Alternatively, Charbonnel & Zahn (2007) suggest that the double-diffusive mechanism called “thermohaline instability” should be at play. In principle, both these phenomena might also occur on the AGB, though detailed models are just emerging (Cantiello & Langer 2008). Finally, Busso et al. (2007) explore the possibility that circulation of partially processed matter can be accounted for by the magnetic buoyancy induced by a stellar dynamo operating on the RGB and on the AGB. That CBP is probably active on the AGB has recently been demonstrated by Uttenthaler et al. (2007b, 2008).

Among the AGB stars, those with carbon-rich chemistry (C-type, $C/O > 1$ due to the dredge-up of freshly synthesised $^{12}\text{C}$) have been studied more intensively for their Li content than those with oxygen-rich chemistry (M-type, $C/O < 1$) in the past. This may partly have a historical reason because of the early detection of carbon stars with a strong Li resonance line (McKellar 1940; Torres-Peimbert et al. 1964), but also an observational reason. Although the molecular line blanketing mainly caused by the CN and C$_2$ molecules in the spectral vicinity of the Li line in C-stars is strong, that of the TiO molecule in oxygen-rich stars of the same effective temperature is even more severe. The lower limit of Li abundance that can be measured is thus higher for O-rich stars than for C-rich stars. In both cases, a Li abundance determination can only be achieved with the help of spectral synthesis techniques including large numbers of molecular lines. Thus, the counterparts to the catalogues of Li abundance measurements in C-stars (Denn et al. 1991; Boffin et al. 1993) include only relatively small tables of M-type giants (Luck & Lambert 1982). Even in this last work, a number of the observed stars are supergiants and non-variable giants that are rather in the RGB than in the AGB phase of evolution.

There are, however, M-type AGB stars that are known to be very rich in Li. This type of star has been observed in the Magellanic Clouds (Smith et al. 1995), and very recently also in the Milky Way galaxy (Garcia-Hernández et al. 2007). These objects are intermediate-mass ($M \simeq 4 – 8 M_\odot$) TP-AGB stars with a convective envelope penetrating the H-burning shell, thus nuclear-burning occurs partly under convective conditions. This process is generally known as hot bottom burning (HBB; Iben 1973). Under these conditions, carbon, on the one hand, is converted into nitrogen, keeping the C/O ratio below 1, and on the other hand $^7$Li is produced very efficiently by the Cameron-Fowler mechanism. The Li abundance on the surface of HBB stars can be higher than the initial abundance of the interstellar medium from which they formed. We do not intend to deal with this kind of stars in the present paper, but rather with the less massive AGB stars that have not (yet) dredged up enough carbon to have C/O > 1 and are not massive enough to remain O-rich due to the operation of HBB. Nevertheless, by inspecting their bolometric magnitudes, we will check whether our Li-rich objects belong to this group of stars.

The correlation of Tc and Li was studied for a sample of Galactic S-type (C/O $\simeq 1$) stars by Vanture et al. (2007). Uttenthaler et al. (2007b) present Li abundances and their correlation with Tc in a homogeneous sample of O-rich AGB stars located in the Galactic bulge. Here, we want to increase the sample of O-rich AGB stars whose Li abundance has been measured, and study its correlation with the presence of Tc in this type of stars. These measurements will be useful for understanding the interaction between CBP mechanisms and 3DUP in AGB stars.

The paper is structured in the following way. In Sect. 2, the sample and the observations are described and bolometric magnitudes of the sample stars derived; in Sect. 3 we present the analysis of the spectra, results concerning the presence of Tc and the abundance of Li; in Sect. 4 the results are discussed in view of a possible enrichment mechanism of Li, and we take a closer look at two of the sample stars; Sect. 5 summarises the work.

2. Sample and observations

The sample used in this study originally goes back to the search for Tc in Galactic-disk AGB variables in the solar neighbourhood, based on parallaxes measured with the Hipparcos satellite (Lebzelter & Hron 2003). Primary targets for that study were those stars that had not been searched for Tc in the past and objects without a definite decision on their Tc content. The original spectra of that study are reanalysed in this work. An exception here is the star V441 Cyg, whose observation and analysis was initiated by the work of Vanture et al. (2007). A refined method for detecting Tc described in Sect. 3.1 has led to some re-classifications in the sample, which we describe in the present study.
The general appearance of the spectra is dominated by strong bands of the TiO molecule (except of the carbon star TW Hor, of course), clearly verifying their oxygen-rich nature. Some of the stars also show significant bands of the ZrO molecule, indicating that some s-process enrichment has taken place. Only stars that are identified as Tc-rich (see below) also show bands of ZrO, and conversely no Tc-poor star shows any clear sign of ZrO absorption bands. Thus, none of our sample stars is extrinsically enriched in s-process elements by, e.g., mass transfer from a binary companion. However, the absorption bands of the LaO molecule cannot be clearly identified in any of our sample stars, as is sometimes the case in S-type stars.

2.1. Bolometric magnitude determination

To derive absolute $K$-magnitudes, we used the log$P - K$ relations from Ita et al. (1994). For stars classified as Miras we used Ita’s relation C including their separation for targets with $J - K < 1.4$ and $J - K > 1.4$. For semi-regular variables we used sequence B or C'. Naturally, this approach includes some uncertainties. In

**Table 1.** Important characteristics of the sample stars.

| Name   | Sp. type | Var. type | $P$ [days] | $K$ [mag] | $J - K$ [mag] | Ref. | $M_{bol}$ [12–25] |
|--------|----------|-----------|------------|-----------|---------------|------|-------------------|
| U Cet  | M4       | M         | 234.76     | 2.73      | 1.11          | 1    | 4.60              |
| W Cet  | M7       | M         | 351.31     | 2.14      | 1.23          | 1    | 5.07              |
| V441 Cyg | M4S      | SRA       | 288.00     | 1.69      | 1.39          | 3    | 5.56              |
| W Eri  | M7       | M         | 376.63     | 1.78      | 1.42          | 1    | 5.08 - 0.90       |
| S Gru  | M7       | M         | 401.51     | 0.54      | 1.122         | 1    | 8.35 - 0.87       |
| R Hor  | M7       | M         | 407.60     | 0.88      | 1.24          | 1    | 8.35 - 0.92       |
| T Hor  | M5       | M         | 217.60     | 3.34      | 1.13          | 1    | 4.44 - 1.15       |
| TW Hor | C5(N)    | SRB       | 158.00     | 0.19      | 1.46          | 3    | 4.89 - 1.03       |
| R Hya  | M7       | M         | 388.87     | 2.52      | 1.24          | 1    | 5.18 - 1.08       |
| RU Hya | M6       | M         | 331.50     | 1.60      | 1.18          | 1    | 5.07 - 0.74       |
| Y Lib  | M5       | M         | 275.70     | 3.16      | 1.21          | 1    | 4.72 - 0.73       |
| U Mic  | M6       | M         | 334.29     | 1.80      | 1.22          | 1    | 5.09 - 0.69       |
| Y Scl  | M5       | SRB       | 79.36      | 0.35      | 1.27          | 2    | 4.24 - 0.94       |
| T Tuc  | M4       | M         | 250.30     | 2.96      | 1.18          | 2    | 4.58 - 1.08       |
| ER Vir | M4       | SRB       | 55.00      | 1.44      | 1.10          | 4    | 4.03 - 1.41       |
| EV Vir | M4       | SRB       | 120.00     | 1.55      | 1.15          | 4    | 4.10 - 1.34       |
| RS Vir | M7       | M         | 353.35     | 1.15      | 1.31          | 1    | 5.09 - 0.56       |
| S Vir  | M7       | M         | 378.01     | 0.30      | 1.27          | 1    | 3.21 - 0.98       |

References for near infrared data: 1: Catchpole et al. (1979); 2: Fouquet et al. (1992); 3: Kerschbaum & Hron (1994); 4: Kerschbaum (1995).

1 [http://webviz.u-strasbg.fr/viz-bin/VizieR](http://webviz.u-strasbg.fr/viz-bin/VizieR)
their Table 3, Ita et al. (1994) list a typical width of about 0°/2 of these sequences. This, however, is much less than the uncertainties of absolute $K$-magnitudes derived from parallax measurements, which are only available for a small number of stars in our sample. A larger error comes from the uncertainty of attributing a star to a given pulsation sequence. Several authors agree (Wood et al. 1999; Kiss & Bedding 2003; Lebzelter et al. 2005) that large amplitude variables, classically dubbed Miras, are found on sequence C, which corresponds to fundamental mode pulsation. The risk of a misclassification will thus be low for the Miras. It is much more difficult to attribute the inhomogeneous group of the five semi-regular sample stars correctly. They can be located on any sequence from A to C, and the definition of sequences A, B, and C is less clear. As selection criterion, we chose the light amplitude following the extensive analysis of Kiss & Bedding (2003) for the LMC. As on average the amplitude becomes smaller from sequence C′ to A, we attributed the non-Miras V441 Cyg, Y Scl, and EV Vir to sequence C′, TW Hor and ER Vir to sequence B. It is clear that this classification and the derived luminosities have to be taken with some caution. However, because of the small separation of sequences B and C compared to the difference to sequence C, any misclassification will not change the overall result substantially.

To derive absolute bolometric magnitudes from the absolute $K$-magnitudes, we need to apply a bolometric correction. We adopt the approach outlined in Mekul (2005) using two different relations between blackbody fits and $J−K$ depending on the $K−L$ colour. The inclusion of a second near infrared colour allows for much better treatment of stars at the cool end of the AGB than other formulas found in the literature. Details will be given elsewhere (Kerschbaum et al., in preparation).

We used near-infrared colours from the literature (see Table 1). The $J$ and $K$ band magnitudes were taken from Catchpole et al. (1979), Fouquet et al. (1992), Kerschbaum & Hron (1994) and Kerschbaum (1995), respectively. All infrared measurements were converted to the 2MASS system using the relations given in Carpenter (2001). Where more than one measurement was found we used an average value. While the $K$-magnitudes used to derive the absolute bolometric magnitudes were calculated from a star’s period, the bolometric correction is based on individual near infrared measurements and thus affected by stellar variability. The extensive material presented by Catchpole et al. (1979) allow estimation of the typical uncertainty of the bolometric correction from the variations in the $J−K$ colour. For Miras, this uncertainty can be up to 0°/5. In a few cases no $K−L$ colour was available. We then used an average of the two relations. In all cases the error introduced by this is less than 0°/1. Interstellar extinction has not been taken into account for these rather nearby objects.

Recently, Guandalini & Busso (2008) have published a new set of bolometric magnitudes for mass-losing AGB stars. As a result they give a $P−M_{bol}$ relation for Miras (see their Fig. A.1). Using this relation we calculated $M_{bol}$ for the Miras in our sample. In Fig. 1 we compare the results derived from Guandalini & Busso (2008) with our values of the absolute bolometric magnitude for the stars in common, showing good agreement between the two approaches.

3. Analysis and results

3.1. Analysis with respect to Tc

The radial velocity ($rv$) is the first quantity that we determined from our spectra. It was measured from the TiO band head at 705.4 nm using a cross-correlation technique, with a synthetic MARCS spectrum as template. Sect. 3.2.1 gives more details on the used MARCS models. We chose this TiO feature because the SNR of the observed spectra is much higher at this wavelength than at the wavelength of the Tc lines, and the TiO features are formed in the stellar atmosphere close to the atomic (Tc) lines. For TW Hor, the $rv$ was measured from atomic lines in the vicinity of the Tc lines, due to the absence of TiO bands in carbon stars. The precision of the $rv$ measurement is of the order of 1 km s$^{-1}$ or better. The differences to literature values are usually small (a few km s$^{-1}$), and can be fully explained by $rv$ variations caused by the stellar pulsation.

We corrected the observed spectra by the measured $rv$ shift to check them for the Tc lines using the flux-ratio method introduced by Uttenthaler et al. (2007a). In this method, the mean flux in a small wavelength interval around a quasi-contingent point close to the Tc line is divided by the mean flux in a small wavelength interval centred on the Tc line itself. This ratio can be calculated for all of the seven identified Tc lines (398.497, 403.163, 404.911 and 409.567, 423.819, 426.227, and 429.706 nm), and plots of the ratios from different lines clearly separate the Tc-poor from the Tc-rich stars. If the Tc lines are absent, the ratio will be close to 1.0, but significantly more than 1.0 if they are present. Figure 2 shows such a plot for the lines at 423.819 and 426.227 nm for our sample stars; plots involving other Tc lines are very similar and reveal the same Tc-rich stars. The Tc-rich stars that clearly separate from the Tc-poor ones are identified in the plot with their name. The error bars on the symbols in Fig. 2 were directly derived from the SNR of the observed spectra.

We want to briefly explain the advantages of the flux-ratio method over previous methods of deciding on the presence of Tc. The method previously applied uses the central wavelength of the Tc line blend at 429.706 nm (e.g. Little et al. 1987; Van Eck & Jorissen 1999, and references therein). This Tc line is blended with a line of chromium. If Tc is present, the central wavelength is shifted to a somewhat longer wavelength than in the absence of Tc. However, the shift is not large, thus the separation between Tc-poor and Tc-rich stars is not very large either. Every uncertainty of the local wavelength scale has a direct impact on the central wavelength of the blend, thus adding uncertainty to the classification with respect to Tc. Due to the stellar pulsation and the velocity fields in the atmosphere, lines formed at different layers have a slightly different $rv$ shift. This
shift also depends on the pulsation phase at which the observations were done. The result is that intermediate cases are classified as “Tc doubtful”, “Tc possible”, and “Tc probable”. Figure 2 shows that, with our flux-ratio method, the gap between Tc-poor and Tc-rich stars is so large compared to the uncertainty that no room is left for these intermediate cases. The uncertainty of the wavelength scale has only a very small impact on this method. We can thus very clearly decide on “Tc yes” or “Tc no”. We conclude that the flux-ratio method delivers more reliable results than the central wavelength method.

Table 2 summarises the radial velocity shifts measured from the spectra and the updated Tc classification. With respect to previous classifications, there are three changes: V441 Cyg, TW Hor, and R Hya are Tc-poor compared to the previous classifications, there are three changes: V441 Cyg, TW Hor, and R Hya are Tc-poor compared to Garcia-Hernández et al. (2007), who apply this method to the stellar temperature. We thus followed a procedure similar to García-Hernández et al. (2007), who apply this method to

Table 2. Quantities measured from the spectra: radial velocity, Tc content, effective temperature, and Li abundance of the sample stars.

| Name   | \( \nu_r \) [km s\(^{-1}\)] | Tc?  | \( T_{\text{eff}} \) | \( \log \varepsilon(\text{Li}) \) |
|--------|-----------------|------|----------------|----------------|
| U Cet  | 19.0            | no   | 3300           | \( \leq 0.0 \) |
| W Cet  | +5.8            | yes  | 3100           | +0.8           |
| V441 Cyg | -61.7         | yes  | 3400           | +4.6           |
| W Eri  | +17.8           | no   | 2950           | +0.4           |
| S Grz  | -18.4           | no   | 2900           | +0.8           |
| R Hor  | +56.0           | yes  | 2900           | +0.6           |
| T Hor  | +44.9           | no   | 3300           | \( \leq 0.0 \) |
| TW Hor | +14.5           | yes  | 3000           | -1.5           |
| R Hya  | -15.7           | no   | 3100           | \( \leq 0.0 \) |
| RU Hya | +0.4            | no   | 3300           | \( \leq 0.0 \) |
| Y Lib  | +9.3            | no   | 3100           | +0.9           |
| U Mic  | -61.0           | no   | 2900           | +0.6           |
| Y Scl  | +30.0           | no   | 3200           | +1.0           |
| T Tuc  | -37.9           | no   | 3300           | \( \leq 0.0 \) |
| ER Vir | +8.5            | no   | 3500           | \( \leq 0.0 \) |
| EV Vir | -44.5           | no   | 3500           | \( \leq 0.0 \) |
| RS Vir | -15.9           | no   | 2900           | +1.0           |
| S Vir  | +7.2            | yes  | 2800           | +0.5           |

We used the same modified \( \chi^2 \) test as these authors to fit model data \( Y_{\text{synth}} \) to observed data \( Y_{\text{obs}} \), which is expressed in the form

\[
\chi^2 = \sum_{i=1}^{N} \frac{(Y_{\text{obs},i} - Y_{\text{synth},i})(x_1 \ldots x_M))^2}{Y_{\text{obs},i}},
\]

with \( N \) the number of data points and \( M \) the number of free parameters. The synthetic spectra are based on COMARCS atmospheric models. COMARCS is a revised version of MARCS (Jörgensen et al. 1992) with spherical radiative transfer routines from Nordlund (1984) and new opacity data from the COMA program (Aringer 2000). The only model parameters that we varied in this procedure were the effective temperature and the metallicity. The other stellar parameters have a very limited impact on the spectral appearance, hence on the results of this analysis (see also García-Hernández et al. 2007, for a more detailed discussion). For the surface gravity \( \log g \) [cm s\(^{-1}\)], micro-turbulent velocity \( \xi \), and the mass \( M \), we chose values typical for red giant stars of 0.0, 3 km s\(^{-1}\), and 1 \( M_\odot \). Since the precise C/O ratio cannot be determined from our optical data (near-IR spectra would be required to do so), we fixed it at the solar value of 0.48, although in principle it might deviate from that value, particularly for the Tc-rich sample stars. Once the C/O ratio approaches 1, the chemistry and thus the dominant features in the spectrum will change significantly. Two stars of our sample are classified as MS or S-type (W Cet and V441 Cyg), and only for these objects do we expect that the assumption of a constant C/O might deteriorate the results to some degree. We come back to this point in the next section.

We chose three metallicity values for the grid of model atmospheres: 0.3, 1.0, and 1.6 times the solar metallicity. The temperature ranges between 2600 and 3600 K in steps of 100 K, with intermediate steps at 2950 and 3150 K for the solar metallicity models. From this grid of model atmospheres, synthetic spectra were calculated in the two spectral pieces 668–674 nm (covering the Li line at 670.8 nm and the TiO \( \gamma(1,0) \) Rc and TiO \( \gamma(1,0) \) Rb band-heads) and 700–710 nm (covering the strong TiO \( \gamma(0,0) \) Ra band-head at \( \sim 705 \) nm and the TiO \( \gamma(0,0) \) Rb band head). Atomic lines from the VALD database (Kupka et al. 1999) and TiO lines from the list of Schwenke (1998) were taken into account in the spectral synthesis. Other molecular line data of

Fig. 2. Ratio of the continuum flux to line core flux for the two Tc lines at 423.819 and 426.227 nm. The quasi-continuum points were taken in the range 423.940–423.970 nm and 426.130–426.150 nm, respectively, the line core flux was measured in the range 423.805–423.835 nm and 426.220–426.240 nm, respectively. While the Tc-poor stars gather around ratios 1.0 (lower left corner), the Tc-rich stars are displaced to the upper right by the Tc line absorption. The dashed lines represent the upper limits of the ratios found for the Tc-poor bulge stars analysed in Uttenthaler et al. (2007a).
less impact on the spectral ranges under consideration were also taken into account; these data are summarised in Table 1 of Cristallo et al. (2007).

Prior to the $\chi^2$ minimisation fitting, the model spectra were convolved with a Gaussian to a resolution of $R = \lambda / \Delta \lambda = 50,000$ (except for V441 Cyg, for which the spectra are convolved to $R = 65,000$). An additional macro-turbulence of 3 km s$^{-1}$ was assumed. This proves an acceptable value for all except two stars, namely V441 Cyg and Y Sco, for which a higher value of 6 km s$^{-1}$ had to be adopted to make a satisfactory fit to the spectra.

Although the metallicities adopted for the atmospheric model grid cover a quite wide range, it turned out that the temperature at which $\chi^2$ becomes minimal does not strongly depend on the metallicity. The $\chi^2$ minimum for the spectral piece including the Li line is quite flat for many stars, thus the adopted temperature was mostly fixed by the second piece between 700–710 nm. For the spectral synthesis to determine Li abundances (see next section), we therefore adopted the model with solar metallicity, with a temperature that satisfactorily fits both spectral pieces. There is some indication in the literature that solar metallicity is a good assumption for solar neighbourhood AGB stars (e.g. Vanture & Wallerstein 2002; García-Hernández et al. 2007). After finishing this procedure, we found that the adopted effective temperature correlates well with the $(J−K)$ colour, as can be expected: cooler stars have higher (redder) $(J − K)$ colour than hotter stars. The adopted temperatures are summarised in the fourth column of Table 2. We estimate that the precision of the temperature determination is ±100 K.

### 3.2.2. Li abundances

With this temperature, spectral synthesis calculations of the Li line doublet were performed to measure the Li abundance, using the MARCS models with solar metallicity. The log $gf$ values from the VALD database were adopted for the 670.8 nm Li doublet (log $gf = −0.009$ and −0.309 for the component at the shorter and longer wavelength, respectively). The Li abundance was varied in steps of 0.1 dex, and the observed-minus-calculated flux at the wavelength of the Li line was monitored to determine the Li abundance in the atmosphere of each sample star. The abundance that left practically a zero flux difference was finally adopted. The last column of Table 2 gives the measured Li abundances on the log $\epsilon$ scale (log $\epsilon$(Li) = log $N$(Li)/$N$(H) + 12). The solar photospheric Li abundance on this scale is $\epsilon$(Li) = +1.1. We also used our model spectra to verify that the observed absorption around the Li line cannot come from a line of cerium, which is observed to be a “substitute” for Li in the hotter barium stars and post-AGB stars (Lambert et al. 1993; Reyniers et al. 2002).

From the uncertainty of the temperature, the stellar parameter with the strongest influence on the Li line strength, we estimate an abundance uncertainty of ±0.4 dex. Taking the uncertainties of the other stellar parameters into account, which are harder to quantify, the total uncertainty on log $\epsilon$(Li) is estimated to be up to ±0.6 dex, being larger for the cooler stars. The relative uncertainty within the sample, however, is probably less than this.

A number of stars in the sample has no significant Li line absorption, their spectra are satisfyingly fit with negligible Li abundance in the spectral synthesis. It is difficult to state a precise upper limit to their atmospheric Li abundance. In the vicinity of the Li line, positive and negative residuals are present in an observed-minus-calculated flux plot, due to imperfect spectral modelling. Besides errors on the adopted stellar parameters, neglecting velocity fields in the atmosphere (due to stellar pulsations) by using hydrostatic models leads to persistent observed-minus-calculated flux residuals. Also, the line lists (mostly TiO) are certainly not without flaws at the high resolution of our spectra. The stars with no detectable Li line absorption are listed with log $\epsilon$(Li) ≤ 0.0 in Table 2, an abundance that would certainly not be detectable with our methods anymore. The carbon-star TW Hor was analysed by Kipper (2004), who determined a log $\epsilon$(Li) = −1.5 from another UVES spectrum of this object. We adopt this value of the Li abundance for TW Hor in Table 2. We also compared our spectrum of TW Hor with the one used by Kipper (2004) and found negligible variation between them. The low Li abundance of the carbon-star TW Hor would not be detectable in oxygen-rich stars of the same effective temperature, because of the increased molecular absorption in M-type stars in this spectral region. In the following we focus on the oxygen-rich stars. Figure 3 shows sample spectra of two stars (R Hya and RS Vir) with very different Li abundances, along with a best-fitting model spectrum. The Li content of R Hya is below the detection threshold, whereas RS Vir is found to have Li at the solar photospheric level.

The very high Li abundance of V441 Cyg is remarkable. As noted above, this star deviates from the trend towards higher (redder) $J − K$ colours at lower temperatures: despite its rather high temperature estimate of 3400 K, a $J − K = 1.39$ is found. Vanture & Wallerstein (2002) estimate $T_{\text{eff}} = 3100$ K from its spectral type. This low temperature is hardly compatible with our fit to the 700–710 nm spectral region. While there is some disagreement on the near-IR photometry (Wang & Chen 2002), the combination of red $J − K$ but weak TiO bands could be caused by a high C/O ratio. From our models we found that a synthetic spectrum with C/O = 0.9 and a temperature of 3200 K also reasonably fits the 700–710 nm region. We thus repeated the Li abundance measurement adopting C/O = 0.9 and $T_{\text{eff}} = 3200$ K and derived log $\epsilon$(Li) = 4.1, which is still a factor of 1000 higher than the solar photospheric abundance! However, Plez et al. (2003) demonstrate that atomic and some molecular lines (such as from ZrO and LaO) strengthen even more when the C/O ratio approaches 1. To find the Li abundance that may be regarded as a lower limit, we constructed a MARCS model with a C/O ratio of 0.99 and $T_{\text{eff}} = 3400$ K, but otherwise unaltered stellar parameters. Using this model, we find log $\epsilon$(Li) = 3.1 for V441 Cyg. The TiO bands are still well fit by the model at this high a C/O ratio.

The equivalent width of the Li I 670.8 nm line in V441 Cyg is approximately 730 mÅ, surpassing that of many of the super-Li rich stars identified in the Magellanic Clouds (Smith et al. 1995), and the line core flux is ~6% of the local quasi-continuum level. Also, the Li line at 812.63 nm was identified in V441 Cyg. A spectrum synthesis of this line yielded a Li abundance lower by 0.8 dex (at solar C/O) than was found from the 670.8 nm Li line. However, the spectral fit in the vicinity of the 812.6 nm line was not as good as that around the 670.8 nm line, which caused problems in defining the quasi-continuum level.

We repeated the Li abundance measurement with the C/O ratio increased to 0.99 for W Cet, the other S star in our sample. This exercise yielded log $\epsilon$(Li) = −2.0, which may again be regarded as a lower limit for the Li abundance. The Li detection would still be significant, because the detection threshold will also decrease markedly with C/O approaching 1. The observed spectrum of W Cet is still incompatible with negligible Li content, if C/O = 0.99 is adopted for the model atmosphere. For
consistency, we keep the Li abundances as determined with the C/O = 0.48 models in Table 2 and in the analysis.

We would also like to note that we did not identify significant LaO bands in any of our oxygen-rich stars, thus we may assume that indeed none of them has a C/O ratio above 0.99.

Besides V441 Cyg, only one of our sample stars has previously been investigated for its Li content, namely RS Vir (García-Hernández et al. 2007). In contrast to our measurement (Table 2), García-Hernández et al. (2007) find no significant Li line absorption in that star, and state an upper limit of log $\epsilon$(Li) < 0.5 instead. Also, the temperature determinations of this star differ somewhat, 2900 K in the present work compared to 2700 K in García-Hernández et al. (2007). We identify two possible explanations for this discrepancy.

First, two different TiO line lists were applied to derive stellar temperatures. One of them might yield systematically lower temperatures, which would decrease the measured Li abundance considerably. To investigate this possibility, we calculated model spectra using the TiO line list of Plez (1998), as used by García-Hernández et al. (2007), and repeated the $\chi^2$ minimisation procedure (Sect. 3.2.1). Only the sequence of models with solar metallicities was used for this. From this we find that the temperatures found using the two TiO line lists hardly differ from each other, with the Plez list delivering temperatures at most 50 K higher than the Schwenke list. We conclude that the different line lists used cannot explain the discrepancy found in the temperature and Li content of RS Vir. From this experiment with the two TiO line lists, we also find that the list of Schwenke (1998) yields slightly lower residuals than that of Plez (1998), particularly in the vicinity of the 670.8 nm Li line. This might also explain why our detection limit is somewhat lower than that of García-Hernández et al. (2007).

Second, the two spectra have been taken at different epochs, with different instruments. The temperature variation over the cycle of stellar pulsation could be responsible for the difference of 200 K found by the two studies. According to the AAVSO visual light curve, our spectrum was taken just 30 days before maximum, when the light curve was still sharply rising. García-Hernández et al. (2007) observed RS Vir during their fourth run between 21–24 February 1997. This date is just a few tens of days before a visual light maximum of the AAVSO light curve, too, but three pulsation cycles before our UVES observations. With the pulsational phase at the two observations being so similar, it is hard to imagine that the photospheric temperature could be different by 200 K, even for a Mira variable. Assuming a Li abundance constant on short time-scales, it is very unlikely that the line would go undetected in the observations of García-Hernández et al. (2007). The atmospheric structure of a Mira star certainly cannot be described perfectly with a hydrostatic model, and line strengths might vary considerably with the pulsation phase, even from cycle to cycle. It would be interesting to obtain another spectrum of RS Vir to exclude a variable Li line strength, as has been reported for a number of carbon-stars by Boffin et al. (1993).

A portion of the spectrum of RS Vir around the 670.8 nm Li line is displayed in Fig. 3, with the Li line clearly present.

**Fig. 3.** Examples of observed spectra (black graph with squares) of two stars with very different Li abundances, along with a best-fitting model spectrum (grey graph). The dashed lines indicate the laboratory wavelengths of the Li doublet.
formation from Marigo et al. (2008). The isochrones have been cut off once the model stars become C-rich.

In Fig. 4 we show the location of our stars in a $T_{\text{eff}}$ vs. $M_{\odot}$ diagram using the data given in Table 1, along with two isochrones from Marigo et al. (2008). Most stars nicely follow a trend of increasing luminosity with cooler temperature (higher $T_{\text{eff}}$). Stars with and without Tc are marked by different symbols. In agreement with earlier studies (e.g. Lebzelter & Hron 2003; Uttenthaler et al. 2007a), we find no Tc-rich stars below $M_{\odot} \sim 4.8$. This is another confirmation of the lower luminosity limit for third dredge up predicted by various stellar evolution models. As in earlier studies, we also find here a few stars without Tc above the luminosity limit. We refer to the discussion in Lebzelter & Hron (2003) that suggests that these stars might have too low an envelope mass for third dredge up to occur.

The data points in Fig. 4 are labelled with the derived Li-abundances from Table 2. Standard theories predict a Li abundance on the AGB below log $\epsilon$(Li) = 1.5. Only one star in our sample exceeds this value, namely V441 Cyg. We discuss this star in more detail in Sect. 4.1. For the other stars, there seems to be a tendency to higher Li abundance with higher luminosity or with lower temperature. This contradicts the observations of giants summarised in Michaud & Charbonneau (1991) and Mallik (1999), as they find a decrease in the average Li abundance towards lower temperature. In Fig. 5 we show our sample, together with the results for the giants presented by Luck & Lambert (1982) and Mallik (1999) in a $T_{\text{eff}}$ vs. log $\epsilon$(Li) plot. Our sample extends the previous dataset towards cooler temperatures. This extension reveals that the trend to decreasing Li abundance with lower temperature stops and may even be reversed at the cool end.

The decline in the Li abundance as a function of temperature is typically attributed to two effects (Mallik 1999): first, the surface abundance will be reduced by a deepening of the convective envelope as the stars evolve towards and up the giant branch. Second, mass loss should erode outer Li-rich layers during the advanced stages of stellar evolution.

4. Discussion

In Fig. 4 we show the location of our stars in a $T_{\text{eff}}$ vs. $M_{\odot}$ diagram using the data given in Table 1, along with two isochrones from Marigo et al. (2008). Most stars nicely follow a trend of increasing luminosity with cooler temperature (higher $T_{\text{eff}}$). Stars with and without Tc are marked by different symbols. In agreement with earlier studies (e.g. Lebzelter & Hron 2003; Uttenthaler et al. 2007a), we find no Tc-rich stars below $M_{\odot} \sim 4.8$. This is another confirmation of the lower luminosity limit for third dredge up predicted by various stellar evolution models. As in earlier studies, we also find here a few stars without Tc above the luminosity limit. We refer to the discussion in Lebzelter & Hron (2003) that suggests that these stars might have too low an envelope mass for third dredge up to occur.

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At the lowest luminosities we find in our sample only stars with a strong depletion of their Li abundance (see Fig. 4). These stars also have the highest temperature, thus link our sample to the one of Mallik (1999). A deep extension of the convective envelope results in the destruction of most of the Li. Lines of this element again appear in the spectrum at about $M_{\odot} = -4.7$, i.e. at a slightly lower luminosity than the threshold level for Tc occurrence. This suggests that production of Li sets in at some point. This is supported by Li preferentially being detected in sample stars with long pulsation periods ($P \approx 280$ d) and redder IRAS [12]–[25] colours. Based on the derived luminosities, HBB may be safely excluded as the production mechanism for all but one star.

Uttenthaler et al. (2007b) found four AGB stars in the Galactic bulge with a detectable Li abundance of log $\epsilon$(Li) between 0.8 and 2.0 (at an error of 0.4 dex) and an effective temperature around 3000 K. These results agree nicely with our findings. Uttenthaler et al. identify extra-mixing (e.g. Boothroyd & Sackmann 1999) as the most likely explanation for the reappearance of Li on the stellar surface. We speculate that the same mechanism is at work in the Li-enhanced stars of our sample. The lowest luminosity of a Li-enhanced star in the sample of Uttenthaler et al. (2007b) is in good agreement with the lower luminosity limit found among the targets studied here.

In this sample we cannot distinguish whether this change in Li abundance is coming from a difference in mass or as a result of stellar evolution or both. However, when combining our findings with the ones from Uttenthaler et al. (2007b), there seems to be a lower luminosity limit for any Li production mechanism to set in. The existence of such a limit would favour an internal mechanism over an external one (e.g. surface contamination by a companion – see Uttenthaler et al. 2007b). We note further that mass loss increases substantially during the AGB phase. As mass loss should reduce the surface Li abundance, the detection of an increase in Li abundance on the upper AGB strongly suggests a production of this element inside the star.

3 We use here the term “enhanced” to express a Li abundance above our detection threshold corresponding to log $\epsilon$(Li) = 0. This has to be distinguished from Li rich objects with an abundance exceeding the average Galactic value.
Concerning a possible relation between the Li abundance and the occurrence of Tc, we find that all Tc-rich stars show also at least a mild enrichment of Li relative to the values found for the lowest luminosity stars of our sample. We also find Li-enhanced stars without Tc and luminous stars that show no detectable abundance of neither of the two elements. Furthermore, Vanture et al. (2007b) also found Tc rich stars with no Li-enhancement. This mixture of possibilities indicates the involvement of a further parameter besides the stellar luminosity. As we have no indications of a strong scatter in metallicty in our sample, we may assume that mass is the discriminating factor. There are some indications that extra-mixing occurs more effectively among stars of lower mass, which may lead to an enhancement of surface Li in these objects (e.g. Cantiello & Langer 2008).

If we want to compare our results with the work of Vanture et al. (2007), who find objects with all four combinations of Tc-rich, Tc-poor, Li-rich, and Li-poor, we face the problem that Vanture et al. define stars as Li-rich if log \( \epsilon(\text{Li}) \) \( \geq 1.0 \). All other stars are defined as Li-poor. With this approach, only two stars, RS Vir and V441 Cyg would be classified as Li rich, with the first one at the lower limit. In that sense we would find one Tc-rich/Li-rich star (see below), one Tc-poor/Li-rich star, four (five if we include TW Hor) Tc-rich/Li-poor stars and a couple of Tc-poor/Li-poor stars. This means that all four classes from Vanture et al. (2007) would be present in our sample. However, taking into account the uncertainties in the Li abundance and the obvious scatter of Li abundances between log \( \epsilon(\text{Li}) \) = 0 and 1, we think that the Vanture et al. classes oversimplify the picture. Our understanding would certainly profit from finding an abundance limit between mildly Li-enhanced low-mass AGB stars and luminous Li-rich AGB stars producing this element by HBB in order to disentangle two different production mechanisms.

That all four combinations of Tc-rich, Tc-poor, Li-rich, and Li-poor are found can be understood at least qualitatively from the theoretical point of view. Assuming that \( ^7\text{He} \) is left from the RGB phase, thermohaline mixing (Cantiello & Langer 2008) can connect the H-burning shell of a TP-AGB star with the convective envelope and thus transport \( ^7\text{Be} \) to cool layers where it may decay to Li that can be observed on the surface. This mechanism is found to be more efficient in low-mass stars (\( > 1.5 M_\odot \), Cantiello & Langer 2008). This scenario is not constrained to stars undergoing 3DUP events, although the faster mixing during 3DUP would ensure that even more \( ^7\text{Be} \) survives. In higher mass stars (\( \geq 3 M_\odot \)), thermohaline mixing cannot connect the H-burning shell with the convective envelope. Nevertheless, a \( ^7\text{Be} \)-rich pocket can build up above the H-burning shell that can be dredged to the surface after a TP, even before formal 3DUP occurs. The \( ^7\text{Be} \)-rich pocket would be dredged to the surface in any 3DUP event, which may account for our finding of Li in every Tc-rich star in the current sample. The requirement that some \( ^7\text{He} \) is preserved from the RGB phase also introduces a mass threshold above which extra mixing can work on the AGB, because for stars of too low an initial mass, all \( ^7\text{He} \) would be consumed by efficient extra-mixing already on the RGB. Thus, thermohaline mixing critically depends on the mixing history of the star.

In the magnetic buoyancy scenario (Guandalini et al. 2009), the mixing is thought to arise from magnetic bubbles with locally increased magnetic pressure, thus a decreased density. The magnetic field might be sustained by an \( \sigma - \Omega \) dynamo produced by a region of rotational shear below the convective envelope. Fields of different strengths descending from different initial rotational velocities may explain the observed spread in Li abundances. Independent from 3DUP, Li may be produced on the AGB by fast mixing rates (provided a \(^3\text{He} \) reservoir is still present from the RGB), or destroyed by slow mixing rates.

Quantitative predictions of models of extra mixing are still rather uncertain and require parameter fine-tuning by observations. Depending on the adopted efficiency parameter of thermohaline mixing, Cantiello & Langer (2008) predict a surface Li enrichment of \(-0.05 \) dex during one inter-pulse period of a \( 3 M_\odot \) TP-AGB model star. After a number of 3DUP events, the surface Li abundance may thus increase above the detection threshold in a cool atmosphere. Thermohaline mixing is expected to be more efficient in lower mass stars, so the surface Li abundance could be increased by larger amounts than for the described case of a \( 3 M_\odot \) star. It should be noted that the interaction of thermohaline mixing with magneto-rotational instabilities is important, but only full magneto-hydrodynamical simulations can lead to a better understanding of these interactions.

The magnetic buoyancy picture, on the other hand, predicts an upper limit on Li production at the level of log \( \epsilon(\text{Li}) = 2 \pm 2.5 \). This upper limit is set by assuming a short phase of very fast mixing (a few km s\(^{-1} \)) of magnetised bubbles, in which no burning of the material occurs, and the Li enrichment of the envelope is set by the amount of “normal” \( ^7\text{Be} \). That is that produced near the H-burning shell. The Li abundances below this upper limit can be easily reproduced by assuming someLi destruction by a slower transport of the material, such that some nuclear burning occurs during the transfer to the envelope. If magnetic fields are the origin of the extra mixing, both fast and slow regimes of circulation can explain very different outcomes with only a single physical mechanism.

To conclude, super-Li rich stars such as V441 Cyg cannot be easily explained by the magnetic buoyancy scenario, but the rest of our sample would be described well. To decide whether thermohaline mixing could be the dominant mechanism, more information on the masses and mixing histories of the stars would be required.

We end this discussion with a closer look onto two of our sample stars. As far as we know, the reclassification of W Eri as Tc-poor has no great consequences on understanding the nature of this star. However, the re-classification of V441 Cyg and R Hya as Tc-rich and Tc-poor, respectively, has important consequences, and we thus devote the following two sections to these two objects.

4.1. V441 Cygni

Even though the SNR of the spectrum of V441 Cyg is low, it is clear from Fig. 2 that this star indeed has Tc in its atmosphere. It is thus an intrinsic S-star. As further evidence, its spectrum around the three strongest Tc lines is shown in Fig. 6. Also Wang & Chen (2002) list V441 Cyg as “not a good candidate Tc-deficient S star” based on its near- and mid-IR photometry.

Vanture et al. (2007) investigate a sample of 59 Galactic S-stars for the correlation of Tc and Li and find all four possible combinations of Tc-rich and -poor, and Li-rich and -poor in their sample. However, the group of Tc-poor, Li-rich S-stars is formed by only one object, namely V441 Cyg. Vanture et al. (2007) thus call it a “unique” object. There was good reason for doubt because V441 Cyg actually has never been checked for its Tc content in the literature, hence our FOCES observations. As shown above, there is no Li-rich (not Li-enhanced?) and Tc-poor S-type star known at the moment.

We thus show that V441 Cyg is Tc- and Li-rich and that it needs to be moved to “group 2” as defined by
Fig. 6. FOCES spectrum of V441 Cyg around the three strongest TcI lines. The spectrum has been smoothed with a 5 pixel boxcar. The dashed line marks the laboratory wavelength of the respective line. Clearly, all three TcI lines are present.

Vanture et al. (2007). They offer two possibilities for interpreting this group of stars. The first interpretation is that intrinsic (Tc-rich) S-stars with high Li-abundance are intermediate-mass ($M \geq 4 M_\odot$) TP-AGB stars experiencing HBB, thus producing Li in their atmospheres and destroying C via CN cycling. This picture is supported by the low average Galactic latitude of the stars in group 2 (14°, excluding two relatively nearby stars). However, the bolometric magnitude, which is available for only four stars of the Vanture et al. (2007) sample, instead argues against this interpretation, since none of them has $M_{\text{bol}} \leq -6.60$. Vanture et al. (2007) thus suggest that their sample consists of a mix of low- and intermediate-mass stars. The second interpretation thus concerns low-mass S-stars, which might be the result of extra-mixing processes on the TP-AGB (see discussion above). The existence of Li-rich C-stars (Boffin et al. 1993) suggests that low-mass Li-rich S-stars could also exist, and have not yet dredged-up enough carbon to reach $C/O > 1$.

Which of the two offered interpretations holds for V441 Cyg? It is located at a very low Galactic latitude of $b \sim -1°$, and our estimate of its bolometric magnitude ($M_{\text{bol}} = -5.66$) is not far below the approximate limit for HBB. Concerning the uncertainties in determining the luminosity we note that only if the star were a fundamental mode pulsator, we would expect a lower luminosity. This definitely argues in favour of the intermediate-mass HBB interpretation. However, García-Hernández et al. (2007) find that Li-rich Galactic OH/IR stars, thought to be intermediate-mass AGB stars with a very high mass-loss rate, do not exhibit significant Zr enhancements. On the other hand, the s-element Rb is observed to be enriched in these stars (García-Hernández et al. 2006). This might stem from the activation of the $^{22}\text{Ne}(\alpha,n)^{25}\text{Mg}$ neutron source rather than the $^{13}\text{C}(\alpha,n)^{16}\text{O}$ neutron source in these more massive stars. Thus, enrichment in Rb is another indicator of high mass. Unfortunately, we did not succeed to derive a reliable Rb abundance from our spectrum of V441 Cyg, because the Rb resonance line at 780.0 nm is completely dominated by a blue-shifted circumstellar component that makes it impossible to determine the photospheric Rb abundance. Nevertheless, we can interpret this as no enhancement of Rb in the photosphere of V441 Cyg, suggesting that it is too low in mass to activate the $^{22}\text{Ne}$ neutron source. The light curve of V441 Cyg changes with a period of 288 d in a semi-regular way, and the IRAS $[12]-[25]$ colour, defined as $-2.5\log(F_{12}/F_{25})$, has a value of $-1.28$. Only three of our sample stars are bluer than that, which suggests only low obscuration by the circumstellar envelope. The variability characteristics, in particular the low amplitude of pulsation at this high luminosity, could be interpreted as a consequence of a high stellar mass, but is difficult to quantify.

To summarise, the evidence on the mass of V441 Cyg is not entirely conclusive, and we cannot clearly decide on which of the interpretations offered by Vanture et al. (2007) holds for this star. There are a number of other peculiar intrinsic S-stars with high Li abundance, e.g. R And and T Sgr. The Rb abundance has been measured in the former by Wallerstein (1992), and a neutron density at the s-process site of $10^8$ cm$^{-1}$ was derived, indicative for the $^{13}\text{C}$ neutron source operating in low-mass stars. An analysis and comparison of these stars would be be very rewarding, which we plan to present in a forthcoming paper.

Finally, Fig. 7 reproduces a small piece of spectrum of V441 Cyg around the 670.8 nm Li resonance line, along with the best-fitting synthetic spectrum based on a MARCS model atmosphere with $T_{\text{eff}} = 3400$ K and solar metallicity, assuming $\log \epsilon(\text{Li}) = +4.6$. There is a prominent blue wing in the Li line, which we did not try to fit. This feature may be interpreted as indication of a Li-rich stellar wind that cannot be reproduced with our hydrostatic models. Such a wind feature is somewhat surprising, given the rather blue IRAS colours of this star. Because the temperature is probably lower in the wind than in the photosphere, more Li atoms are present in the ground state, and the wing is deeper than the photospheric line component. Thus, we possibly see V441 Cyg in a stage where it enriches the ISM with freshly produced Li.
4.2. R Hya

R Hya has already been classified as Tc-rich a long time ago, albeit with only a low Tc line intensity (Merrill 1952b). Spectrograph tracings of R Hya taken at different phases of its pulsation cycle can be found in Merrill (1952a). These spectrographs cover the Tc I lines at 398.497 and 404.911 nm, but both are absent at all observed pulsational phases. Also in our high-quality, high-resolution UVES spectra of R Hya, we are unable to detect any of the Tc lines. We find no increase in ZrO band strength, wether in R Hya or in any other Tc-poor star in our sample. We thus conclude that, with the spectrographs available at the times of Merrill, a precise decision about the presence of weak absorption lines was not possible, and a misidentification occurred in this particular case that has continued in the literature ever since. We find R Hya to be the most luminous Tc-poor star in our sample, with approximately 10 000 solar luminosities. From detailed AGB evolution models (Cristallo et al. 2009), it is known that a 3DUP episode, if it takes place, follows a TP with some time delay. For instance, for a 2 $M_\odot$ model of solar metallicity, the first 3DUP episode takes place ~670 years after the preceding TP (Cristallo, private communication). Thus, abundance changes of s-process elements and $^{13}$C on the stellar surface also become visible only with a time delay. Wood & Zarro (1981) suggest that a TP could have occurred in R Hya about 550 years ago. If the decrease in pulsation period observed in R Hya was indeed caused by a recent TP, we may be able to detect surface abundance changes (e.g. Tc) in the future, say in a few 100 years, if this past TP is followed by a 3DUP event.

Alternatively, Zijlstra et al. (2002) suggest that the period decrease observed in R Hya could just as well be caused by a nonlinear instability leading to an internal relaxation of the stellar structure. While not detecting Tc does not strongly favour one or the other scenario, it indicates that possible TPs are not strong enough to drive 3DUP in R Hya.

5. Summary and conclusions

We analysed high-resolution optical spectra of a sample of 17 M-type (oxygen-rich) and one C-type (carbon-rich) AGB variables for the presence of Tc and the abundance of Li. We employed a flux-ratio method to decide on the presence of the 3rd dredge-up indicator Tc in the stellar atmosphere, and measured the abundance of the temperature-sensitive element Li with spectral synthesis techniques of the 670.8 nm Li resonance line using MARCS model atmospheres. Bolometric magnitudes were established from near-IR photometry and pulsation periods. The lower luminosity limit for 3DUP to occur, established in previous works, has been confirmed. We re-classified three sample stars with respect to their Tc content, namely that R Hya and W Eri are Tc-poor, and V441 Cyg is Tc-rich. We thus suggest that R Hya has not yet experienced a dredge-up of freshly produced s-elements, but, regarding the possibility that it recently underwent a TP, might have a 3DUP episode in the future. V441 Cyg, on the other hand, is an intrinsic S-star. Lithium is detected in ten sample stars (with a log $\epsilon$(Li) > 0). After combining these abundances with bolometric magnitude estimates, we find that Li is more abundant in more luminous and cool stars. All Tc-rich sample stars are found to contain also some Li in their atmosphere. We thus suggest that this fragile element could be replenished in the stellar atmosphere by some (extra-mixing) process that is only active in the more luminous objects. This could also be connected to a mass effect within the sample. The S-star V441 Cyg is found to be super-Li rich, with a higher Li abundance than the solar photospheric value probably by a factor 1000. The gathered evidence does not allow us to clearly conclude whether this object is an intermediate-mass AGB star ($M > 4 M_\odot$) producing Li by the HBB mechanism, or a low-mass star with extremely efficient extra-mixing processes. The data obtained in this study may be useful for constraining theoretical models of such extra-mixing processes.

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For the s-process elements to be enhanced, it takes at least two 3DUP episodes, one to build up a $^{12}$C pocket in the inter-shell region as neutron source, and another one to actually mix the s-process products to the surface. C enhancement should be present only after one 3DUP episode.
