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Letter to the Editor

# Hot bottom burning and s-process nucleosynthesis in massive AGB stars at the beginning of the thermally-pulsing phase\*

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#### ABSTRACT

We report the first spectroscopic identification of massive Galactic asymptotic giant branch (AGB) stars at the beginning of the thermal pulse (TP) phase. These stars are the most Li-rich massive AGBs found to date, super Li-rich AGBs with log  $\varepsilon$  (Li) ~ 3–4. The high Li overabundances are accompanied by weak or no s-process element (i.e. Rb and Zr) enhancements. A comparison of our observations with the most recent hot bottom burning (HBB) and s-process nucleosynthesis models confirms that HBB is strongly activated during the first TPs but the <sup>22</sup>Ne neutron source needs many more TP and third dredge-up episodes to produce enough Rb at the stellar surface. We also show that the short-lived element Tc, usually used as an indicator of AGB genuineness, is not detected in massive AGBs, which is in agreement with the theoretical predictions when the <sup>22</sup>Ne neutron source dominates the s-process nucleosynthesis.

**Key words.** stars: AGB and post-AGB – stars: abundances – stars: evolution – nuclear reactions, nucleosynthesis, abundances – stars: atmospheres – stars: late-type

#### 1. Introduction

Low– and intermediate-mass  $(0.8 < M < 8 M_{\odot})$  stars end their lives with a phase of strong mass loss and thermal pulses (TP) on the asymptotic giant branch (AGB, Herwig 2005), and are one of the main contributors to the chemical enrichment (e.g. C, N, Li, F, and s-process elements) of the interstellar medium. After each TP the surface convective zone moves inwards, and may reach internal layers contaminated by  $3\alpha$  nucleosynthesis, enriched in C. This mixing episode is known as third dredge-up (TDU). After many TDUs the surface C exceeds the O content, transforming originally O-rich stars into C-rich stars. However, this applies only to AGB stars in the mass range from  $\sim 1.5$ to  $3-4 M_{\odot}$ . More massive stars experience hot bottom burning (HBB, Sackmann & Boothroyd 1992), i.e. proton-capture nucleosynthesis at the base of the outer envelope that favours the conversion of C to N by the CN-cycle and reconversion of the C-rich to an O-rich atmosphere. The HBB process is activated when the temperature at the bottom of the envelope reaches 40 MK, the same required to ignite the Cameron & Fowler (1971) mechanism (Mazzitelli et al. 1999), by which great amounts of Li can be produced in the surface regions. The detection of Li overabundances in massive O-rich AGB stars both in our Galaxy (García-Hernández et al. 2007) and in the Magellanic Clouds (MCs; e.g. Plez et al. 1993; García-Hernández et al. 2009) has confirmed the activation of HBB in the more massive AGB stars.

Theoretical nucleosynthesis models also predict the presence of the elements (e.g. Rb, Zr, and Sr) that can be made by *slow* neutron captures (the s process) and are dredged up to the stellar surface. According to the most recent models,  ${}^{13}C(\alpha,n){}^{16}O$  is

the preferred neutron source for  $\sim 1-3 M_{\odot}$ , while for more massive stars neutrons are mainly released by  $^{22}\text{Ne}(\alpha, n)^{25}\text{Mg}$  (e.g. Karakas 2010; van Raai et al. 2012; Karakas et al. 2012). The  $^{22}\text{Ne}$  neutron source requires higher temperatures and produces higher neutron densities than the  $^{13}\text{C}$  source. The relative abundance of Rb to other nearby s-elements such as Zr is very sensitive to the neutron density owing to the operation of branchings in the s-process path at  $^{85}\text{Kr}$  and  $^{86}\text{Rb}$  (Lambert et al. 1995; Abia et al. 2001; van Raai et al. 2012). In this context, the [Rb/Zr] ratio is a powerful discriminant of the operation of the  $^{13}\text{C}$  versus the  $^{22}\text{Ne}$  neutron source in AGB stars.

A small group of Galactic stars showing OH maser emission, known as OH/IR stars, have been identified as massive  $(4-8 M_{\odot})$ O-rich HBB AGB stars showing strong Rb overabundances coupled with weak Zr enhancements (García-Hernández et al. 2006, 2007). This provides the first observational evidence that <sup>22</sup>Ne is indeed the dominant neutron source in massive Rb-rich AGB stars. However, this study was intentionally biased towards the redder and more extreme Galactic OH/IR stars, which experience very strong mass-loss rates (up to  $\sim 10^{-4} - 10^{-5} M_{\odot}/\text{yr}$ ) and are expected to be at the end of the thermally-pulsing (TP) AGB phase. A very advanced evolutionary AGB stage is also suggested by the large variations in the measured Li abundances  $(-1.0 \le \log \varepsilon(\text{Li}) \le 2.6$ ; see van Raai et al. 2012); the Lirich stars in that sample display Li abundances larger than solar, but significantly smaller than those found in a few super Li-rich Galactic AGB stars (with  $\log \varepsilon$ (Li) > 3–4; e.g. Abia et al. 1999)<sup>1</sup>.

<sup>\*</sup> Appendix A is available in electronic form at http://www.aanda.org

<sup>&</sup>lt;sup>1</sup> We note that a few super Li-rich AGBs were found in the MCs (e.g. Plez et al. 1993) but these are less massive ( $\sim 3-5 M_{\odot}$ ) Rb-poor HBB-AGBs where the <sup>13</sup>C neutron source dominates the s-process nucleosynthesis (see García-Hernández et al. 2006, 2009).

Interestingly, HBB models predict that massive AGB stars experience a super Li-rich phase (log  $\varepsilon$ (Li) ~ 4) at the beginning of the TP phase (e.g. Mazzitelli et al. 1999; van Raai et al. 2012). Yet, to date, no super Li-rich massive Galactic AGB stars have been unambiguously identified (see e.g. Uttenthaler & Lebzelter 2010; Uttenthaler et al. 2011). In this Letter we report the first detections of super Li-rich massive AGB stars in our Galaxy. The extreme Li overabundances found together with the lack of s-process element enhancements are consistent with these stars being truly massive O-rich AGB stars at the beginning of the TP phase.

## 2. Sample, optical observations, and chemical abundance analysis

Our sample is composed of the Galactic disc O-rich AGB stars RU Cyg, SV Cas, R Cen, and RU Ari. Their AGB status is deduced from their relatively long pulsation periods  $(\sim 200-500 \text{ days})$ , large amplitude variability, late spectral type (>M5), and infrared excess (see García-Hernández et al. 2007). All stars show similar infrared excesses and IRAS colours (R Cen and RU Ari are the bluest and reddest sources, respectively), but very different circumstellar maser emission from O-based molecules such as SiO, H<sub>2</sub>O, and OH. In Table A.1 we list the four AGB stars together with their Galactic coordinates, present-day variability periods<sup>2</sup>, and maser information. An evolutionary sequence of increasing mass-loss from SiO, to H<sub>2</sub>O and OH maser emission is expected in these stars (Lewis 1989; Habing 1996). Thus, the OH/IR star RU Ari is presumably more evolved (and/or more massive) than the other three AGBs for which no OH maser emission has been detected. Also, defining marks of the three non-OH/IR AGBs are their complex (e.g. double maxima) and changing variability properties. The dominant period of the Mira-like star R Cen has decreased from ~500 days in 2000 (Hawkins et al. 2001) to the present value of 251 days while the other two stars have increased their dominant periods from  $\sim 200-300$  days to  $\sim 450$  days. It has been speculated that the changing period is related to a recent TP in AGB stars (see e.g. Wood & Zarro 1981; Uttenthaler et al. 2011).

The optical observations of the stars RU Cyg, SV Cas, and RU Ari presented here are part of our recent high-resolution ( $R \sim$  $60\,000$ ) optical spectroscopic survey of a large sample (~100) of relatively blue Galactic O-rich AGB stars not previously studied. This survey has been carried out in several observing runs from 2006 to 2008 by using the Tull (Tull et al. 1995) and SARG spectrographs at the 2.7 m Harlan J. Smith (HJS) Telescope and at the Telescopio Nazionale Galileo, respectively; the optical spectra and the abundance analysis for the whole sample will be presented in a future paper. In particular, the optical spectra reported here were taken in the wavelength range ~3650–9500 Å ( $R \sim$  $60\,000$  with the 1.2" slit and the grating E2) at the HJS telescope. On the other hand, the unpublished high-resolution ( $R \sim 50000$ ) optical spectrum of R Cen was taken with the ESO-VLT UVES spectrograph (with the 0.7'' slit), covering the ~3770-4900, 6670-8470, and 8650-10500 Å spectral regions. The star R Cen was observed within the ESO programme 65.L-0317(A) that was devoted to studying AGB stars in the Galactic bulge (GB; see e.g. Uttenthaler et al. 2007). However, R Cen is a lowlatitude ( $b = +1.2^{\circ}$ ) Galactic disc AGB star and displays a Li I 6708 Å line that is much stronger than in the AGBs studied by Uttenthaler et al. (2007). The exposure times varied between a few seconds (R Cen) and 3–5 min (RU Cyg and SV Cas) for the bluer AGBs and 20 minutes for the more obscured star RU Ari. A signal-to-noise ratio (S/N) of  $\geq$ 30–50 at 4200 Å and in excess of 100 at wavelengths longer than 5900 Å was achieved in the blue AGBs. The only exception was the redder AGB star RU Ari for which a S/N higher than 10 was achieved at 5924 Å (the Tc I line) and higher than 40 at  $\lambda > 6400$  Å.

The two-dimensional optical *echelle* spectra were reduced to single-order one-dimensional spectra using standard astronomical tasks. We are mainly interested in the wavelength regions around the Li I 6708 Å and Rb I 7800 Å resonance lines and around the ZrO 6474 Å bandhead. The Galactic O-rich AGB stars analysed here are bright enough in the 4000-6000 Å region, permitting us to search for the Tc absorption lines (e.g. at ~4238, 4262, 4297, and 5924 Å) for the first time. This is in strong contrast with the more obscured (OH/IR) massive Rb-rich AGB stars previously studied in our Galaxy (García-Hernández et al. 2006, 2007) that are too faint at wavelengths below 6000 Å. Indeed, the blue AGBs in our sample do not display the still unidentified molecular bands that are clearly present in obscured massive Rb-rich AGB spectra (e.g. at ~7400-7600 Å; see García-Hernández et al. 2009). These unidentified molecular bands are also detected in the much redder (OH/IR)AGB star RU Ari. This spectroscopic difference permit us to doublecheck the Zr abundance derived from the ZrO molecular bands with that estimated from the lack of the Zr I lines in the 7400–7600 Å region in the blue AGBs (see below).

The chemical abundance analysis follows the procedure previouly used by us in Galactic O-rich AGB stars (see García-Hernández et al. 2006, 2007 for more details). In short, we used the latest version (v12.1.1) of the TURBOSPECTRUM package (Alvarez & Plez 1998; Plez 2012) with line-blanketed model atmospheres and up-to-date molecular/atomic linelists to construct a grid of synthetic spectra appropriate for cool O-rich AGB stars in the Galactic disc:  $T_{\rm eff} = 2600-3500$  K in steps of 100 K, FWHM = 200-600 mÅ in steps of 50 mÅ,  $\log g = -0.5$ ,  $\xi = 3$  km s<sup>-1</sup>, and solar metallicity ([M/H] = 0.0).

The observations were compared to the synthetic spectra in the regions 6455-6499, 6670-6730, and 7775-7835 Å, covering the ZrO 6474 Å bandhead, the Li I 6708 Å line, and the Rb I 7800 Å line (Figs. A.1 and A.2). The best fit to the TiO bandheads and the pseudocontinuum around the atomic lines provided the  $T_{\rm eff}$ , which was found to be  $3000 \pm 100$  K for all sample stars. The abundances (or upper limits) of Li, Rb, and Zr were obtained by adjusting the Li I and Rb I lines and the ZrO molecular bands, respectively. In the blue AGBs, we note that the Zr abundance derived from the ZrO molecular bands is consistent with the lack of the Zr I lines in the 7400–7600 Å region. The spectroscopic  $T_{\rm eff}$  and abundances are given in Table A.1, where we also list the abundance uncertainties estimated for each star. The three bluer AGB stars show strong Li enhancements (log  $\varepsilon$ (Li)  $\ge$  2) together with no (or small) Rb and Zr overabundances (log  $\varepsilon$ (Rb, Zr) ~ 2.6  $\pm$  0.3). However, the redder AGB RU Ari displays a very high Rb content accompanied by no Li and no (or weak) Zr (see Sect. 4).

Finally, we have searched for the presence of the strong Tc I lines at ~4238, 4262, and 4297 Å and the much weaker Tc I 5924 Å line by following the method described by Uttenthaler et al. (2011). We note that the bluest AGB R Cen was not observed around the Tc I 5924 Å line and the reddest AGB star RU Ari is too faint around the stronger Tc I lines

<sup>&</sup>lt;sup>2</sup> Present-day periods have been determined by us from AAVSO (http://www.aavso.org) visual light curves (Uttenthaler et al. 2011).



**Fig. 1.** *Left panel*: HBB-FST predictions of the Li abundance versus time from the beginning of the AGB (in Myr). The horizontal lines represent the observed values of  $\log_{\mathcal{E}}(\text{Li}) = 2.0, 3.5, \text{ and } 4.3$ . *Right panel*: HBB-MLT Li, Rb, Zr, and Tc predictions for a 5  $M_{\odot}$  model with a delayed superwind. We note that the Tc abundance is an upper limit because the trend of the half-life of  ${}^{99}$ Tc – decreasing with temperature from terrestrial 0.22 Myr to ~3 yr at the peak temperature of ~350 MK – is not included in the model (though we do not expect large differences, see Mathews et al. 1986).

at ~4200–4300 Å. Our Tc search proved to be negative and all sample stars are non-Tc stars (see an example in Fig. A.3). The non-detection of Tc is also suggested by spectrum synthesis around the Tc I 5924 Å line<sup>3</sup> (see Fig. A.2). Our synthetic spectra suggest that Tc is not detectable (log $\varepsilon$ (Tc) < 0.0) in our stars, although the Tc I 5924 Å line is not very sensitive to the Tc content.

#### 3. The super Li-rich massive AGB stars

The stars SV Cas and R Cen are among the most Li-rich (super Li-rich with  $\log \varepsilon(\text{Li}) > 3-4$ ) O-rich (M-type) AGB stars found in our Galaxy<sup>4</sup>. The high Li overabundances observed in these Galactic disc O-rich AGBs are most likely explained by Li-enrichment due to HBB. The evolution of the Li abundance in HBB-AGB stars strongly depends on several stellar parameters such as progenitor mass, metallicity, mass loss, and convection model (e.g. Mazzitelli et al. 1999; van Raai et al. 2012). The treatment of convection and of mass loss are the most important ingredients in determining the duration of HBB and the variation of the surface chemistry during the AGB phase. This particularly holds in the range of masses experiencing HBB (Ventura & D'Antona 2005aa,b). Thus, we compare our observations with up-to-date solar metallicity HBB model predictions with very different prescriptions for mass loss and convection: i) models with the Blöcker (1995) recipe for mass loss and the full spectrum of turbulence convective mixing (HBB-FST; e.g. Mazzitelli et al. 1999); and ii) models with the Vassiliadis & Wood (1993, VW93) delayed mass loss and the mixing length theory for convection (HBB-MLT; see discussion in Karakas et al. 2012).

The temporal variation of the surface Li abundance in up-todate HBB-FST models of 3.5  $M_{\odot} \leq M \leq 6 M_{\odot}$  is displayed in Fig. 1 (left panel). The new models reach higher Li values compared to those previously published by Mazzitellli et al. (1999) in which only the 6  $M_{\odot}$  model reached log  $\varepsilon$ (Li) > 4. The corresponding Li predictions from the most recent HBB-MLT models (Karakas et al. 2012) are very similar with the exception that the 4  $M_{\odot}$  model does not become Li-rich (Karakas 2010). Figure 1 (right panel) shows these predictions for a 5  $M_{\odot}$  model. There are two obvious differences between the two sets of models. First, the Li minima in the HBB-FST models are deeper than in the HBB-MLT models, probably because of the different efficiency of the convection model. When the TP is on (or has just extinguished), the HBB-FST models are cooler than the HBB-MLT models and this stops Li production for a while, leaving room for Li destruction via proton capture. Second, the evolution of the HBB-FST models (and consequently the duration of the Li-rich phase) is shorter than their HBB-MLT counterparts. The stronger HBB predicted by the FST model (Ventura & D'Antona 2005a) leads to a fast increase in the stellar luminosity. The use of the Blöcker mass loss recipe in the HBB-FST models further enhances the difference in the evolutionary times of the two sets of models (Ventura & D'Antona 2005b).

Figure 1 shows that  $\log \varepsilon(\text{Li}) \sim 4$  is reached during the first TPs. In the HBB-FST scenario this occurs at the 3rd, 5th, and 11th TP for the 6, 5, and 4  $M_{\odot}$  models, respectively; in the HBB-MLT framework at the 7th and 14th TP for the 6 and 5  $M_{\odot}$  models, respectively. The HBB models also predict 3 <  ${}^{12}C/{}^{13}C < 20$  during the super Li-rich phase, as expected. The HBB-FST models with mass below 4  $M_{\odot}$  (Fig. 1, left panel) are also expected to become Li-rich but only in the late AGB phase when the many TP and TDU episodes would favour an enhancement of s-process elements like Rb (and Zr), which is not observed (see Sect. 4). In short, we conclude that our observations of super Li-rich AGBs are consistent with AGB stars of ~4–6  $M_{\odot}$  at the beginning of the TP phase. The situation may be more complex for the AGB star RU Cyg with  $\log \varepsilon(\text{Li}) = 2$ . This star is probably in an inter-pulse period, on its way to becoming a super Li-rich star, or has just been one. An early AGB stage for these blue HBB-AGB stars is also suggested by other observational properties such as the low changing periods, low infrared excess, and no OH maser emission (Table A.1) and seems to be corroborated by the specific s-process nucleosynthesis experienced by these stars (see below).

## 4. The s-process in massive AGBs at the beginning of the thermally-pulsing phase

Remarkably, the three bluer AGBs display high Li overabundances accompanied by very weak or no Rb and Zr enhancements (Table A.1) while the redder OH/IR AGB RU Ari shows a chemical abundance pattern (high Rb together with no Li and weak Zr) that is typical of Rb-rich massive Galactic AGBs where the <sup>22</sup>Ne neutron source dominates the s-process nucleosynthesis (García-Hernández et al. 2006, 2007). It is to be noted here

<sup>&</sup>lt;sup>3</sup> The atomic parameters were taken from Palmeri et al. (2005).

<sup>&</sup>lt;sup>4</sup> We mote that the O-rich and Tc-poor (M-type) AGB star R Nor was previously found to be extremely enriched in Li (with  $\log \varepsilon(\text{Li}) = 4.6$ ) by Uttenthaler et al. (2011). The star R Nor (with  $T_{\text{eff}} = 3000 \pm 100$  K) is a spectroscopic twin of R Cen. Our spectrum synthesis confirms that R Nor is a super Li-rich (with  $\log \varepsilon(\text{Li}) = 4.0$ ) AGB with no (or weak) Zr ( $\log \varepsilon(\text{Zr}) = 2.6 \pm 0.2$ ) enhancement. However, the R Nor spectrum does not cover the Rb I lines at 7800 and 7947 Å. We expect R Nor to be non-enriched in Rb, being another example of super Li-rich massive AGBs at the beginning of the TP phase (see text).

that the [Rb/Zr] ratios observed in Rb-rich massive OH/IR AGBs such as RU Ari are much larger than predicted by the s-process models (see García-Hernández et al. 2009). The authors van Raai et al. (2012) discuss several possibilities (e.g. a failure of the present model atmospheres which may give to Rb overestimations, condensation of Zr to dust, etc.) that could explain this Rb/Zr mismatch. However, the situation is very different in the super Li-rich massive AGB stars presented here. These stars are very blue (little circumstellar dust, no OH maser emission) and are not as extreme as the more evolved and Rb-rich AGBs. Thus, the present model atmospheres and the derived abundances in the super Li-rich massive AGBs are expected to be more reliable (see also Sect. 2).

The short-lived element Tc (usually used as an indicator of an intrinsic AGB star, see below), however, is not detected (i.e.  $\log \epsilon(Tc) < 0$ ) in all sample stars<sup>5</sup>. The lack of Tc can be explained by the operation of the <sup>22</sup>Ne neutron source in massive AGB stars. The s-process nucleosynthesis models that better reproduce the large Rb overabundances observed in these stars are the delayed superwind models by Karakas et al. (2012), where the production of s-process elements is dominated by the <sup>22</sup>Ne neutron source. Their solar metallicity 5 and 6  $M_{\odot}$  models show that the super Li-rich phase is reached at the beginning of the TP phase, but it is not until much later (i.e. by the 33rd and 30th TP, respectively) that the s-process abundances (e.g. Rb) start to rise. Interestingly,  $\log \varepsilon(Tc) < 0$  during all AGB evolution. This is shown in Fig. 1 (right panel) where we display the Rb, Zr, and Tc predictions for a 5  $M_{\odot}$  model with a delayed superwind (Karakas et al. 2012). The activation of the <sup>13</sup>C neutron source predicts a much higher and faster Tc production (also Zr production but at a much slower rate), which is not observed. Models that include a <sup>13</sup>C-rich region (the <sup>13</sup>C pocket) in the He intershell of massive AGB stars (see Karakas et al. 2012; Lugaro et al. 2012) predict a fast increase of the Tc abundance at the beginning of the TP phase or during the super Li-rich phase; e.g.  $\log \varepsilon(\text{Tc}) > 0$  by the 13th TP in a 5  $M_{\odot}$  model (see Fig. A.4). The production of Tc depends on the neutron exposure experienced by the intershell material, specifically, if its value is high enough to allow bypassing the first s-process peak at Sr, Y, Zr to reach Tc. The neutron exposure from the  $^{22}$ Ne source builds up in time, pulse after pulse, which is why the Tc abundance linearly increases with the pulse number. On the other hand, the neutron exposure in the <sup>13</sup>C pocket is larger and the same in each <sup>13</sup>C pocket, which means that Tc is already produced in the very first <sup>13</sup>C pocket. Thus, we conclude that the lack of Tc in massive AGB stars is the consequence of <sup>22</sup>Ne being the dominant neutron source at the s-process site, as predicted by Goriely & Siess (2004).

The detection of Tc in s-process enriched (MS-, S-, SC-, and C-type) AGB stars has been widely used as an indicator of AGB genuineness ("intrinsic" stars), while its non-detection is indicative of binary systems ("extrinsic" stars; see e.g. Van Eck & Jorissen 1999; Abia et al. 2002). This is correct if the <sup>13</sup>C neutron source dominates the s-process nucleosynthesis, as in low-mass (~1-3  $M_{\odot}$ ) AGB stars. However, we have shown here that the use of Tc as an indicator of AGB genuineness is not valid for more massive AGB stars for which the <sup>22</sup>Ne is the dominant neutron source. Notably, many O-rich (M-type) Mira-like stars without Tc, among them our sample star R Cen, were found by Little et al. (1987). We propose that an important fraction of these Tc-poor stars may be super Li-rich massive AGBs at the beginning of the TP phase. Indeed, Little et al. (1987) found that  ${}^{12}C/{}^{13}C \sim 8$  for the three Miras without Tc in their sample, which is very near to the equilibrium value expected for strong HBB AGB stars.

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<sup>&</sup>lt;sup>5</sup> We note that the detection threshold for Tc in AGB stars is  $\log \varepsilon(\text{Tc}) \sim 0$  (see Fig. 15 in Goriely & Mowlavi 2000).

## Appendix A: Table A.1 and Figs. A.1–A.4

Table A.1. Sample of early massive AGBs: spectroscopic  $T_{eff}$  and derived Li, Rb, and Zr abundances<sup>*a*</sup>.

Star	Gal. Coor. (l, b)	T <sub>eff</sub> K	$\log \varepsilon(\text{Li}) \\ \log N(\text{Li}) + 12$	$\log \varepsilon(\text{Rb}) \\ \log N(\text{Rb}) + 12$	$\log \varepsilon(\text{Zr}) \\ \log N(\text{Zr}) + 12$	Tc	Period <sup>b</sup> (days)	Masers SiO/H <sub>2</sub> O/OH	Ref. <sup>c</sup>
RU Cyg	(97.37,+1.20)	3000	$2.0 \pm 0.5$	$<2.6 \pm 0.3$	$2.6 \pm 0.2$	No	442	No/No/No	1/1/1
SV Cas	(111.83, -9.04)	3000	$3.5 \pm 0.5$	$2.6 \pm 0.3$	$2.7 \pm 0.2$	No	456	No//	2//
R Cen <sup>d</sup>	(313.42, +1.21)	3000	$4.3 \pm 0.5$	$2.6 \pm 0.3$		No	251	No/Yes/No	1/1/1
RU Ari	(161.47, -41.90)	3000	No	$4.5 \pm 0.7$	${<}2.6\pm0.2$	No	357	Yes/Yes/Yes	3/1/1

**Notes.** <sup>(a)</sup> The abundance uncertainties represent the formal errors due to the sensitivity of the derived abundances to slight changes in the model atmosphere parameters ( $\Delta T_{\text{eff}} = \pm 100 \text{ K}$ ,  $\Delta [M/H] = \pm 0.3$ ,  $\Delta \xi = \pm 1 \text{ km s}^{-1}$ ,  $\Delta \log g = +0.5$ ,  $\Delta FWHM = 50 \text{ mÅ}$ ) for each star. <sup>(b)</sup> Present-day pulsation periods derived by us from AAVSO data. <sup>(c)</sup> References for the SiO, H<sub>2</sub>O, and OH maser observations. <sup>(d)</sup> R Cen was not observed around the ZrO 6474 Å bandhead, but its spectrum around the weaker (and less sensitive to the Zr content) ZrO bands near 6925 Å is identical to the other stars.

References. (1) Benson et al. (1990); (2) Spencer et al. (1981); (3) Deguchi et al. (2012).



**Fig. A.1.** High-resolution optical spectra (in black) and best model fits (in red) in the Li I 6708 Å region (*left panel*) and Rb I 7800 Å region (*right panel*) for the AGB stars RU Ari, R Cen, SV Cas, and RU Cyg. The derived Li and Rb abundances (in the usual scale log N(X) + 12) are indicated. Synthetic spectra obtained for Li and Rb abundances shifted +0.5 dex (in blue) and -0.5 dex (in green) (these values are ±1.0 for Li in R Cen and SV Cas) from the adopted values are also shown. We note that Li is not detected in the extreme OH/IR AGB star RU Ari, which displays a strong Rb I line that is not detected in the other stars.



**Fig. A.2.** High-resolution optical spectra (in black) and best model fits (in red) in the ZrO 6474 Å region (*left panel*) and the Tc I 5924 Å region (*right panel*) for the AGB stars RU Ari, SV Cas, and RU Cyg. The derived Zr abundances and Tc upper limits (in the usual scale  $\log N(X) + 12$ ) are indicated. Synthetic spectra obtained for Zr abundances shifted +0.5 dex (in blue) and -0.5 dex (in green) from the adopted values are also shown. For the less sensitive Tc I 5924 Å line, synthetic spectra obtained for Tc abundances shifted +5.0 dex (in blue) are shown. We note that none of the stars are in our sample is found to be enriched in Zr or Tc.



**Fig. A.3.** High-resolution optical spectra of the non-Tc AGB star R Cen (in black; this paper) and the Tc AGB star S Her (in red; taken from Uttenthaler et al. 2011) around the Tc I line at 4238 Å. The wavelength of the Tc line is marked with a dashed vertical line. We note that S Her displays a strong Tc I line that is completely absent in R Cen.



Fig. A.4. Temporal evolution of the Li, Rb, Zr, and Tc abundances as predicted by the HBB-MLT 5  $M_{\odot}$  model with a <sup>13</sup>C-rich region (the <sup>13</sup>C pocket) and a delayed superwind (Karakas et al. 2012). We include a  ${}^{13}\hat{C}$  pocket by inserting protons into the top of the He-intershell (with a mass =  $1 \times 10^{-4} M_{\odot}$ ) at the deepest extent of each TDU episode. We refer to Karakas et al. (2012) and Lugaro et al. (2012) for details of this procedure. Tc (also Zr although at a slower rate) is quickly produced by the <sup>13</sup>C neutron source;  $\log \varepsilon(Tc) > 0$  at the beginning of the super Li-rich phase (log  $\varepsilon$ (Li) ~ 4). The evolution of Rb is not greatly affected by the inclusion of the <sup>13</sup>C pocket, but Zr is more affected, being even more abundant than Rb during the super Li-rich phase. We note that the Tc abundance is an upper limit because the trend of the half-life of 99Tc, decreasing with the temperature, is not included. However, the difference would be very small because the 99 Tc half-life changes only from terrestrial 0.22 Myr to 0.11 Myr at the temperature of 100 MK typical of the <sup>13</sup>C pocket, which means that <sup>99</sup>Tc behaves as a stable nucleus during this neutron flux.