COMPLEX ORGANIC AND INORGANIC COMPOUNDS IN SHELLS OF LITHIUM-RICH K GIANT STARS

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ABSTRACT

Hydrocarbon organic material, as found in the interstellar medium, exists in complex mixtures of aromatic and aliphatic forms. It is considered to originate from carbon-enriched giant stars during their final stages of evolution, when very strong mass loss occurs in a few thousand years on their way to becoming planetary nebulae. We show here that the same organic compounds appear to be formed in previous stages of the evolution of giant stars, more specifically, during the first-ascending giant branch K-type stars. According to our model, this happens only when these stars are being abruptly enriched with lithium, together with the formation of a circumstellar shell with a strong mass loss during just a few thousand years. This sudden mass loss is, on average, a thousand times larger than that of normal Li-poor K giant stars. This shell would later be detached, especially when the star stops its Li enrichment and a rapid photospheric Li depletion occurs. In order to gain extra carbon-based material to form the organic hydrocarbons, as well as to explain the presence of complex inorganic compounds in these stars, we propose an interaction of these strong winds with the remaining asteroidal/cometary disks that already existed around these stars since they were dwarf A-type stars. The mechanism of interaction presented here is successful in explaining the presence of inorganic compounds; however, it is unable to produce new carbon-free atoms to form the organic hydrocarbon compounds. Finally, we discuss some suggestions and speculations that can eventually help solve the long-standing puzzle of Li-rich giants.

Key words: astrochemistry – stars: evolution – stars: late-type – stars: winds, outflows

1. INTRODUCTION

Since the late 1970s, organic compounds have been detected by means of unidentified infrared emission (UIE) in several cosmic environments, e.g., the interstellar medium (ISM), galaxies, post-AGB stars, pre-planetary nebulae (PPNs), and young protoplanetary disks (Bauschlicher et al. 2009; Cerro-gone et al. 2009; Acke et al. 2010; García-Hernández et al. 2011; Salama et al. 2011; Li & Draine 2012). Nevertheless, the mechanisms for the formation of these compounds are still obscure, and the nature of the carriers of UIE is still under debate (Kwok & Zhang 2011, 2013). Are they free-flying gas molecules of polycyclic aromatic hydrocarbons (PAHs) or solid mixed aromatic/aliphatic organic nanoparticles (MAONs)? Hydrocarbons are very rarely detected in oxygen-rich giant stars, except for some post-AGB binaries with circumstellar disks (Giielen et al. 2011) or some planetary nebulae (Guzman-Ramirez et al. 2014). Among the first-ascending giant stars, aromatics were detected, for the first time, in the super Li-rich K giant HD 233517 (Jura et al. 2006). These authors invoked a hypothetical recently formed disk to explain the presence of aromatics. In this paper, we supplement our model of connecting Li enhancement and infrared excesses (de la Reza et al. 1996, 1997; de la Reza & Drake 2012) with the Spitzer mid-infrared spectra of seven Li-rich K giants. In addition to the hydrocarbon organic compounds, we report here the presence of peculiar inorganic compounds in the spectra of first-ascending K giant stars. In fact, these spectra are completely different from those of normal K giants (Sloan et al. 2015). We propose that oxygen-rich K giants, which are also momentarily Li rich, can eventually obtain new carbon by partially perturbing disks around them, and thus form hydrocarbons. These disks are the debris disks that have existed since the stars were ~A5 dwarfs (de la Reza & Chavero 2014). As they suddenly become Li-rich, owing probably to the processes that are described in Section 4, there is a mass-loss ejection of dust and gas that is, on average, a thousand times larger than that occurring in a normal K star in the first-ascending giant branch. This mass loss leads to the formation of a circumstellar shell. In de la Reza & Drake (2012) it is proposed that this shell emerges from the stellar surface and remains attached to the star during the Li-enrichment phase but gets detached and ejected when the Li enrichment ceases. The photosphere of the star with a detached shell depletes rapidly, attaining the normal low Li abundance of K giant stars. This fast Li-rich episode occurs at the rate of 1% of Li-rich K giants in the Galaxy (Kumar et al. 2011; de la Reza & Drake 2012) and thus appears to be a universal phenomenon. This means that all K giant stars could pass by this short Li-rich episode, since the same rate has been found in other galaxies (Kirby et al. 2012).

The proposed shell-disk interaction model is used to explain the several features of inorganic origin of K giants shown in this work. This is the first time, to our knowledge, that a collection of emission-line features superposed on a strong continuum emission (see Section 2) is detected in first-ascending giant stars. These spectra were discovered in the Spitzer Space Telescope archive, and our main motivation in this work is to discuss possible reasons for their presence.

2. THE OBSERVED MID-IR SPECTRA

2.1. Observations

This work is based on the mid-IR spectra of seven K giant stars. Five of them are first-ascending giant stars (red giant branch [RGB]): HD 233517, PDS 365 (IRAS 13313-5838),
PDS 100 (IRAS 19285+0517), PDS 68 (IRAS 13539-4153), and IRAS 17596-3952. The two remaining stars, IRAS 12327-6523 and IRAS 17582-2619, can be classified as early-AGB stars. Two other K giant stars, HD 30834 and HD 146850, are also considered, for comparison purposes. All spectra shown here were obtained from archives of the Cornell Atlas of...
Spitzer/IRS sources (CASSIS; Lebouteiller et al. 2011). All the spectra were observed in the wavelength interval of 5–38 \( \mu m \), with the exception of IRAS 17582-2619, which shows data from 5 to 13 \( \mu m \) only. The spectra of four RGB stars, PDS 365, PDS 100, PDS 68, and IRAS 17596-3952, all of which have the property of being Li-rich or super Li-rich giants, are presented in Figure 1. A similar spectrum of HD 233517 can be seen in Jura et al. (2006). In Figure 2, even more detailed parts of the spectra of PDS 365 and PDS 100 are presented, showing the spectral emission feature at 6.26 \( \mu m \). The spectra of the two early-AGB stars are presented in Figure 3, and the structureless spectra of the two comparison Li K giant stars HD 30834 and HD 146850 are shown in Figure 4. All spectra were observed in 2006, except that of IRAS 17582-2619. The latter was observed in 2007. CASSIS considers the sources as point-like, except for PDS 365, which is taken as an extended source of \( \sim 2'' \), and IRAS 17596-3952 (\( \sim 3'' \)). Appropriate best extractions have been applied individually by CASSIS. We performed order and flux matching (for different aperture sizes) to the extracted spectra.

2.2. Stellar Properties and Compositions

Some of the main stellar properties of the seven Li-rich K giant stars are presented in Table 1. Out of the five RGB stars, three are located at the luminosity bump, and the other two (PDS 68 and HD 233517), the two super Li-rich stars, are located very near to this luminosity bump region. This is the region where the giant star locally slows down its evolution, and it corresponds to stellar luminosities and effective temperatures of \( \log(L/L_\odot) = 1.45–1.90 \) and \( T_{\text{eff}} = 4450–4600 \) K (Kumar & Reddy 2009). The remaining two stars are early-AGB stars, having the lower limit of Li abundance of Li-rich giant stars. The Li abundance \( \log \epsilon (\text{Li}) \) is measured with respect to the number of hydrogen atoms with \( \log \epsilon (\text{H}) = 12. \) The standard theory of stellar evolution predicts a maximum of \( \log \epsilon (\text{Li}) = 1.4 \) for the RGB phase of stars as the Li is expected to be depleted (Iben 1967, 1991).

In Table 1, together with some important stellar parameters, we have included the most important spectral UIE features with their respective and most probable aromatic, aliphatic, and inorganic identifications. As an example, we show in Figure 2

\[ \log \epsilon (\text{Li}) = \log(N_{\text{Li}}/N_{\text{H}}) + 12. \]  

The Li abundance in the ISM is \( \log \epsilon (\text{Li}) = 3.2. \)

The aromatic features at 6.26 \( \mu m \) of two stars from this work. In general, aromatic features appear as narrow structures, and aliphatic plateaus are broad in mid-IR spectra (Kwok & Zhang 2011, 2013). Also, a new condition is observed here, with aromatic and aliphatic compounds coexisting and developing in the absence of a strong UV radiation. We find that UIE features appear in the mid-IR spectra, as is the case of RGB stars, only in those stars that have a strong continuum emission, in agreement with the general cases mentioned by Kwok & Zhang (2013). This continuum emission is clearly seen in all spectra of the Li-rich RGB stars, from 5–10 \( \mu m \) up to 38 \( \mu m \) as shown in Figure 1.

As mentioned in Section 1, two problems are faced here. One is that of the origin of the organic compounds, which are considered to be formed a priori in the shells. The other is the origin of the inorganic compounds, which, at least for the five RGB stars, could be the result of the wind-disk interaction that will be discussed in Section 3.

To our knowledge, no organic compounds have been found in debris disks, even in young objects such as HR 4796 A (Köhler et al. 2008), but only in gas-rich protoplanetary disks. We then consider that the organic compounds are probably formed in the shell winds. The UIE phenomenon is a complex one (Kwok & Zhang 2013), and we are still far from understanding the detailed formation of these UIE features.
corresponding to the organic compounds presented in Table 1. Identifying the carriers of these UIEs and selecting one of the two scenarios mentioned in Section 1 is the first step toward making progress in this field. Are these UIE carriers 2D free-flying PAH molecules? Or are they 3D solid structures like amorphous nanoparticles (MAONs) containing a much larger number of carbon atoms than those of PAHs? This subject has been largely discussed in Kwok & Zhang (2013). In this work, we find two important observed properties that are in favor of the MAON scenario, in agreement with the conclusions of Kwok & Zhang (2011, 2013). One of them is the strong correlation found here between the presence of UIE in the RGB star’s spectra and the presence of a strong underlying continuum in emission. This is because this continuum can only be due to large (micron-sized) solid state particles. The second property is that we detected 8 and 12 μm plateau features (see Table 1) that, according to Kwok & Zhang (2013), are of aliphatic origin and would have no place in the PAH scenario.

All these evidences lead us to propose that the mechanism for formation of the organic compounds in the emerging shells of Li-rich K giant stars has some similarities to those found in carbon-rich PPNs. These similarities are (1) the presence of a negligible UV continuum radiation in both cases and (2) that this phenomenon requires similar formation timescales, of the order of a few thousand years. The differences are that in the case of the PPNs, stellar mass losses are two orders of magnitude larger than in the case of these Li-rich K giant stars. Also, carbon particles are intrinsically part of the winds in the case of carbon-rich PPNs, whereas in our scenario of Li K giant stars, carbon is supposed to, in principle, come from the wind shell interaction with disks.

### 3. THE SHELL-DISK INTERACTION MODEL

In the 1990s Gregório-Hetem et al. (1993) realized that a large majority of Li K giant stars were IR sources measured by *IRAS*. In a diagram based on fluxes at 12, 25, and 60 μm, they found that these sources were distributed in mainly two regions: one of them formed by faint visual stars characterized by excesses at 25 μm, and the other one formed by bright stars with excesses at 60 μm. There is also a third region constituted by normal Li-poor K giant stars without IR excesses. In de la Reza et al. (1996, 1997) we constructed a simple model connecting those three regions. This model considered that departing from the non-IR excess region, each star being recently and abruptly enriched with 7Li, is related to the ejection of a shell of gas and dust from the star to the ISM. In this way, the shell near the star radiates at 25 μm, whereas far away it radiates at 60 μm. When the shell is completely ejected, the star returns to the origin, closing the loop of these changes. In de la Reza & Drake (2012) we introduced a more realistic description of the emergence of the shells. In Figure 5 we present this model, and the figure caption gives more details on the model. With the selected values in the figure, a complete loop is realized in ~80,000 yr. This model can be verified either by directly imaging these shells or by analyzing their spectra at corresponding wavelengths. This is what we are trying to do in the present work by means of spectra centered at ~25 μm. Let us invoke a wind shell-disk interaction scenario to explain the presence of complex inorganic compounds observed in the shells and to examine how to obtain extra free carbon-based material, eventually necessary to produce the organic compounds. Because we are facing short timescales, but very strong winds, with mass losses about 1000 times larger than those of normal RGB stars, we only consider here the stellar wind drag acting on a debris disk, supposedly the residual disk from when the K giant star was an A-type star in the main sequence.

The emerging shells, supposedly spherical and attached to the star at this stage, could result from a sudden internal transport of matter connected with an also sudden 7Li enrichment of the stellar surface (see Section 4). Following our model, this is represented by the stars labeled in red in Figure 5. These circumstellar shells can reach distances of the order of 800 AU, with a minimum expansion velocity of 2 km/s during 2000 yr (de la Reza & Drake 2012). Then, any body b of a disk rotating around the central star will suffer, in principle, a drag during the time period that is the lifetime of the shell. It is only during this period that the radiation emitted by the shell is concentrated in the mid-IR region, the explored spectral region of this work.
estimate the critical radius of the body suffering the drag as
\[
R_b^C \approx \left( \frac{3 M_\odot}{16\pi} \right) V_w^{-1} D^{-5/2} \rho_b^{-1} G^{1/2} (M_b^{1/2}) \Delta t. \tag{2}
\]

Any body with a radius larger than \( R_b^C \) will not suffer the drag and will survive at the corresponding distance \( D \). In this scenario, it is expected that a debris disk of a dwarf A-type star entering into the post-main-sequence phase could suffer important transformations in its structure. In fact, detecting debris disks in the RGB phase is a difficult task (Bonsor & Wyatt 2010). This is probably due to their less dusty material. More success can be obtained when observing sub-giant stars, especially those hosting planets.

Typical main-sequence debris disks are appropriate for our case as those spatially resolved corresponding to A3–A6 stars, such as those belonging to the star \( \beta \) Pictoris (Vandenbussche et al. 2010) and HR 8799 (Su et al. 2009; Matthews et al. 2014). These disks have an internal radius smaller than 10 AU and an external radius near 2000 AU. We can now estimate the value of the critical radius \( R_b^C \) for our case by considering typical values as those presented in Figure 5. We have \( M_b = 10^{-7} M_\odot \) yr\(^{-1} \), \( V_w = 2 \) km s\(^{-1} \). All kinds of stellar photospheric rotational velocities are represented here, even with a smaller fraction of rapid rotators (Drake et al. 2002). Here the axes are defined by \( \lambda_3 = \lambda_1 \), \( \log(\lambda_3) \), \( \log(\lambda_3) \), where \( \lambda_3 \) is the density flux. In general, at the right part of the diagram, where the shells labeled in red are located, are faint and distant K giants that have been detected as a sub-product in the PDS survey, dedicated to searching for \( \beta \) Tauri type stars (Gregorio-Hetem et al. 1992; Torres et al. 1995). On the contrary, objects at the left part are bright and nearby K giants. Due to this different space volume in the Galaxy, we were able to detect in the right part generally more rare K giants presenting rapid processes, as is the case here of the recent emergence of a shell characterized by an excess at 25 \( \mu \)m in times of 1000-2000 yr following the model. Also, because of this, the nearby shells at the left show longer phenomena up to 80,000 yr. Here these shells appear detached with excesses only at 60 \( \mu \)m. Note that at the shell emergence region at the right of the diagram, almost all objects are Li rich. This is not the case at the left, where there exist several Li-poor K giants rapidly Li depleted following the model, with a vanishing shell.

If we consider a star with a mass \( M_e \) and a shell formed by a mass loss \( M_b \), the gas/dust wind density will be \( \rho_w = M_b / 4 \pi D^2 V_w \), where \( V_w \) is the wind velocity and \( D \) the distance of body in the disk to the central star. Let us consider the mass loss \( M_e \) of a star, defined as the rate of shell mass encountered by a spherical body in the disk with radius \( R_b \) and density \( \rho_b \). This encountered rate is defined by \( M_e = (\pi/2) R_b V_b \), where \( V_b = (GM_e/D)^{1/2} \). By replacing \( \rho_w \) and \( V_b \) and integrating over the wind lifetime \( \Delta t \), we obtain

\[
M_e \approx R_b^2 \left( \frac{M_b}{4\pi} \right) \left( \int_{V_w} D^{-5/2} \rho_b^{-1} G^{1/2} (M_b)^{1/2} \Delta t \right). \tag{1}
\]

If \( M_e \) of the shell is equal to the mass of the body, this can suffer the drag, lose momentum, and will spiral toward the star. In this case we have \( M_e = 4\pi \rho_b R_b^3 / 3 \), which enables us to
The case. As far as the internal models are concerned, the most these stars would be predominantly rapid rotators, which is not strong emissions at 10 and 18.5 emission typical of RGB stars. Its spectrum contains two 12327-6523 appears not to present a strong continuum possible amorphous inorganic material that could originate its own stellar wind. Because of its low mass loss, it is expected that crystallization is inefficient due to the lower dust formation temperatures expected for these low mass rates (Suh 2002). The other star, IRAS 17582-2619, even with a short observed spectral interval, appears to show an increasing emission continuum (Figure 3, right panel). We have tentatively identified the emission at 8.7 μm as an aliphatic plateau.

All the shell spectra discussed up to now represent emerging shells attached to the stars, which are represented by red points in Figure 5. Nevertheless, the spectra of the two Li K giant stars HD 30834 and HD 146850 shown in Figure 4 are completely different. They are characterized by the absence of a continuum in emission and also by the total absence of UIE features. The shapes of these structureless spectra are similar to those of ordinary K giants (Sloan et al. 2015). The positions of these two objects in Figure 5 (blue points) indicate for our model that their shells are already detached, leaving free the zone that would emit at ~25 μm and emitting only at 60 μm far away from the star.

Finally, it is important to mention that the shell-disk interaction can introduce a non-spherical geometry in our scenario and show important optical polarization signals. In fact, two of our sources, PDS 100 and PDS 68, exhibit a large degree of polarization (Pereyra et al. 2006).

4. SOME CONSIDERATIONS ON THE LITHIUM ENRICHMENT PROCESSES

More than 30 yr have elapsed since the discovery of the first Li-rich K giant star, and no self-consistent models have appeared explaining this Li-enrichment phenomenon excluded by the standard theory of stellar evolution. Stellar internal or external scenarios have appeared trying to solve this “Li-rich puzzle.” Concerning the external approach based in general on the engulfing of a planet (Siess & Livio 1999), strong observational evidences have worked against this scenario, such as the absence of a simultaneous 6Be and 6Li enrichment together with 7Li. Also, due to the gain of planet momentum, these stars would be predominantly rapid rotators, which is not the case. As far as the internal models are concerned, the most appropriate for the cyclical model discussed here, the situation is the following: all scenarios are based on the Cameron–Fowler 6Be mechanism (Cameron & Fowler 1971) to create new 7Li. However, all low-mass stellar models, as is the case here, require a rapid outward transport of the 7Be in order to avoid its destruction before it could decay into 7Li in the cool external convective envelope (CE) and enrich the stellar surface with fresh 3Li. Theoretical difficulties arise by the fact that, in the absence of a rapid mixing mechanism, the models respond well, explaining the enrichment of other elements such as 13C and also the normal 7Li depletion. However, different 1D evolution codes used for the 7Li depletion seem to produce different Li abundances (Lattanzio et al. 2015). The two scenarios, a rapid and a slow mixing, are then somewhat opposite. To conciliate them, the rapid process must be concentrated in short evolutionary episodes in an otherwise normal slow and long evolutionary process. This is what we propose in this work.

Eggleton et al. (2008) detected the appearance of an instability relating the top of the H-burning zone and the bottom of the CE by means of 3D stellar models of low-mass giants. This non-convective mixing is produced by the reaction 3He (3He, 2p) 4He on top of the H-burning zone, inducing a molecular weight inversion. This happens precisely at the luminosity bump (LB), where we found all the RGB Li-rich K giants reported in this paper. This mixing process is supposed to destroy a large part of the 3He. However, if under certain short timescales part of 4He is used to create 7Be by means of 7Be (e−, νν) 7Li. Nevertheless, the velocities of 1 ms−1 proposed by Eggleton et al. (2008) are probably not large enough to produce the required excess of 7Li. At this point, we can speculate and explore a new mechanism for this rapid transport. This is achieved by relating this scenario to the internal angular momentum (AM) loss necessary to reduce the stellar core rotation of these giant stars. In fact, recent asteroseismology measurements of the CoRoT and Kepler satellites have shown that at the sub-giant stages, the stellar cores appear to suffer a spin-up (Deheuvels et al. 2014). This spin-up is transformed into an important core spin-down at a later stage when the stars advance in the RGB (Mosser et al. 2012). These low core rotations appear at the upper RGB and in the He-burning clump giants (Cantiello et al. 2014). These two regions are where Li-rich K giants exist. We speculate that the internal AM transport mechanism—whatever it is—can act in a continuous way but has peaks at the LB in order to produce the Li enhancement, while the gain of AM by the envelope could eventually produce the observed shells presented in this work.

As far as the more massive (2 M⊙) clump Li-rich giants are concerned (see, e.g., Carlberg et al. 2014), the phenomenology can be different because these stars, having already experienced the He flash, can eventually generate hydrogen flashes (Schlattl et al. 2001) that could be involved in the 7Li creation and contribute to the reduction of the core rotation velocities.

5. RESULTS AND CONCLUSIONS

We detected several emission lines related to hydrocarbon organic and other inorganic materials in the Spitzer mid-IR spectra of seven K giant stars. Five of them are first-ascending giants, and two are apparently early-AGB stars. These emission features appear, especially in the case of the RGB stars, superposed to a strong underlying continuum emission between 5 and 38 μm. To our knowledge, this is the first time, at least for first-ascending giant stars, that this collection of continuum and lines in emission is found. Concerning the five RGB stars,
all of them are Li-rich or super Li-rich, even reaching very high Li abundance values \((\log e(\text{Li}) = 4.3)\). Also, all of them are located at or very near the luminosity bump. We suggest that the continuum emission in the RGB stars is due to an emerging circumstellar shell attached to the star that is associated with the rapid Li surface enrichment. This emergence process, as indicated in our model represented in Figure 5 by stars with red labels, occurs in very short episodes \((\text{of the order of } 1000–2000 \ \text{yr})\). A general, internal stellar evolutionary process that can eventually be at the origin of this rapid Li enrichment, together with a circumstellar shell formation, is discussed in Section 4.

The hydrocarbon organic compounds, consisting of aromatic and aliphatic components, are supposed to be formed in the winds of the expanding shell. The details of this formation are, however, unknown, but we consider that they could be formed in a similar way to that in carbon-rich PPNs. This is because the timescales are similar in both cases and also both evolved without the presence of a strong UV radiation field. Further, in contrast to the carbon-rich PPN scenario, we are here in a case of dual chemistry in which hydrocarbons are formed in an oxygen-rich wind.

We postulate a priori that a source of fresh carbon, to supply the formation of organic compounds in the shell, could be the result of shell wind dragging on a debris disk surviving from the main-sequence stage when these giants were A-type dwarfs. We are unable, however, to find a physical process that can furnish new carbon in our shell-disk scenario. However, because these organic features are observed, this leaves an open possibility that the used carbon could be that of the original star itself. This problem can possibly be solved in the future, when the carriers of organic UIE features will mostly be definitively discovered. These are 2D free-flying PAH molecules or 3D solid MAONs.

In this work we found properties supporting the MAON scenario by observing pure aliphatic plateaus and, mainly, by finding a strong correlation between UIE features and a strong underlying emission continuum in the five RGB stars. This continuum emission would be due to the emission of micron-sized solid state particles forming the circumstellar shells according to the MAON scenario.

Nevertheless, the action of this shell-disk interaction is successful in explaining the presence of the observed inorganic compounds in the shell. This is due to the effect of the dragging action on expected disks in the RGB phase. Due to the short \((1000–2000 \ \text{yr})\) action of a strong wind, correlated to the Li stellar enrichment, with mass-loss values more than 1000 times that of the normal mass loss of a giant star, only the inner parts of the debris disks are eroded. This dragging process removes particles less than some centimeters in size, leaving larger bodies unaltered. All these small particles, at least those in the micron-sized scale, remain in the expanding shell during the very rapid stages observed in these emerging new Li stars. The existence of these micron-sized particles is, in fact, inferred by the observation of the continuum emission spectra in all the RGB stars. Also the presence of micron-sized particles is observed in a direct case of shell-disk interaction. This is the case of one of the super Li-rich RGB stars, where micron-sized crystalline enstatite particles, typical inner debris disk particles, are injected into the shell. We also expect that this wind-disk interaction can, in principle, form non-spherical geometries that could be detected with ALMA. Furthermore, optical polarimetric observations showed that at least two stars (one is the star showing the enstatite signatures) of these emerging very Li-rich giants exhibit polarization signals.

We can conclude that if this episodic Li-enrichment process is indeed a universal phenomenon as evidenced by Galactic and extragalactic observations, we are facing a new source of organics in the ISM.

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