

# Long chain *n*-alkanes and their carbon isotopes in lichen species from western Hubei Province: implication for geological records

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**Abstract** Five coticolous lichen samples were collected from western Hubei Province of China to analyze the long chain *n*-alkanes and their carbon isotope compositions. The *n*-alkanes range in carbon number from C<sub>17</sub> to C<sub>33</sub> with strong odd-over-even predominance between C<sub>21</sub> and C<sub>33</sub>. Lichens are dominated by *n*-C<sub>29</sub> in the samples of Dajiuahu, Shennongjia Mountain, but by both *n*-C<sub>23</sub> and *n*-C<sub>29</sub> at Qizimei Mountain. This difference may result from the different environmental conditions in these two sites. The δ<sup>13</sup>C values of long chain *n*-alkanes in lichen samples show the signature of C3 plants. Based on compound-specific carbon isotopic values and previous results, we state that alkane homologs > C<sub>23</sub> mainly originate from the symbiotic fungi, while symbiotic algae only contribute trace amount of long chain alkanes. Of great interesting is the occurrence of long chain 3-methylalkanes in the Qizimei samples. These *anteiso* compounds range from C<sub>24</sub> to C<sub>32</sub>, displaying obvious even-over-odd predominance. This study reveals that the association of long chain 3-methylalkanes with *n*-C<sub>23</sub> alkane might be used as proxies to reconstruct the paleoecological implications of lichens in Earth history.

**Keywords** lichen, alkane, 3-methylalkanes, *n*-C<sub>23</sub> alkane, compound specific carbon isotope

## 1 Introduction

Lichens are composite organisms consisting of a fungus and an alga (usually a green alga or a cyanobacterium). The symbiotic alga provides carbon or nitrogen nutrient for the symbiotic fungus, while the symbiotic fungus provides

suitable humidity and sunlight condition for the symbiotic alga. Such symbiosis makes lichens very strong adaptation and stress resistance. Thus, lichens are often the first to settle in some extreme environments, such as deserts and Antarctica, and were early colonized plants of land in Earth history (Heckman et al., 2001; Yuan et al., 2005; Karatygin et al., 2009). However, the poor preservation as fossils hinders to investigate the evolution history of lichens and their effect on the early land ecosystem (Fu et al., 2007; Rikkinen and Poinar, 2008).

Previous researchers have investigated lichen lipids. Jia et al. (2008) conducted the analysis of neutral monosaccharides in several lichen species from a UK peat bog. Sasaki et al. (2005) analyzed carbohydrate, glycolipid and lipid components of the photobiont of *Dictyonema glabratum*. Many studies also investigated the distributions of alkanes in extant lichen species (Gaskell et al., 1973; Catalano et al., 1976; Dembitsky, 1992; Zygadlo et al., 1993; Piervittori et al., 1996; Ficken et al., 1998; Torres et al., 2003; Goss and Wilhelm, 2009). To the best of our knowledge, no study has reported about lipids in Chinese lichen species, although the lichen diversity is high in China (Wu, 1987; Wei, 1991).

Long chain alkanes have been successfully used as chemotaxonomic tools of cyanobacteria (Köster et al., 1999), *Sphagnum* (Nott et al., 2000) and other higher plants (Schwark et al., 2002; Huang et al., 2011). In addition, compound-specific carbon isotopes can provide useful information to distinguish plant groups with different carbon metabolic pathways, such as C3 and C4 plants (Collister et al., 1994). In this study, we conducted the lipid analysis of several lichen species collected from the mountainous area of western Hubei Province. We focused on the long chain alkanes and their carbon isotopic features in order to develop the specific indicators of these lichen species.

## 2 Materials and methods

The lichen samples were collected from the Dajiuhe National Wetland Park and the Qizimei Mountain National Nature Preserve, western Hubei Province, China. The lichens habit on branches or stems of trees. Five samples including six species were investigated. Two samples, LI-2 and LI-4, are from a mixture of two species, respectively (Table 1).

After air-dried and crushed into small pieces, the pre-cleaned lichen samples were ultrasonically extracted with  $\text{CH}_2\text{Cl}_2$  (5 min, repeated four times). Internal standard (cholane, Chiron, Norway) was added before extraction. The extracts were fractionated into aliphatic, aromatic and polar fractions using silica column chromatography with hexane,  $\text{CH}_2\text{Cl}_2$  and methanol as eluting solvents, respectively.

The aliphatic fraction was analyzed by gas chromatography-mass spectrometry (GC-MS). A HP 6890 GC equipped with a DB-5MS column (60 m  $\times$  0.25 mm i.d., film thickness 0.25  $\mu\text{m}$ ) and interfaced to a HP 5973 mass selective detector was used. The oven temperature was ramped from 70°C to 210°C at 10°C/min and then to 300°C (held 30 min) at 3°C/min. He was used as carrier gas at a constant flow (1 mL/min). Compounds were identified by comparing with alkane standards and NIST02 library. Abundances were calculated by comparison of peak areas with those of known quantities standards.

The stable carbon isotope compositions of individual long chain *n*-alkanes were determined using a Finnigan Trace GC attached to a Finnigan Delta Plus XP isotope ratio mass spectrometer. Samples were injected in splitless mode (1  $\mu\text{L}$ ), with the injector temperature at 290°C. Separation was achieved using a DB-5MS column (60 m  $\times$  0.25 mm i.d., film thickness 0.25  $\mu\text{m}$ ). The GC oven temperature was programmed from 50°C (held 1 min) to 210°C at 10°C/min, and then to 310°C (held 20 min) at 2°C/min. He was the carrier gas (1.4 mL/min). Instrument performance was checked before and after each run using an *n*-alkane mixture with known  $\delta^{13}\text{C}$  values (Chiron, Norway). Reproducibility of the carbon isotope composition for specific compounds was better than  $\pm 0.5\text{‰}$  (standard deviation), based on at least duplicate analyses. Results are reported in the  $\delta$  notation (‰) relative to the Vienna Pee Dee Belemnite (VPDB) standard.

## 3 Results and discussion

### 3.1 *n*-alkanes

The lichen samples analyzed contain *n*-alkanes ranging from *n*-C<sub>17</sub> to *n*-C<sub>33</sub>, dominated by long chain homologs (*n*-C<sub>21</sub>–*n*-C<sub>33</sub>; Fig. 1). Such distribution pattern is consistent with previous results (Gaskell et al., 1973; Catalano et al., 1976; Zygadlo et al., 1993; Piervittori et al., 1996; Ficken et al., 1998; Torres et al., 2003). The long chain homologs show obvious odd-over-even predominance, with the carbon predominance index (CPI) being 3.5–8.2 (Table 2), a nature of typical higher plants (Ficken et al., 2000; Bi et al., 2005).

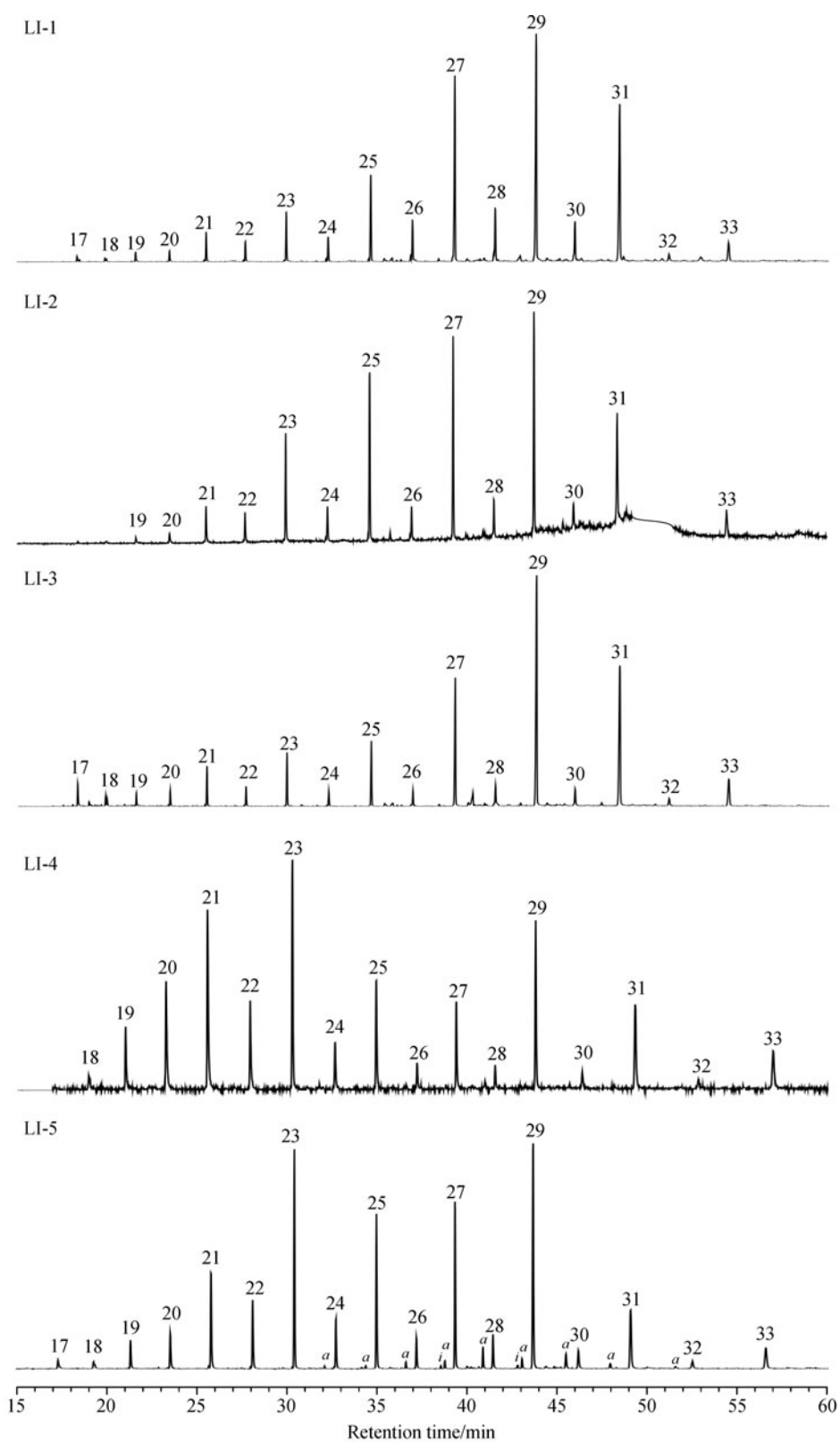
The short chain homologs may be derived from photobiont (cyanobacteria or green algae). Photobiont (*Scytonema* sp.) separated from *Dictyomema glabratum* contained *n*-alkanes with a predominance of homologs < C<sub>20</sub> (Sasaki et al., 2005). Cyanobacteria extracts normally contain high abundance of *n*-C<sub>17</sub> alkane (Han and Calvin, 1969). Gaskell et al. (1973) also observed methylheptadecanes, typical biomarkers of cyanobacteria (Köster et al., 1999), from lichen *Siphula ceratites* in Norway.

The long chain homologs in these lichen samples probably originate from mycobionts. A study (Torres et al., 2003) showed that the amount of alkanes in the mycobiont of *Xanthoria parietina* was one order of magnitude higher than that of their photosynthetic partner. The published fungal spores were all dominated by *n*-C<sub>27</sub>, *n*-C<sub>29</sub> and *n*-C<sub>31</sub> alkanes (Weete, 1972; Ladygina et al., 2006).

The distribution patterns of lichen alkanes are different between Dajiuhe and Qizimei, even for the same species such as *Ramalina intermediella* (Fig. 1). The three samples collected from Dajiuhe are all dominated by *n*-C<sub>29</sub> alkane, which is a common feature of published lichen alkanes. On the contrary, the two Qizimei lichen samples show bimodal distribution dominated by *n*-C<sub>23</sub> and *n*-C<sub>29</sub>. The bimodal pattern has not been reported in previous studies of lichen alkanes. Such difference may result from climate difference between the sampling sites. Dajiuhe has an annual mean temperature of 7.2°C and annual mean precipitation of 1560 mm, while the annual mean temperature is 8.9°C and annual mean precipitation is 1869 mm at Chunmuying Town, Qizimei. Thus, it is warmer and wetter in Qizimei

**Table 1** Plant species, sampling location, elevation and sampling time

	Species name	Location	Altitude/m	Time
LI-1	<i>Ramalina intermediella</i> Vain.	Dajiuhe	1700	September, 2009
LI-2	<i>Cetrelia olivetorum</i> (Nyl.) W.L. Culb. & C.F. Culb., <i>Parmotrema chinense</i> (Osbeck) Hale & Ahti	Dajiuhe	1700	September, 2009
LI-3	<i>Lobaria yunnanensis</i> Yoshim.	Dajiuhe	1700	September, 2009
LI-4	<i>Lobaria isidiosa</i> (Müll. Arg.) Vain., <i>Cetrelia chicitae</i> (W.L. Culb.) W.L. Culb. & C.F. Culb.	Qizimei	1900	August, 2009
LI-5	<i>Ramalina intermediella</i> Vain.	Qizimei	1900	August, 2009



**Fig. 1** The  $m/z$  85 chromatographs of alkanes in lichen samples. The numbers labeled on peaks refer the carbon number. 'a' refers anteiso-alkanes. 'i' refers iso-alkanes

**Table 2** The concentration ( $\mu\text{g/g}$  dry weight), CPI and ACL of *n*-alkanes in lichen samples

	LI-1	LI-2	LI-3	LI-4	LI-5
<i>n</i> -C <sub>17</sub>	0.1		0.4	0.1	0.2
<i>n</i> -C <sub>18</sub>	0.0		0.1	0.3	0.1
<i>n</i> -C <sub>19</sub>	0.2	0.1	0.2	0.7	0.4
<i>n</i> -C <sub>20</sub>	0.2	0.2	0.2	1.5	0.6
<i>n</i> -C <sub>21</sub>	0.5	0.5	0.6	2.4	1.4
<i>n</i> -C <sub>22</sub>	0.3	0.4	0.3	1.1	1.0
<i>n</i> -C <sub>23</sub>	0.8	1.4	0.8	2.6	2.8
<i>n</i> -C <sub>24</sub>	0.4	0.5	0.2	0.6	0.8
<i>n</i> -C <sub>25</sub>	1.5	2.3	1.0	1.3	2.2
<i>n</i> -C <sub>26</sub>	0.7	0.5	0.2	0.3	0.6
<i>n</i> -C <sub>27</sub>	3.5	2.7	2.2	0.9	2.5
<i>n</i> -C <sub>28</sub>	1.0	0.5	0.3	0.3	0.5
<i>n</i> -C <sub>29</sub>	5.0	2.9	4.9	1.9	3.9
<i>n</i> -C <sub>30</sub>	0.8	0.4	0.3	0.3	0.4
<i>n</i> -C <sub>31</sub>	4.0	1.8	3.7	1.5	1.8
<i>n</i> -C <sub>32</sub>	0.2	0.0	0.2	0.2	0.3
<i>n</i> -C <sub>33</sub>	0.6	0.6	0.8	0.8	0.9
CPI*	4.5	5.1	8.2	3.5	4.0
ACL**	28.5	27.5	28.8	27.2	27.3

Notes: \*  $\text{CPI} = \frac{(C_{23}+C_{25}+C_{27}+C_{29}+C_{31})+(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})}{2(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})}$

\*\*  $\text{ACL} = \frac{23 \times C_{23} + 25 \times C_{25} + 27 \times C_{27} + 29 \times C_{29} + 31 \times C_{31} + 33 \times C_{33}}{C_{23} + C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}$

than that in Dajiuhu. In leaf cuticles, the main physiological function of long chain *n*-alkanes is to reduce the water loss (Jetter et al., 2006). Plants growing in arid conditions synthesized the larger proportions of longer chain homologs relative to their counterparts growing in humid conditions (Dodd et al., 1999). Since the temperature can affect the leaf water loss through manifesting transpiration, some researchers argued that the temperature was the dominant controller for the chain length of long chain *n*-alkanes (Poynter et al., 1989). If the temperature acts as the dominant factor, lichen species should have a longer average chain length in Qizimei than that in

Dajiuhu, which is contradictory with our data. Therefore, we deduce that the different distribution of lichen alkanes between Dajiuhu and Qizimei more likely results from the humid difference.

Four out of five lichen samples were conducted for compound specific carbon isotope analysis of long chain *n*-alkanes. The carbon isotopic values vary between  $-31.4\text{‰}$  and  $-38.3\text{‰}$  (Table 3), falling into the range of C3 plants (Collister et al., 1994). The alkane  $\delta^{13}\text{C}$  values in LI-1 decreased with increasing carbon number. However, the other three samples do not show the similar trends. The  $\delta^{13}\text{C}$  values of *n*-C<sub>23</sub> alkane are more depleted in this study than that in the Antarctic soils ( $-30.4\text{‰}$  to  $-26.6\text{‰}$ ; Matsumoto et al., 2010). This difference suggests that *n*-C<sub>23</sub> alkane in the Antarctic soils may have a mixed source or result from the climatic conditions quite different from our sampling sites.

### 3.2 Branched alkanes

The two lichen samples collected from Qizimei contain some long chain branched alkanes (Fig. 1), mainly *iso*-(2-methyl) and *anteiso*-(3-methyl) isomers. LI-4 only contains trace of branched alkanes. In some unidentified lichen samples collected from Qizimei, the long chain branched alkanes are also obvious (unpublished data). In LI-5, 3-methylalkanes range from *a*-C<sub>24</sub> to *a*-C<sub>32</sub>, dominated by *a*-C<sub>28</sub> with a strong even-over-odd predominance. The 2-methylalkane series in LI-5 include *i*-C<sub>27</sub>, *i*-C<sub>29</sub> and *i*-C<sub>31</sub>, with *i*-C<sub>31</sub> being a little higher in abundance than the other two compounds. 3-methylalkanes also occurred in *S. ceratites* (*a*-C<sub>22</sub>–*a*-C<sub>26</sub>) and was dominated by *a*-C<sub>26</sub> (Gaskell et al., 1973). This carbon range is a little smaller than that of the Qizimei lichen samples.

### 3.3 Geological implications

So far, the dominance of C<sub>23</sub> *n*-alkane has been only observed in *Sphagnum* (Nott et al., 2000; Huang et al., 2010), submerged/floating aquatic macrophytes (Ficken et al., 2000), seagrass and associated sediments (Mead et al., 2005; Xu et al., 2006), Antarctic soils (Matsumoto et al., 2010) and laminated carbonates from the Franconian Alb, SW-Germany (van Kaam-Peters et al., 1997; Schwark

**Table 3** The  $\delta^{13}\text{C}$  values of long chain *n*-alkanes in the lichen samples

	LI-1	LI-2	LI-3	LI-5
<i>n</i> -C <sub>21</sub>			$-35.0$	
<i>n</i> -C <sub>23</sub>	$-32.3$	$-36.3$	$-32.6$	$-34.3$
<i>n</i> -C <sub>25</sub>	$-33.2$	$-33.8$	$-31.8$	$-33.0$
<i>n</i> -C <sub>27</sub>	$-33.9$	$-31.4$	$-38.3$	$-31.7$
<i>n</i> -C <sub>29</sub>	$-35.7$	$-32.5$	$-34.0$	$-32.6$
<i>n</i> -C <sub>31</sub>	$-37.4$	n.a.*	$-35.8$	$-33.6$

Note: \* not available

et al., 1998). The relatively heavy  $\delta^{13}\text{C}$  values of *n*-C<sub>23</sub> alkane in the Franconian have been interpreted as the input from some special algae (Schwark et al., 1998), while Matsumoto et al. (2010) attributed lichens as the major source of *n*-C<sub>23</sub> alkane in Antarctic soils. In fact, common rust fungus (*Puccinia graminis* f. sp. *avenae*) contained high abundant *n*-C<sub>23</sub> alkane in its airborne urediospores (Laseter and Valle, 1971). More works are needed to investigate lichen species in more sites to testify the *n*-C<sub>23</sub> indication to some specific lichen groups or environmental condition.

Long chain 3-methylalkanes have been detected in various geological samples, including lacustrine sediments (Fukushima et al., 1996, 2005), the Antarctic rock samples (Matsumoto et al., 1992), modern microbial mats (Kenig et al., 1995), and ancient sediments (Chaffee et al., 1986; Summons, 1987), and some higher plants (Pautler et al., 2010; Huang et al., 2011). Although the short chain 3-methylalkanes (C<sub>16</sub>–C<sub>21</sub>) have been identified in cyanobacterial cultures (Köster et al., 1999), the source of long chain 3-methylalkanes is still under debate (Huang et al., 2011). Matsumoto et al. (1992) attributed the *a*-C<sub>20</sub>–*a*-C<sub>30</sub> alkanes in Antarctica rocks to the inputs from heterotrophic bacteria or symbiotic processes. However, as our results revealed, it is possible that lichens contribute 3-methyl compounds identified in ancient sediments or rocks.

Above discussion suggests that the *n*-C<sub>23</sub> alkane and long chain 3-methyl alkanes have the potential to be acted as an indicator of lichens. If we combine with these two features, together with carbon isotope and morphological evidences, we can be more confident to discuss the evolution history of lichens and their response to environmental changes.

## 4 Conclusions

This study investigated the distribution of long chain alkanes and their carbon isotope in the lichen samples collected from Dajiuhe and Qizimei, western Hubei Province. The coticolous lichen samples are dominated by long chain *n*-alkanes (*n*-C<sub>21</sub>–*n*-C<sub>33</sub>), showing strong odd-over-even predominance and similar with the signatures of higher plants. The  $\delta^{13}\text{C}$  values of long chain *n*-alkanes show a pattern similar to C3 plants. The lichen samples collected in Qizimei are featured by the relatively high abundance of *n*-C<sub>23</sub> alkane and even predominant long chain 3-methylalkanes. These features have the potential to be acted as the indicators of lichens and be used to reconstruct the evolution history of lichens and their response to environmental changes.

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