Molecular organic geochemical peculiarities of lacustrine core sediments in Fildes Peninsula, King George Island, Antarctica

ZHANG Gan, SHENG Guoying, PENG Ping'an & ZHENG Honghan

Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
Correspondence should be addressed to Zhang Gan (email: zhanggan@gig.ac.cn)

Abstract The peculiarities of lipids in lacustrine core sediments from Fildes Peninsula, King George Island, Antarctica, are reported. The origin of high-molecular-weight n-alkanes, alkenes, fatty acids, alcohols is supposed to be related to the abundant moss occurring in the sediments. Abundant *iso*- and *anteiso*-fatty acids that occur in the sediments indicate a relatively strong bacterial activity in non-ice-cover zone than in other regions in Antarctica. The $C_{18:2}$ unsaturated fatty acids mainly originate from autochthonous algae in the sediment pool, and the $C_{18:2}/C_{18:0}$ ratios in the profile are controlled more by paleotemperatures than source assemblies. Long-chain alkenones were identified in freshwater lacustrine sediment in Antarctica for the first time, of which *Prymnesiophyceae* is assumed to be the source organism. High relative abundance of $C_{37:4}$ homologue in long-chain alkenone well correlates to the severely cold climate in Antarctica.

Keywords: Antarctica, lacustrine sediment, lipids, source, paleoclimate.

Fildes Peninsula is located at 62° 12′59″ S, 58° 57′52″ W on King George Island. The peculiarities of lipid compositions from sediments in Tern Lake and West Lake adjacent to the Great-Wall Station of China, and in Kitech Lake near Russian Bellingshausen Station are reported in the present paper.

1 Sampling and experimental

The three sedimentary cores mentioned above were drilled in April—July 1993. ^{14}C-dating revealed that they constituted a continuous sedimentary sequence from 12 000 aB.P. in the late Pleistocene[1]. The cores were cut into segments at 5 cm intervals and freeze-stored in PE bags until analysis.

Wet sediments were freeze-dried and Soxhlet extracted with DCM for 72 h. The extracts after solvent evaporation was refluxed with 15 mL 1 mol/L KOH in MeOH for saponification at 80℃ for 2 h. Neutral lipids were LLE extracted with 15mL DCM after 10 mL distilled water was added. Then the pH value of the water phase was adjusted to 1 by concentrated KOH solution, and the fatty acids were extracted with 15 mL DCM. Both neutral and acidic fraction was dehydrated with anhydrous Na_2SO_4. The neutral lipids were further separated into (hydrocarbon+alketone) and alcohol fractions by means of silica gel column chramatography, and the latter fraction was silylated with BSTFA (50 μL, 70℃, 30 min) prior to gas chromatography. Fatty acids were methylated with BF_3/MeOH (14%). The GC and GC-MS conditions were described elsewhere[2], and a new Micromass Platform GC-MS was employed. $C_{24}D_{50}$ was used as internal standards for quantification.

2 Result and discussion

(i) Hydrocarbons. Alkanes in the sediments showed a unimodal distribution with a carbon number range of C_{16}—C_{33} mostly maximizing at C_{23}. Similar to the sediments from Richardson Lake in Riiser-Larson region, East Antarctica, our sediments contained abundant moss relics. It was reported that the alkanes in Richardson Lake contained relics of *Bryum* sp., a saline water moss showed a C_{max} at C_{21}, secondly maximizing at C_{23}[3], and those in a permafrost bog sediment from Qinghai-Xizang (Tibet) Plateau with abundant moss relics also showed a C_{max} at C_{23}[4]. Hence, we suggest that alkanes in Fildes lacustrine sediments might also mainly originate from the abundant moss relics (*Drepanocladus* sp., *Amblysbegiaceae*).

Abundant alkenes were also observed in the sediments, with a carbon range of $C_{20:1}$—$C_{25:1}$

maximizing at $C_{23:1}$ or $C_{25:1}$. No polyunsaturated alkenes were detected. In many samples, the relative concentrations of n-$C_{23:1}$ or $C_{25:1}$ were higher than those of the corresponding alkanes. Similar C_{max} characteristic, i. e. C_{23} or C_{25}, may indicate that alkenes were derived from the same source as alkanes. In other Antarctic regions, Akiyama et al. reported alkenes in Richardson Lake in Enderby Island distributed in the carbon range of $C_{27:1}$—$C_{29:1}$[3]. Volkman et al. detected $C_{29:1}$ and n-C_{34} alkenes with 1—4 double bonds in Ace Lake in Vestfold Oasis[5], and Matsumoto et al. found mono-alkenes within C_{17}—C_{19} carbon range, which were supposed to be derived from epibenthic algae, in Vanda Lake in McMurdo Dry Valley[6]. These, however, were all different from our results. The presence of abundant alkenes indicated good preservation conditions for organic matter in Antarctic environment and weak hydrogenation process in early diagenesis.

Isoprenoid hydrocarbons in the sediments were mainly pristane, phytane and in some samples phyt-di-ene. The ratios of Ph/Pr were greater than 1 except for in one smaple, indicating an anaerobic sedimentary environment related to lacustrine-swamp sedimentation.

The components of triterpanoids in the samples were characteristic of abundant hopenes, comprised mainly of hop-22(29)-ene and hop-17(21)-ene. This is the same as triterpanoids detected in Ace Lake[5] in Antarctica. Bacteria and fungus were considered to be the main sources of these hopenes[7].

(ii) Fatty acids. Fatty acids in the samples displayed a bimodal distribution in the carbon range of C_{10}—C_{32} maximizing at C_{16} and C_{24}. Strong even/odd predominance was observed with an average EOP of 6.2. C_{max} at C_{24} well corresponds with that at C_{23} in alkanes, suggesting that the long-chain alkanes were derived from their fatty acid counterparts by decarboxylation.

Abundant C_{15}—C_{17} *iso-* and *anteiso*-fatty acids were identified in the sediments, and in some samples the concentration of *iso*-C_{15} fatty acid even exceeded that of n-C_{15} fatty acid and became the major peak in GC traces. It is suggested that the bacterial activity in non-ice-sheet zone as Foldes Peninsula is stronger than in other regions in Antarctica.

The unsaturated fatty acids were characteristic of abundant $C_{16:1}$, $C_{18:1\Delta9}$, $C_{18:1\Delta11}$ and $C_{18:2}$. As compared with those in Gucheng Lake in Nanjing, East China[8], Antarctic sediments showed a much higher $C_{18:2}/C_{18:0}$ ratio (mostly$>$0.2 while in Gucheng Lake$<$0.1=. It was reported that many organisms tend to synthesize more unsaturated fatty acids in lower temperature environment in order to maintain the fluidity of their cell membranes[9]. So the high value of $C_{18:2}/C_{18:0}$ ratios[10] in Antarctic sediments was evidently related to the severely cold climate in Antarctica. The down-core variations of $C_{18:2}/C_{18:0}$ ratios in the sedimentary profile assigned cold events in 11 000, 9 000 and 3 000 aB.P. in Antarctica, among them the cold event in 9 000 a B. P. was the strongest one as well as the shortest one.

(iii) Alcohols. Alcohols identified in the samples included normal alcohols, phytol and sterols, and were characteristic of high amount of phytol and sterols. Phytol always occurred as the highest peak in GC traces of alcohol fraction. Sterols accounted for 20%—60% of the total amount of alcohols.

Normal alcohols were distributed in the carbon range of C_{14}—C_{30}, parallel with alkanes. The average EOP of normal alcohols was 5.3. C_{max} in most samples was at C_{24}, while in some samples at C_{26} or C_{28}. It was reported that normal alcohols were possibly derived from emerged macrophytes[11]. In this case, they may originate from mosses in the region.

Sterols detected in the sediments were mainly comprised of various isomers of C_{27}—C_{29} 4-demethylsterols, though in some samples a small amount of 4-methyl-sitosterol was found. The ratios of $5\alpha C_{27}/(5\alpha C_{27}+\Delta^5\text{-}C_{27})$ and $5\alpha C_{29}/(5\alpha C_{29}+\Delta^5 C_{29})$ of sterols were in the range of 0.07—0.42 and 0.03—0.52 respectively, without significant linear down-core trend. This indicated that the early diagenesis process in Antarctic lacustrine environment was weak, and suggested that the relative concentration of stanols and stenols in the sediments might be controlled by the original source properties.

We observed obvious negative correlation between the autochthonous and terrigenous contribution indices ACI $[(C_{27}\Delta^5+C_{27}\Delta^0+C_{28}\Delta^{5,22})/\Sigma\text{sterols}]$ and TCI $[(C_{29}\Delta^5+C_{28}\Delta^0)/\Sigma\text{sterols}]$[12]. It was interesting to note that the $C_{18:2}/C_{18:0}$ ratios of fatty acids showed similar down-core variations (fig. 1). Since ACI index virtually reflected the relative contribution from autochthonous algae to sedimentary sterols, and TCI here may probably reflect the contribution from mosses, the relationship between $C_{18:2}/C_{18:0}$ ratios and ACI index of sterols may suggest that the $C_{18:2}$ unsaturated fatty acids mainly originated from algae in the sediment pool. This further indicated that the $C_{18:2}/C_{18:0}$ ratios in the sedimentary profile were controlled more by paleotemperatures than source assemblies, and can serve as a possible paleotemperature indicator.

(iv) Ketones. Ketones detected in the lacustrine sediments included phytone and trace amount of low molecular weight methyl alketones ($<C_{22}$). We identified in two sediments in Kitech Lake long-chain (C_{37}—C_{39}) alketones, which were reported to be significant in paleothermometry[13]. The long-chain alketones maximized at $C_{37:4}$ (fig. 2), as was obviously different from those detected in tropical sediments in which $C_{37:2}$ alketone was the most abundant homologue and without $C_{37:4}$[14]. The high unsaturation degree characteristic of long-chain alketones might be the reflection of the severely cold climate in Antarctica, or the difference in source organisms as compared to those in other parts of the world.

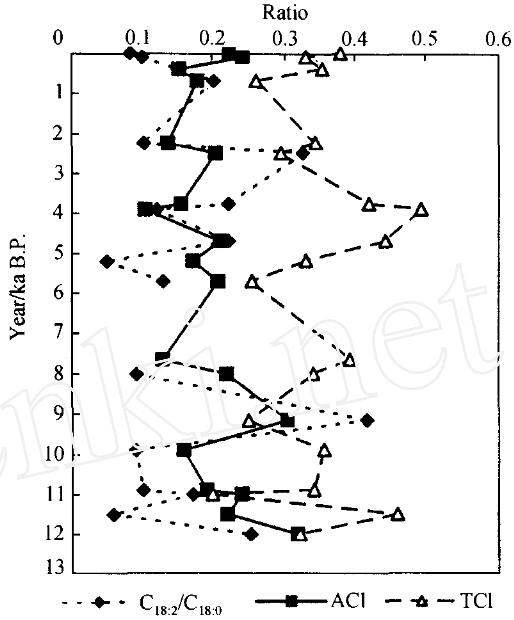

Fig. 1. Down-core variations of $C_{18:2}/C_{18:0}$ ratios of fatty acids drawn with ACI and TCI sterol indices in lacustrine sediments in Fildes Peninsula, King George Island, Antarctica.

Generally long-chain alketones were considered to be bio-specific to *E.Hexuly* and *G.Oceanica* of *Prymnesiophyceae*. However, there is no evidence that these two algae occur in Antarctic environment probably because they are not capable of tolerating the extremely low water temperature. Volkman et al. detected these compounds in an Antarctic saline lake, Ace Lake in Vestfold Hills. Li et al.[15] and Sheng et al.[16] reported the occurrence of long-chain alketones in inland salt lakes

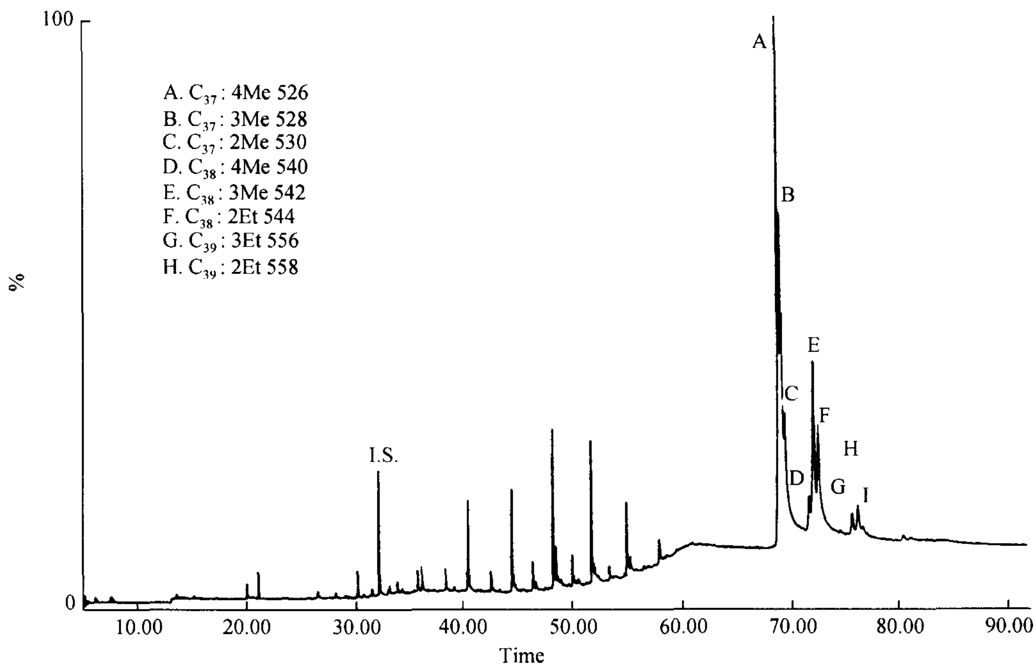

Fig. 2. Gas chromatography of (hydrocarbon+alketone) fraction in a sediment sample from Kitech Lake, Fildes Peninsula, King George Island, Antarctica.

in China and suggested they might originate from specific salt or half-salt species of *Prymnesiophyceae* or *Silico-flagellateae*. Cranwell reported the presence of alkenones in sediments of freshwater lakes in UK and suggested that they might also be derived from some species of *Prymnesiophyceae*[17]. Since Tern Lake is a freshwater lake, a certain freshwater species of *Prymnesiophyceae* source could be suggested to be the long-chain alketones in the sediments.

(v) Concluding remarks.

(1) The distribution of normal alkanes maximized at C_{23}, which might originate from mosses.

(2) Abundant *iso-* and *anteiso*-fatty acids occurring in the sediments indicated a stronger bacterial activity in non-ice-cover zone than in other regions in Antarctica.

(3) The $C_{18:2}/C_{18:0}$ ratios of fatty acids displayed a positive relationship with the ACI index of sterols, which suggested that the $C_{18:2}$ unsaturated fatty acids mainly originated from autochthonous algae in the sediment pool, indicating that the $C_{18:2}/C_{18:0}$ ratios in the sedimentary profile were controlled more by paleotemperatures than by source assemblies.

(4) Long-chain alkenones were identified in freshwater lacustrine sediment in Antarctica for the first time, of which *Prymnesiophyceae* was assumed to be the source organism. High relative abundance of $C_{37:4}$ homologue in long-chain alkenone well correlated to the severely cold climate in Antarctica.

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