



# Geochemical analyses of a Himalayan snowpit profile: implications for atmospheric pollution and climate

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## Abstract

Organic compounds, extracted from snow and ice from the Dasuopu glacier, on the Qinghai-Tibetan Plateau in South-west China at an altitude of 7000 m above sea level (asl), were identified through pre-enrichment, solvent extraction and subsequent GC–MS analysis. The average concentration of the extractable organic matter reached 45.4 µg/l. C<sub>15</sub>–C<sub>33</sub> *n*-alkanes, C<sub>6</sub>–C<sub>18</sub> *n*-alkanoic acids, C<sub>24</sub>–C<sub>31</sub> *n*-alkan-2-ones and esters were derived from subtropical higher plants, as well as marine algae and bacteria. Organic compounds, indicative of petroleum residues such as automobile and diesel exhaust were also unexpectedly identified in the glacial snow. These included *n*-alkanes, alkylcyclohexanes, pristane, phytane, extended C<sub>19</sub>–C<sub>29</sub> tricyclic terpanes, a C<sub>24</sub> tetracyclic terpane, C<sub>27</sub>–C<sub>35</sub> αβ hopanes, and C<sub>27</sub>–C<sub>29</sub> steranes. Their presence indicates that the remote mountainous region and, to some extent, the middle-upper troposphere are polluted by human activities. Concentrations of some organic compounds, and total extractable organic matter, display a weak seasonal variation, postulated to be related to the location of middle-upper troposphere. The C<sub>17</sub> *n*-alkane abundance and some molecular ratios exhibit a stronger seasonal variation, which may signify strong climatic change. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Dasuopu glacier; Middle-upper troposphere; Summer monsoon; Petroleum residues; Pollution; Aeolian transport

## 1. Introduction

Organic constituents, especially high molecular-weight, solvent-soluble compounds have been studied in the lower troposphere from urban, rural and oceanic aerosols (Ketseridis et al., 1976; Simoneit, 1977, 1979, 1980, 1982, 1984; Simoneit et al., 1977, 1991a, b; Cautreels and van Cauwenberghe, 1978; Eichmann et al., 1979; Matsumoto and Hanya, 1980), and have been shown to have natural biogenic, geologic and synthetic origins. They are present in exceedingly low concentra-

tions but are significant components in the global cycling of organic carbon.

Organic matter in snow and ice is scavenged from the atmosphere and deposited by the precipitation of snow and by dust particles. Emphasis has been made in many glaciology studies on the presence of CO<sub>2</sub>, CH<sub>4</sub>, light carboxylic acids (acetic, formic and methanesulfonic acids) and certain synthetic micropollutants in polar snow (Nefel et al., 1985; Ivey et al., 1986; Keene and Galloway, 1986; Barnola et al., 1987; Raynaud et al., 1993; Maupetit, 1994). However, only a few studies have been made on extractable organic matter in snow or glaciers (Lunde et al., 1977; Meyers and Hites, 1982), particularly on the biomarkers that could be used to identify organic matter sources. This is partly due to the difficulty of obtaining enough samples. The potential significance of climatic and environmental changes

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deduced from these organic compounds in glaciers and ice cores, like those already obtained from oceanic sediments, should encourage new research.

The Qinghai-Tibetan plateau plays an important role in affecting the climate of the Northern Hemisphere and probably also the Southern Hemisphere. This investigation attempts to present (1) the composition and relative seasonal variation of the extractable organic matter in

the Dasuopu glacier on the Qinghai-Tibetan plateau, and (2) its climatic and environmental implications. The results of this study on samples from 7000 m asl may also help to elucidate the difference, in organic content, between the lower and middle-upper troposphere.

## 2. Experimental

The snowpit samples were collected from the remote Dasuopu glacier in Xixiabangma, the highest peak (8012 m asl) in the northern branch of the Central Himalayas in the south Qinghai-Tibetan plateau, China (Fig. 1). From the Dasuopu glacier, which is about 120 km northwest of Mount Everest, three ice cores greater than 150 m in length were recovered to study the climatic and environmental records. Six samples were taken in descending order from a 240-cm-deep snowpit profile (from 7000 m asl) for this geochemical study: each sample is from a 40 cm interval. The samples with  $\delta^{18}\text{O}$  dating are listed in Table 1. All snow and ice samples were allowed to melt (taking 2 days per sample) in precleaned enamelware at an altitude of 5800 m asl. Melt water volume of these samples ranges from 21.1 to 24.92 L. Concentrated HCl was added to the melt water to bring the pH to 2. The trace organic matter in the melt water was then enriched, in-situ, using a pre-purified mix of GDX-102 and GDX-105. After enrichment of the organic matter, both ends of the packed columns were sealed and taken back to the laboratory. At low temperature (about 15°C), the adsorbed organic matter was slowly extracted with 30 ml of dichloromethane.  $\text{Na}_2\text{SO}_4$ , activated for 24 h at 450°C, was used to dry the extracted material. The organic extract was concentrated on a rotary evaporator under reduced pressure and then transferred to a small vial. Following

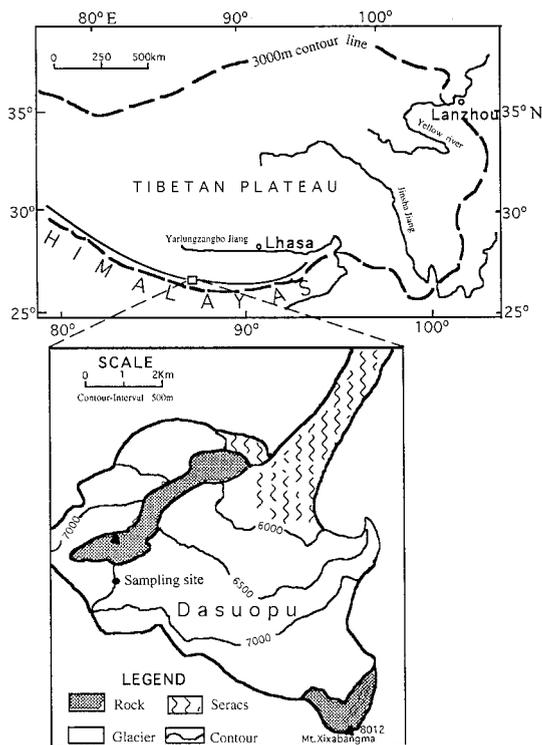


Fig. 1. Sample location.

Table 1  
Sample information and analytical results

Sample no.	Depth <sup>a</sup> (cm)	$\delta^{18}\text{O}$ (‰)	Dating <sup>b</sup>	Melt water (l)	TEY <sup>c</sup>	<i>n</i> -Alkanes <sup>d</sup>		<i>n</i> -Alkanoic acids <sup>e</sup>		<i>n</i> -Alkan-2-ones <sup>f</sup>		
						Content (μg/l)	CPI	Max	CPI	Max	CPI	Max
XFS-4	0/40	-20.6	Summer 1997	21.10	33.8	1.23	1.40	17, 29	0.54	16	3.07	29
XFS-5	40/80	-20.8	Summer 1997	24.15	50.5	1.29	1.30	17, 29	0.67	16	2.13	29
XFS-6	80/120	-19.9	Summer 1997	24.92	44.8	1.25	1.41	17, 29	0.68	16	2.89	29
XFS-7	120/160	-15.0	Winter 1997/96	24.80	41.0	0.86	1.88	20, 29	0.66	16	2.18	29
XFS-8	160/200	-15.4	Winter 1997/96	23.66	55.7	0.57	1.71	20, 29	0.62	16	2.32	29
XFS-9	200/240	-19.2	Summer 1996	21.83	45.6	1.52	1.05	17, 29	0.63	16	2.12	29

<sup>a</sup> Begin/end.

<sup>b</sup>  $\delta^{18}\text{O}$  in the glacier can clearly be divided into summer (May–October) and winter (November–April).

<sup>c</sup> Total extract yield (μg/l).

<sup>d</sup> CPI, carbon preference index;  $\text{CPI} = (\text{C}_{25-33(\text{odd})} + \text{C}_{23-31(\text{odd})}) / 2\text{C}_{24-30(\text{even})}$ ; Max, main peak in carbon distribution.

<sup>e</sup>  $\text{CPI} = 2\text{C}_{7-17(\text{odd})} / (\text{C}_6 + 2\text{C}_{8-16(\text{even})} + \text{C}_{18})$ .

<sup>f</sup>  $\text{CPI} = \text{C}_{25-31(\text{odd})} / \text{C}_{24-30(\text{even})}$ .

evaporation of the remaining solvent, the total extractable organic matter was weighed, and then stored in the refrigerator.

To minimize loss, separation of the extracted organic matter into compound classes was omitted. For GC and GC–MS analysis, 60  $\mu\text{l}$  chloroform was added and 1  $\mu\text{l}$  of this was injected into the instruments. Procedural blanks have also been analyzed to ensure the absence of possible laboratory contaminants.

Gas chromatographic analysis (GC) was undertaken using a Hewlett-Packard 6890 chromatograph equipped with a flame ionization detector (FID). A HP-5 silica capillary column (30 m $\times$ 0.25 mm i.d.; 0.25  $\mu\text{m}$  film thickness) was employed with splitless injection. The oven temperature was ramped at 3°C/min from 70 to 280°C and held at 280°C for 20 min. Helium was used as carrier gas. A Hewlett-Packard 5973A mass spectrometer, interfaced directly with a 6890 *plus* gas chromatograph equipped with a HP-5MS fused silica capillary column (30 m $\times$ 0.25 mm i.d.; 0.25  $\mu\text{m}$  film thickness), was used for biomarker analyses. The operating conditions were as follows: temperature ramped from 70 to 280°C at 3°C/min, held at 280°C for 20 min, carrier gas He; the ionization energy of the mass spectrometer was set at 70 eV, scan range from 40 to 550 amu.

### 3. Results and discussion

The concentration of the total extractable organic matter in the glacier ranges from 33.8 to 55.7  $\mu\text{g/l}$ , with an average at 45.4  $\mu\text{g/l}$  showing no distinct seasonal variation (Table 1). The concentration of *n*-alkanes varies from 0.86 to 1.57  $\mu\text{g/l}$ , averaging 1.29  $\mu\text{g/l}$ . The maximum contents of C<sub>17</sub> and C<sub>29</sub> *n*-alkanes are, respectively, 130 and 220 ng/l. All organic compounds identified are discussed below.

#### 3.1. Organic compounds from biological sources

Organic matter derived from natural organisms includes *n*-alkanes, *n*-alkanoic acids, *n*-alkan-2-ones and esters. Normal alkanes in the glacier range from C<sub>15</sub> to C<sub>33</sub> (Fig. 2a), with two main peaks at C<sub>17</sub> or C<sub>20</sub> and C<sub>29</sub>. A distinct odd-over-even carbon predominance is observed above C<sub>22</sub> (Table 1). This distribution of the *n*-alkanes is believed to be from a mixed source of microorganisms and higher plants. The homologues > C<sub>23</sub> are derived chiefly from the epicuticular waxes of vascular plants, the distribution of which resembles similar data from aerosols (Simoneit, 1977; Eichmann et al., 1979; van Vaeck et al., 1979; Broddin et al., 1980; Matsumoto and Hanya, 1980).

Air masses leading to precipitation in the region are the summer monsoon from the Indian Ocean and from the Bay of Bengal (Fig. 3, lower), and a subtropical

westerly jet stream (Fig. 3, upper) which dominates in the winter. These air masses were responsible for the transportation of subtropical higher plant waxes in the southern Himalayas which are heavily covered with deciduous trees, conifers and grass at different altitudes. The traveling time for air masses from the Indian Ocean to the southern Himalayas was determined to be 4 days (Wushiki, 1977), which is shorter than a 5-day residence time for alkanes in aerosols over the Atlantic ocean (Eichmann et al., 1979). Simoneit (1982) demonstrated that the high molecular-weight *n*-alkanes in petroleum can be detected in the atmosphere, some of which may be mixed with biogenic alkanes. This is also reflected in the *n*-alkane distribution in the glacier, which will be discussed below.

In accord with most geological samples, and aerosols, *n*-alkanes < C<sub>23</sub> in summer samples from the glacier exhibit a main peak at C<sub>17</sub> (Table 1), considered to be from marine algae and microorganisms. It should be noted, however, that some samples from the glacier have another main peak at C<sub>20</sub>, which will be discussed later.

The distribution of the *n*-alkanoic acids, identified in the Dasuopu glacier, ranges from C<sub>6</sub> to C<sub>18</sub> with a maximum at C<sub>16</sub> and a strong even carbon predominance above C<sub>10</sub> (Fig. 2b, Table 1). This distribution pattern is characteristic of a microbial source. Generally, *n*-fatty acids from higher plant waxes show a distribution from C<sub>22</sub> to C<sub>32</sub> with a maximum at C<sub>24</sub> or C<sub>26</sub> and a strong even-over-odd carbon predominance, whereas those from algae and bacteria range between C<sub>12</sub> and C<sub>20</sub> with a maximum at C<sub>16</sub> and also a strong even-over-odd carbon predominance. Lunde et al. (1977) detected heptanoic acid in rain and snow samples from Norway. Compared with *n*-alkanes, the relative concentration of *n*-fatty acids is very low in plant wax, because most of these acids are bound as esters. This may lead to difficulty in detecting long-chain acids from higher plants at high altitude. *n*-Alkanoic acids > C<sub>20</sub> were identified in aerosols from three Chinese cities (Simoneit et al., 1991b), in contrast with those in the glacier. In glaciers, the lack of unstable unsaturated fatty acids, which are indicators of recent biogenesis and which have been identified in aerosols, may be attributed to long-distance transportation in the middle-upper troposphere.

A series of *n*-alkan-2-ones, ranging from C<sub>24</sub> to C<sub>31</sub>, and seldom reported in aerosols, were detected in the glacier (Fig. 2c). These *n*-alkan-2-ones have a maximum at C<sub>29</sub> and a strong odd-over-even carbon predominance (Table 1). Also, 6,10,14-trimethylpentadecan-2-one and nonacosan-15-one were also found. Note that the combination of *n*-fatty acids with *n*-alkan-2-ones exhibits similar distributions as *n*-alkanes. Normal fatty acids in the glacier originated from microbes, as did the short-chain *n*-alkanes. The *n*-alkan-2-ones, peaking at C<sub>29</sub>, were likely derived from higher plants, as were the long-chain *n*-alkanes.

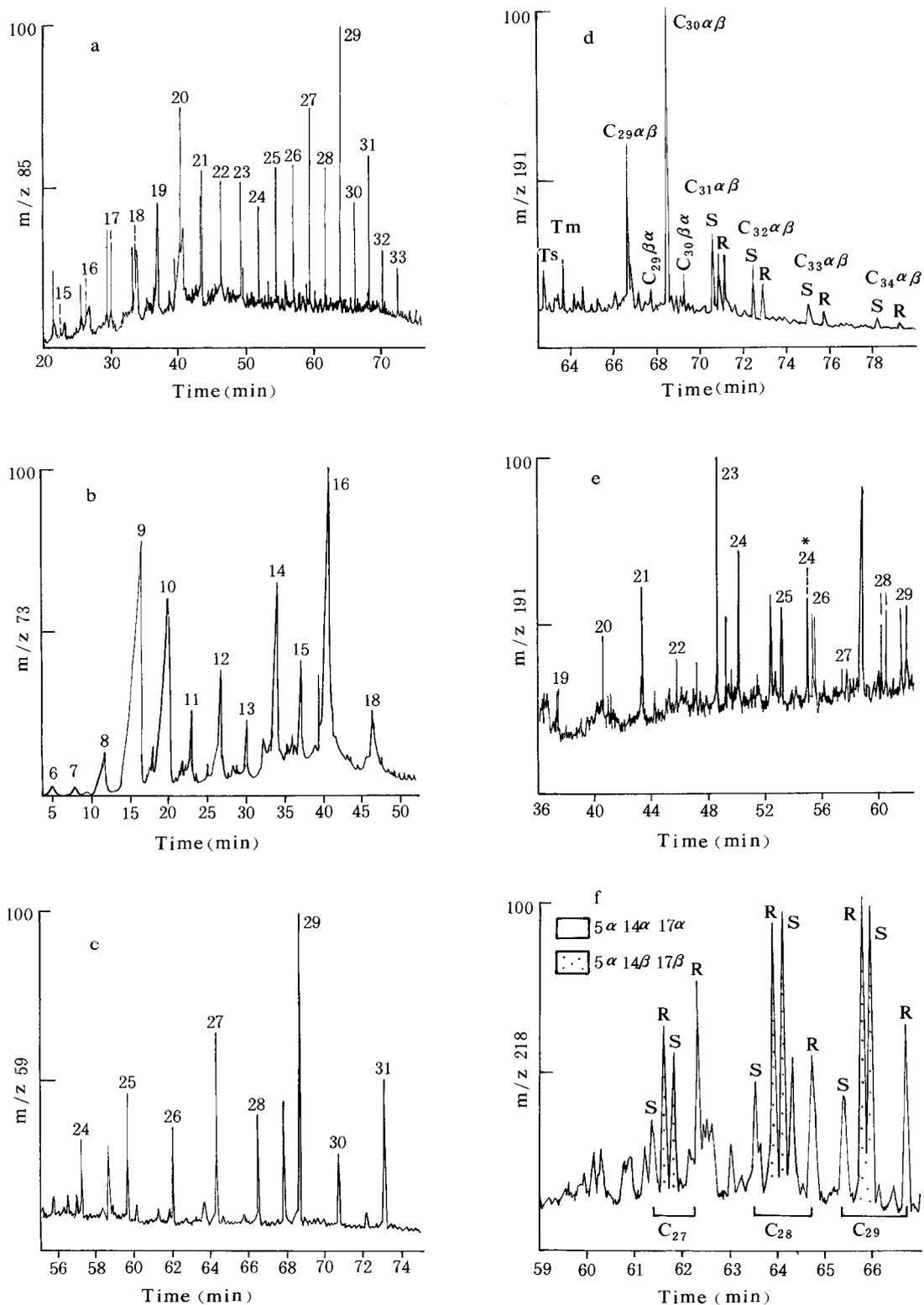


Fig. 2. Mass chromatograms of some typical organic compounds from the glacier: (a)  $m/z$  85 (*n*-alkanes); (b)  $m/z$  73 (*n*-alkanoic acids); (c)  $m/z$  59 (*n*-alkan-2-ones); (d)  $m/z$  191 (triterpanes); (e)  $m/z$  191 (tricyclic terpanes, \* for tetracyclic terpene); (f)  $m/z$  218 (steranes).

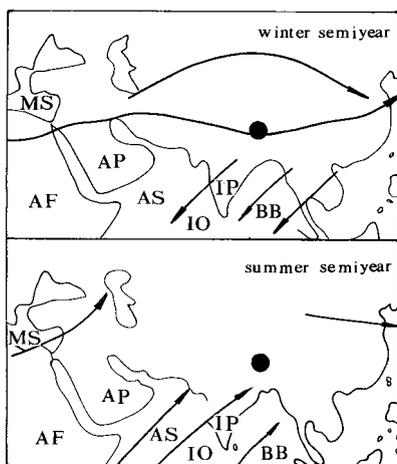


Fig. 3. Schematic illustrations of the air masses (as indicated by arrows) in the study area and its neighbour (from Lockwood, 1965) AF, Africa; AS, Arabian Sea; AP, Arabian Peninsula; BB, Bay of Bengal; IO, Indian Ocean; IP, Indian Peninsula; MS, Mediterranean Sea. The solid circles show the location of the sampling area.

Simoneit (1982) identified a series of fatty alcohols in some aerosols. Similar results were observed by Broddin et al. (1980) and Matsumoto and Hanya (1980). Only a trace amount of 6,10,14-trimethylpentadecan-2-one, a degradation product of phytol, was detected in the aerosols. On the other hand, no fatty alcohols were detected in snow falls by Meyers and Hites (1982) and Lunde et al. (1977) and in this glacial snow. This might imply the transformation of organic matter when scavenged by precipitation from the atmosphere.

Hexadecanoic acid tetradecyl, hexadecanoic acid hexadecyl and hexadecanoic acid octadecyl wax esters were found in the samples. Wax particles are easily released from plant surfaces and can become airborne.

For instance, Simoneit (1982) found a series of  $C_{32}$  to  $C_{40}$  esters in aerosols, presumed to have been derived from a more forested area.

As for most aerosols, no sesqui- and di- terpenoids were found in the glacier, although these terpenoids have been identified in forest soils and in marine sediments. Eichmann et al. (1979) commented that these terpenoids are unstable in the atmosphere and their absence in the glacier may be due to atmospheric oxidation at the altitude of the middle-upper troposphere.

### 3.2. Organic matter from petroleum residues

Petroleum residues are ubiquitous in the environment, especially in sediments (Simoneit, 1984). Their presence in aerosols has been well documented in recent years, except for those in glaciers. Organic compounds originating from petroleum residues were detected in the Dasuopu glacier; they included *n*-alkanes, alkylcyclohexanes, isoprenoids, extended tricyclic terpanes, triterpanes and steranes.

Homologues  $C_{15}$  to  $C_{35}$  *n*-alkanes, from petroleum residues, are often superimposed on naturally occurring biogenic hydrocarbons (Simoneit, 1984). Since *n*-alkanes in petroleum generally show a carbon preference index about 1.0, this has been used by Schneider et al. (1983), Sicre et al. (1987) and Simoneit et al. (1991a) to distinguish plant wax alkanes from fossil fuel alkanes. In this paper, we also used this method (see Simoneit et al., 1991a) to calculate the contribution of petroleum residues (Fig. 4a–f, under the dashed line) and of only the plant wax (Fig. 4g–l). As indicated above, and shown in Fig. 4, some samples from the glacier have another pronounced *n*-alkane main peak at  $C_{20}$  or  $C_{21}$ . In biological materials, *n*-alkanes often peak at  $C_{17}$ ,  $C_{18}$  (from algae and bacteria) and/or  $C_{27}$ ,  $C_{29}$ ,  $C_{31}$  (from higher plants and some fungi) but not at  $C_{20}$ ,  $C_{21}$ . However, diesel exhaust was reported to have *n*-alkanes peaking at  $C_{20}$ ,  $C_{21}$  (Simoneit, 1984). A

Table 2  
Indexes of organic compounds from petroleum residues

Sample no.	Pentacyclic triterpanes		Steranes				
	Tm/Ts <sup>a</sup>	C <sub>31</sub> αβ22S/22R	C <sub>29</sub> S% <sup>b</sup>	C <sub>29</sub> ββ% <sup>c</sup>	C <sub>27</sub> /T <sup>d</sup>	C <sub>28</sub> /T	C <sub>29</sub> /T
XFS-4	1.50	1.47	36.4	43.6	24.7	32.3	43.0
XFS-5	1.33	1.42	34.4	42.5	29.2	32.2	38.3
XFS-6	1.50	1.47	38.3	38.6	29.7	30.5	39.8
XFS-7	1.50	1.47	37.7	42.4	27.6	31.5	40.9
XFS-8	1.50	1.50	34.0	38.3	29.5	31.7	38.8
XFS-9	2.00	1.46	36.2	37.6	29.3	31.8	38.9

<sup>a</sup> 17α-trisnorhopane/18α-trisnorhopane.

<sup>b</sup> C<sub>29</sub> ααα-20S/(20S+20R) (%).

<sup>c</sup> C<sub>29</sub> αββ/(ααα+αββ) (%).

<sup>d</sup> T, total steranes of C<sub>27</sub>, C<sub>28</sub> and C<sub>29</sub>. C<sub>27</sub>/T, C<sub>28</sub>/T and C<sub>29</sub>/T are in %.

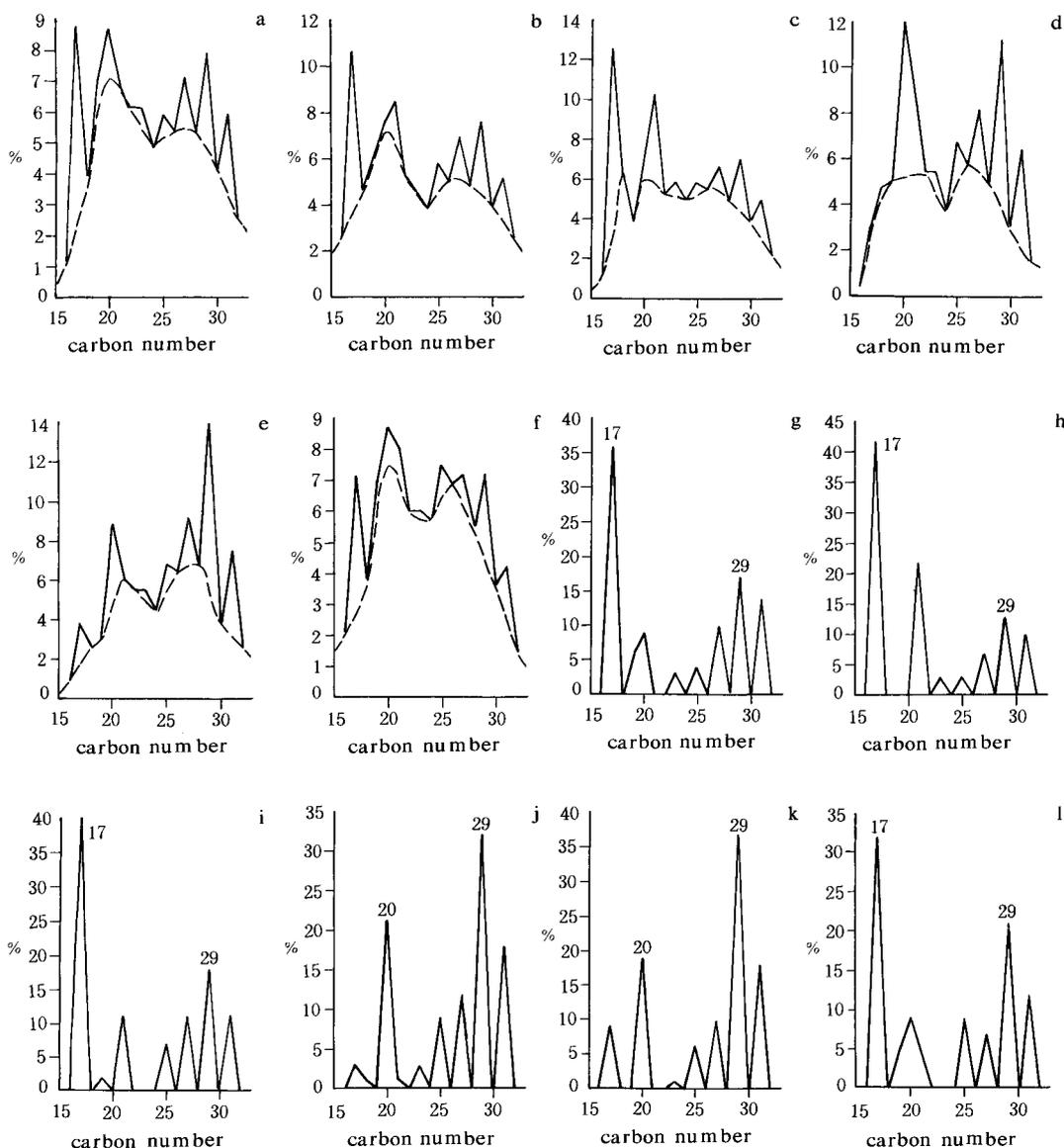


Fig. 4. Distribution diagrams of relative concentrations (%) versus carbon number for *n*-alkanes of the total (a–f) and of only those of plant wax origin (g–l) at different depth of the snowpit profile. The envelope under each dashed line indicates the contribution from petroleum residues. Note that a  $C_{17}$  main peak exists in g, h, i and l related to the strong summer monsoon from the ocean. a, g, 0–40 cm; b, h, 40–80 cm; c, i, 80–120 cm; d, j, 120–160 cm; e, k, 160–200 cm; f, l, 200–240 cm.

$C_{20}$  *n*-alkane peak in the glacier samples is likely related to a partial contribution from diesel exhaust.

Isoprenoid hydrocarbons are widely distributed in geologic samples. Small concentrations of pristane and phytane were identified in the Dasuopu glacier, they are also present in diesel fuel, lubricating oil, and in diesel exhaust gases. Their presence in snow and ice again indicates petroleum residue contamination.

The homologous series of  $C_{20}$ – $C_{27}$  alkylcyclohexanes display no carbon number preference, and have a maximum peak at  $C_{23}$ . In some polluted areas, such as the Lake Tahoe basin (CA, USA), Los Angeles (CA, USA) and the urban areas of Nigeria, alkylcyclohexanes were also observed by Simoneit (1984). These compounds are not present in lipids of recent biogenic origin but are common in petroleum and its distillation products.

Alkylcyclohexanes are major components in auto exhaust but occur only as trace constituents in diesel exhaust (Simoneit, 1984).

The  $C_{27}$  to  $C_{35}$   $17\alpha(H)21\beta(H)$ -hopane series (but not  $C_{28}$ ) and gammacerane were detected in our samples (Fig. 2d); no sesqui- and di-terpenoids were found. The maturity index,  $C_{31}\alpha\beta$   $22S/22R$  (Table 2), reaches 1.42–1.50 in the glacier. Hopanes identified are not of biological configurations but have geological configurations indicating their petroleum origins. Gasoline and diesel fuel do not contain these hopanes, but the compounds are found in auto- and diesel-exhausts (Simoneit, 1984); their formation during combustion in the engines has been proposed by Rogge (1993). Fu (1996) concluded that hopanes, steranes and gammacerane in atmospheric dust were derived from petroleum residues, supporting our belief that the hopanes in the glacier were derived from petroleum residues.

A series of extended tricyclic terpanes with carbon numbers ranging from  $C_{19}$  to  $C_{29}$  were also found in our

samples (Fig. 2e). Two isomers are present for each compound from  $C_{26}$  to  $C_{29}$ . A  $C_{24}$  tetracyclic terpane was also found. They were likely derived from petroleum, as were those in aerosols (Simoneit, 1984).

Steranes identified in the glacier are shown in Fig. 2f. The maturity indices (Table 2),  $C_{29}$   $\alpha\alpha\alpha$   $20S/(20S+20R)$  and  $C_{29}$   $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$ , are 34.0–38.3 and 37.6–43.6%, respectively. The relative contents of  $C_{27}$ ,  $C_{28}$  and  $C_{29}$  steranes in all samples are, respectively, 24.7–29.7, 30.5–32.5 and 38.3–43.0% (Table 2), probably indicating their source as from a bay/estuarine environment. Steranes are not present in gasoline or diesel fuel, but their presence in our samples provide supporting evidence that they were introduced to the atmosphere from vehicle exhausts. It is not clear whether the petroleum-derived compounds in the glacier were transported from the Arabian Peninsula, one of the most concentrated areas of petroleum production in the world, by subtropical westerly jet stream, or carried from vehicle exhaust in the Indian peninsula.

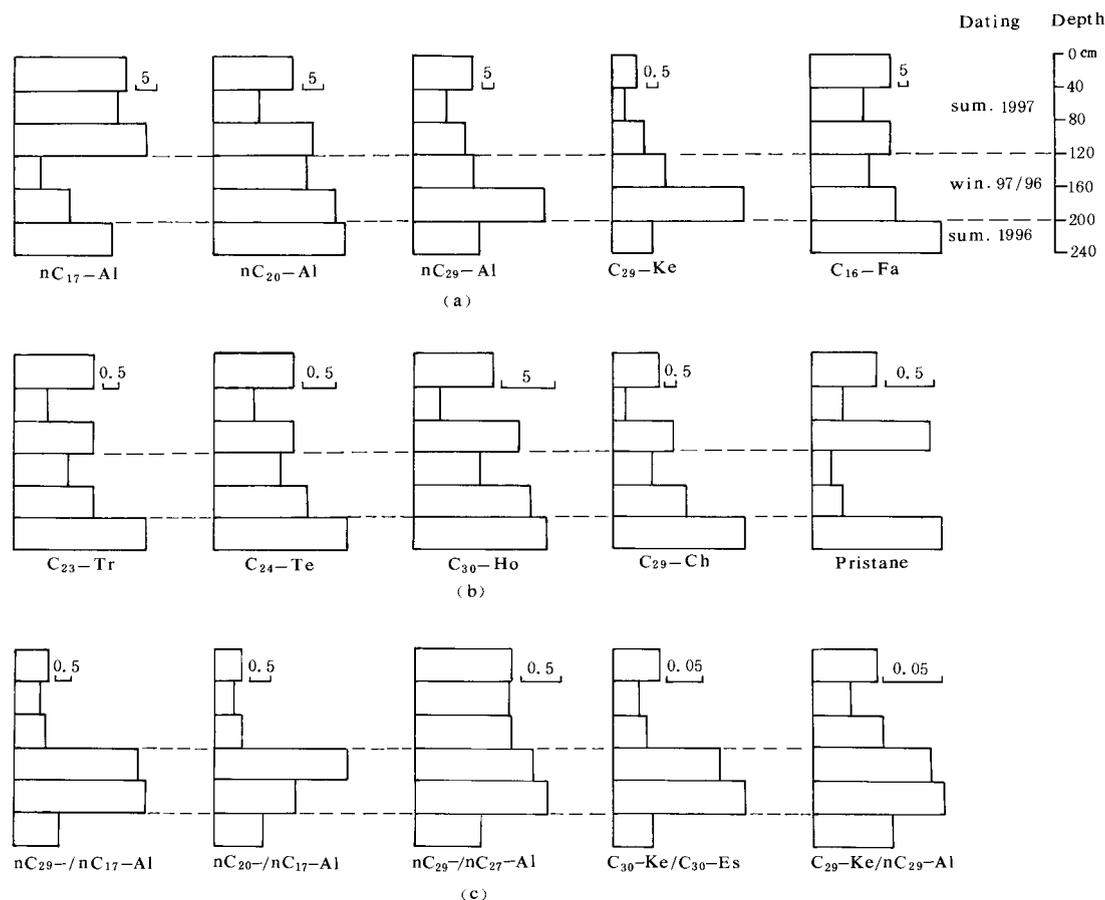


Fig. 5. Seasonal variation of organic compounds and their ratios in the snowpit profile: (a) compounds from natural organisms plus  $n$ -alkanes from petroleum residues; (b) compounds from petroleum residues; (c) organic ratios (for the calculation in a and b, see the text). Al,  $n$ -alkane; Ke, ketone; Fa,  $n$ -alkanoic acid; Tr, tricyclic terpane; Te, tetracyclic terpane; Ho, Hopane; Ch, 24-ethylcholestane; Es, ester; sum, summer; win, winter.

### 3.3. Organic seasonal variation

One advantage of studying organic matter in snowpits, as well as in ice cores, is its relationship to climatic change. It is difficult, and sometimes unnecessary, to quantify the absolute concentrations of all organic compounds. However, it is of some significance to compare the relative concentrations of selected groups of organic compounds. In this paper, the signal intensity of a compound peak in a mass chromatogram on a per ml melt water basis (Fig. 5a and b) was used to display, roughly, the seasonal variation of the relative concentration of each organic compound. This proxy, though not the real concentration, could be practicable for the same compound under the same GC–MS analytical conditions.

Using the  $C_{17}$  *n*-alkane, as representing those from marine algae, microorganisms and partly from petroleum residues, it appears (Fig. 5a) to occur at higher abundance in the summer, than in the winter, and exhibits a strong seasonal variation. Although it could be related to a more flourishing marine biomass in the summer, it more likely implies stronger oceanic air masses during the strong monsoon season. A point of interest is that  $C_{17}$  *n*-alkane concentrations are relatively stable in the summer. Except for a slight increase in the deepest sample,  $C_{16}$  *n*-alkanoic acid shows no apparent seasonal variation.  $C_{29}$  *n*-alkane, as well as  $C_{29}$  ketone, representing compounds from higher plant waxes, display a consistent concentration throughout the profile (Fig. 5a), with the exception of a sharp increase in one sample corresponding to a winter season. The relatively constant concentrations of these compounds may be a result of them originating from ever green deciduous sources, and a longer residence time in the troposphere. The sharp increase in one sample indicates a stronger wind in the winter, resulting in extra input of regional waxes. The  $C_{20}$  *n*-alkane exhibits a slight increase in the winter, probably resulting from less precipitation in the season.

Except for the deepest sample, petroleum-derived compounds (e.g.  $C_{23}$  tricyclic terpane,  $C_{24}$  tetracyclic terpane,  $C_{30}\beta$  hopane and  $C_{29}\alpha\alpha\alpha$ 24R-ethylcholestane) display a slight increase in the winter, due to less snow fall (Fig. 5b). Pristane shows a sharp increase in the transitional periods between seasons. More data are needed to elucidate the sharp increase in the deepest sample.

One should also note the ratios between organic compounds. Fairly strong variations in organic ratios do occur (Fig. 5c). The variation of the *n*-alkane ratios  $C_{29}/C_{17}$  and  $C_{20}/C_{17}$  is mainly caused by the changes of  $C_{17}$  relating to the strong summer monsoon season (Fig. 3). Ester molecules are mainly from plant surfaces and may become airborne in heavy rainfall during the summer in this region. The ratio of  $C_{30}$ -ketone/ $C_{30}$ -ester exhibits this seasonal variation. These variations in molecular ratios reflect the interrelationship between

organisms and the climate. Therefore, these molecular ratios may be used as climatic indicators in the region.

### 3.4. Blanks

Based upon the analyses of procedural blanks from solvents, chemical reagents and the overall procedures, compounds most likely to arise from laboratory contamination were not detected. However, major laboratory contaminants (phthalate esters, mainly dibutyl and diethyl-hexyl) were observed, but with unchanging concentration in all samples: this indicated them to be from the reagents. These contaminants were also encountered in the experimental blanks of Simoneit (1982) and in the snow samples analysed by Lunde et al. (1977).

## 4. Conclusions

Extractable organic matter in a snowpit profile at an altitude of 7000 m asl from the Qinghai-Tibetan Plateau in southwest China is composed of compounds from marine organisms and subtropical higher plants. These compounds include *n*-alkanes, *n*-alkanoic acids, *n*-alkanol-2-ones and esters. Other compounds from petroleum residues include *n*-alkanes, alkylcyclohexanes, tricyclic terpanes, triterpanes and steranes. The latter indicates that the remote middle-upper troposphere is penetrated by anthropogenic pollutants.

Together with the total extracts, most organic compounds such as the  $C_{29}$  *n*-alkane,  $C_{29}$  ketone,  $C_{16}$  *n*-fatty acid and those from petroleum residues display only minor seasonal variations in concentration, because of their location in the middle-upper troposphere. Unstable organic matter, found in aerosols in the lower troposphere is absent in our samples. The lower troposphere is considered to be an active, short-term reservoir for organic compounds. The  $C_{17}$  *n*-alkane and some molecular ratios exhibit a stronger seasonal variation implying climatic changes. The change in  $C_{17}$  *n*-alkane is related to the strong summer monsoon season. Some differences exist between organic matter in the glacier and those in the atmosphere, indicating the transformation of organic matter when precipitated through snow falls.

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