Distribution and significance of steroids in recent sediments in China

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Abstract. In order to study the distribution and geological significance of steroids compounds in the surface sediments, 13 recent sedimentary samples were collected from the rivers in Guangzhou, Jieyang and Yichang, and Fuxian Lake in Kunming. We investigated the distributions of steroids and the mineral compositions in those samples were analysed. Meanwhile, the relationship of mineral composition to the steroid distributions were analysed. The results showed that the mineral composition of the investigated recent sediments varied with different regions. Regular steranes were existed in all of Soxhlet extracts of the investigated sediments, while aromatic steroids were absent in some samples. Meanwhile, aromatic steroids can be generated by both biogeochemical reaction and thermal maturation catalysed by clay minerals. The sediments from the Yichang and Fuxian Lake areas revealed that the clay minerals showed little catalytic effects during the early diag enesis. And the samples from the Guangzhou and Jieyang areas suggested that the microbial reactions had dominant effect during the steroids aromatization. Therefore, the distributions of steroids in those recent sediments mainly influenced by microbial reaction.

1. Introduction
Steroids are well-known “biomarkers” due to their relatively stable skeleton preservation in sedimentary environments for a long geological record and their structural specificity or distribution reflecting their sources [1,2]. The steroids found in sediments are formed from sterols and stanols, biosynthesized by living organisms [3]. Those steroids were the results of numerous transformations. During the early diagenesis, the sterols and stanols will translate to steroid alkene. With further burying, they will transform to thermodynamically more stable products such as steranes, diasteranes and/or aromatic steroids [1,3]. Generally, the distribution and abundance of steroids in sediments were controlled by the original organic input. Meanwhile, clay minerals which closely associated with organic matters in geological systems, had catalytic effects on the transformations of biomarkers [4-6]. Therefore, the distribution characteristics of steroids in sediments must be indicative of the origins of the organic materials in the sediments, and to assess environmental quality. This study analyzed the distribution of steroids and the mineral composition in recent sediments sampled from various rivers and lakes in China. Its main purpose was to clarify the dominated controlling factors on the distribution characteristics of steroids in recent sediments.
2. Materials and methods

2.1. Sampling
Over 30 surface sediments were collected from the various sampling sites in Guangzhou (including XJ-4, BJ-1, DJ-1 and LXH-2), Jieyang (including LF-1, ZCY-2, TP-2 and GK-2), Yichang (including SJH-2, TM-2 and TDH-1), and Fuxian Lake in Kunming (including FXH-3 and FXH-23) areas, the locations of the sampling sites indicated in figure 1. These sediment samples were collected from locations that have some history of domestic and industrial pollution (such as the samples from the Jieyang area; see at figure 1), or in mountains where is less artificial pollution (such as the samples of SJH-2 and TDH from the Yichang area; see at figure 1). Sediment samples were covered by shallow water and only surface sediment samples (approximately 0 to 10 cm deep) were collected. The texture of the sediments ranged from sandy to loamy.

2.2. Analysis
These sediment samples were freeze-dried and powdered into 80–120 mesh. Then the powder was Soxhlet extracted using a mixture of DCM (dichloromethane)/methanol (93:7, v/v) for 72 hours, with excess copper turnings added to the Soxhlet apparatus to remove the extracted element sulfur. Asphaltenes were precipitated from the final extract by adding 50-fold (volume ratio for n-hexane/extracted) cold n-hexane and were then removed by centrifugation. The maltene fractions were then fractionated by silica/alumina (3:1, v/v) column chromatography into saturated, aromatic and polar fractions by elution with n-hexane, DCM/n-hexane (3:1, v/v) and DCM/methanol (2:1, v/v), respectively.

The saturated and aromatic biomarkers were analyzed using a Thermo Scientific Trace GC Ultra gas chromatograph coupled to a Thermo Scientific Trace DSQ II mass spectrometer. A DB-5 fused silica capillary column (30m × 0.25mm × 0.25um i.d.) was used. When the saturated hydrocarbons were analysed, the GC oven was set at 60 °C for 2 min, programmed to 290 °C at 4 °C/min and then remained at this temperature for 25 min. The temperature program for analyzing the aromatic biomarkers was set initially at 80 °C for 2 min, programmed to 290 °C at a rate of 3 °C/min and held for 15 min. Helium was used as a carrier gas with a constant flow rate of 1.5 mL/min. The ion source temperature was set to 250 °C, and the temperature of the injector was set to 290 °C. The ion source was operated in the electron impact (EI) mode with an electron energy level of 70 eV. The GC-MS analyses were carried out in selected ion monitoring mode (SIM). The selected ions that were monitored included m/z 217 (steranes), m/z 231 (triaromatic steranes), and m/z 245 (methyl triaromatic steranes).

The mineral composition was analyzed by X-ray diffraction analysis (XRD) with an OLYMPUS Innova-X BTX. The operating parameters were as follows: working voltage 31 kV with an electric current of 0.4 mA. A Co target was the X-ray light tube, 200 exposures with frequency of 3 times/min, and the 20 ranged from 3° to 55°.

3. Results and discussion

3.1. Mineral composition
The following minerals were identified in the sediments: quartz, feldspar, calcite, dolomite, illite, kaolinite and mentmorillonite (figure 1). Quartz and illite were dominated in all the investigated samples (over more than half of the total minerals). The amounts of quartz in sediments near the Guangzhou area were higher than the illite contents. Whereas, in Jieyang and Yichang areas, the quartz contents in sediments were roughly equal to the illite. In Fuxian Lake, the amounts of quartz in sediments were obviously lower than the illite. Feldspar were detected in the investigated samples except XJ-4 and LF-1, the amounts of feldspar ranged from 2.3% to 21.8%. The feldspar were mainly existed in the sediments in Yichang and Fuxian Lake areas. Except the Yichang area, most sediments from the other areas were existed a small quantity of kaolinite, ranged from 2.8% to 6.2%.
Montmorillonite were only detected in the Fuxian Lake sediments, the contents for samples FXH-3 and FXH-23 were 2.9% and 2.3%, respectively.

Figure 1. Locations of the sampling sites and the mineral composition within corresponding sediments.

River and lake sediments are a deposited integrated body of detrital, clay, authigenic/biogenic minerals and organic matter under various geologic, climatic and hydrologic conditions [7]. Previous studies had shown that the quartz, feldspar and clay minerals in fresh water sediments were mainly controlled by the mineral composition of bedrock within the river basins [7]. Thus, the difference in the mineral composition of sediments from the different regions were mainly because of their mineral compositions of the bedrock.

3.2. Distribution of steroids in the sediments
The results of the steroids distribution of 13 sediment samples from the Guangzhou, Jieyang, Yichang and Kunming areas are compared in figure 2. The steroids distribution include steranes, triaromatic steranes and methyl triaromatic steranes were widely detected in the sediments which from Guangzhou and Jieyang areas. The sediments from Yichang and Fuxian Lake areas, showed low-level contents but completely distribution of regular steranes. Whereas, the aromatic steranes were trace or even hardly detected in the Yichang and Fuxian Lake sediments. The aromatic steroids can only detected in higher temperature (> 300 °C) by laboratory heating experiments of sterols without minerals [8]. Whereas, the aromatic steroids may occurrence in a low temperature (< 70 °C) when the clay minerals presence in the pyrolysis experiments [1,9]. Previous studies documented that the catalyzed effects of clay minerals during the thermal maturation and the biogeochemical reaction from microbial activities can promote the steroids transformed to aromatic steroids in the geological system.
Tannenbaum et al. 1986 [10] indicated that the illite had catalytic effect on the thermal evolution of steroids, and the catalytic effects of montmorillonite were higher than illite.

Figure 2. Selected ion chromatograms from GC-MS analysis of the saturate and aromatic fractions in sediment samples. a. the selected ion profiles m/z 217 for steranes, b. the selected ion profiles m/z 231 for triaromatic steranes, and c. the selected ion profiles m/z 245 for methyl triaromatic steranes. The abbreviation of the biomarkers according to Wu et al. 2018 [12].

In this study, the clay minerals in sediments from the Yichang area only existed illite. While, in the Fuxian Lake, the clay minerals in the recent sediments were consist of illite, kaolinite and montmorillonite (figure 1). However, the aromatic steranes were trace or even hardly detected in the Yichang and Fuxian Lake sediments. This suggested that the clay minerals may not worked during the early diagenesis. Since the bury depth of the investigated sediment samples were very shallow, the influence of thermal stress on the sedimentary organic matter can be ignored. Thus, clay minerals may had little effects on the steroids distribution in these investigated sediments. The aromatic steroids had
widely detected in the sediments which from the Guangzhou and Jieyang areas, may influenced by biogeochemical reaction from microbial activities. In early diagenesis, bio-chemical (microbial) reactions are the dominated dynamic existed in sediments, and they can convert biolipids into more stable geolipids [11]. In developed regions of eastern China, the domestic and industrial pollution can contributed to eutrophication of water. Thus, the microbial activities were more active in the sediments from the Guangzhou and Jieyang areas than the Yichang and Fuxian Lake areas. The distribution of steroids in sediments of eastern China were more widely than western China (figure 2), this was consistent with the conditions of the microbial activities. The widely occurrence of regular steranes in all the samples, suggested that the organic inputs was not the reason for the difference of aromatic steroids varied with different regions. Thus, the distribution of steroids in recent sediments was mainly depended on the microbial reaction, rarely influenced by mineral composition of the sediments.

4. Conclusion
In this study, we investigated the distribution of steroids in recent sediments from some rivers and lakes which located in the west and east of China. The mineral compositions in those samples also be analyzed. Meanwhile, the relationship between mineral compositions and the steroid distributions were analyzed. Our findings suggested that the mineral composition of the investigated recent sediments varied with different regions. The sediments from the Yichang and Fuxian Lake areas revealed that the clay minerals showed little catalytic effects during the early diagenesis. And the samples from the Guangzhou and Jieyang areas suggested that the microbial reactions had dominant effect during the steroids aromatization. Therefore, the distributions of steroids in those recent sediments mainly influenced by microbial reaction.

Acknowledgment
This study was supported by the National Foundation of China (Grant No. 41673044).

References
[1] Schüpfner P Y and Gülaçar F O 2000 Relative stabilities of cholestadienes calculated by molecular mechanics and semi-empirical methods: application to the acid-catalyzed rearrangement reactions of cholesta-3,5-diene Organic Geochemistry 31 1589-96
[2] Hang W and Meinschein W G 1976 Sterols as source indicators of organic materials in sediments Geochimica et Cosmochimica Acta 40 323-30
[3] Mackenzie A S, Lamb N A and Maxwell J R 1982 Steroid hydrocarbons and the thermal history of sediments Nature 295 223-6
[4] Hussler G and Albrecht P 1983 C27–C29 Monoaromatic anthrasteroid hydrocarbons in Cretaceous black shales Nature 304 262-3
[5] Brooks B T 1952 Evidence of Catalytic Action in Petroleum Formation Industrial & Engineering Chemistry 44 2570-7
[6] Wang X, Cai J and Bao Y 2006 Catalysis of clay Mineral to Organic Matter in Hydrocarbon Genesis Marine Origin Petroleum Geology 11 27-38 (in Chinese with English Abstract)
[7] Jin Z D 2011 Composition, Origin and Environmental Interpretation of Minerals in Lake Sediments and Recent Progress Journal of Earth Sciences and Environment 33 34-4 (in Chinese with English Abstract)
[8] Rushdi A I, Ritter G, Grimailt J O and Simoneit B R T 2003 Hydrous pyrolysis of cholesterol under various conditions Organic Geochemistry 34 799-812
[9] Schüpfner P, Finck Y, Houot F and Gülaçar F O 2007 Acid catalysed backbone rearrangement of cholesta-2,4,6-triene: On the origin of ring A and ring B aromatic steroids in recent sediments Organic Geochemistry 38 671-81
[10] Tannenbaum E, Ruth E and Kaplan I R 1986 Steranes and triterpanes generated from kerogen pyrolysis in the absence and presence of minerals Geochimica et Cosmochimica Acta 50 805-12
[11] Mackenzie A S, Brassell S C, Eglinton G and Maxwell J R 1982 Chemical fossils: the geological fate of steroids Science 217 491-504

[12] Wu L, Fang X, Ji S and Geng A 2018 Thermal alteration of biomarkers in the presence of elemental sulfur and sulfur-bearing minerals during hydrous and anhydrous pyrolysis Organic Geochemistry 123 74-89