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Xinping Liang, Sergei Katsev, Quanyou Liu, Gleb S. Pokrovski, Zhijun Jin

► **To cite this version:**

Xinping Liang, Sergei Katsev, Quanyou Liu, Gleb S. Pokrovski, Zhijun Jin. Carbon, iron and sulfur records of lacustrine paleo-environments during the middle Eocene in eastern China. *Science of the Total Environment*, 2024, 956, pp.177270. 10.1016/j.scitotenv.2024.177270 . hal-04775135

**HAL Id: hal-04775135**

**<https://hal.science/hal-04775135v1>**

Submitted on 9 Nov 2024

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# Science of the Total Environment

## Carbon, iron and sulfur records of lacustrine paleo-environments during the middle Eocene in eastern China --Manuscript Draft--

<b>Manuscript Number:</b>	STOTEN-D-24-35639R2
<b>Article Type:</b>	Research Paper
<b>Keywords:</b>	organic carbon burial; ferruginous conditions; volcanism; transgression; paralic lacustrine shale; middle Eocene
<b>Corresponding Author:</b>	Xinping Liang Peking University CHINA
<b>First Author:</b>	Xinping Liang
<b>Order of Authors:</b>	Xinping Liang Sergei Katsev Quanyou Liu Gleb S. Pokrovski Zhijun Jin
<b>Abstract:</b>	<p>It is widely recognized that anoxic conditions facilitate the preservation of organic carbon in marine sediments. However, the specific geological factors that lead to the development of such conditions in paleo-lakes are less well understood. Owing to their smaller size, paleolakes could experience more frequent and stronger changes in geochemical conditions than oceans. Such changes, such as volcanism, hydrothermal fluids, or ocean transgressions, can also strongly affect the lacustrine organic carbon burial thereby complicating sediment diagenesis record. Here, we used total organic carbon content (TOC), organic carbon isotope (<math>\delta^{13}\text{C}_{\text{org}}</math>), iron speciation, and pyrite sulfur isotope (<math>\delta^{34}\text{S}_{\text{py}}</math>) data to establish relationships between organic carbon preservation and anoxic conditions in fine-grained sediments from the middle Eocene lacustrine depositional environments from the Shahejie Formation of the Jiyang Depression, Bohai Bay Basin, eastern China. The results reveal TOC between 1% and 10%, highly-reactive iron to total iron ratios greater than 0.38, and most TOC to total sulfur ratios exceeding 2. These data indicate that the organic-rich shales of the Shahejie Formation were formed as a result of high primary productivity during the warm and humid middle Eocene period, coupled with the efficient preservation of organic matter in anoxic bottom waters. Negative <math>\delta^{13}\text{C}_{\text{org}}</math> and <math>\delta^{34}\text{S}_{\text{py}}</math> excursions recorded in the Shahejie Formation indicate water column conditions to have been influenced by transient volcanic eruptions. Positive <math>\delta^{13}\text{C}_{\text{org}}</math> and negative <math>\delta^{34}\text{S}_{\text{py}}</math> excursions may have been caused by hydrothermal fluids input whereas <math>\delta^{34}\text{S}_{\text{py}}</math> values approaching 20‰ suggest frequent marine transgressions. In particular, despite potential inputs of S into the paleolake by volcanism, hydrothermal fluids, or marine transgressions, bacterial sulfate reduction efficiently depleted the sulfate pool to have created ferruginous geochemistry water conditions for the effective preservation of organic carbon in sediments. Our results establish a direct link between lacustrine shale geochemical signatures and geological phenomena that impact its sedimentation.</p>
<b>Suggested Reviewers:</b>	<p>Jun Shen, Dr. Prof., China University of Geology ( Wuhan ) shenjun@cug.edu.cn Prof. Shen is a global environmentalist with a broad perspective, he published several papers in Nature Communications about volcanism</p> <p>Mingyu Zhao, Dr. Associate Prof., CAS Institute of Geology and Geophysics mingyu.zhao@mail.iggcas.ac.cn Dr. Zhao made a big progress in the sphere interaction and nutrient circulation, some of the papers are published in Nature Geoscience.</p>

	<p>Zhengbing Wang, Dr.  Delft University of Technology  Zheng.Wang@wldelft.nl  Prof. Wang has made great progress in the ecological environment research of estuarine delta and near coastal zones.</p>
	<p>Qiyuan Sun, Dr.  Fujian Normal University  minglei_2008@fjnu.edu.cn  Dr. Sun does research on the formation of organic matter in rivers and lakes for more than 10 years, and can give the comments from a morden perspective.</p>
	<p>Meng Cheng, Dr.  Chengdu University of Technology  mengcheng@cdut.edu.cn  Dr. Cheng knows a lot about the carbon and sulfur cycles in oceans and lakes.</p>
	<p>Jian Cao, Dr.  Nanjing University  jcao@nju.edu.cn</p>
	<p>Xiting Liu, Dr.  Ocean University of China  liuxiting@ouc.edu.cn  former reviewer</p>
<b>Response to Reviewers:</b>	

Dear Editor Wei Ouyang,

We gratefully acknowledge the reviewer's positive evaluation of our work and agree with the comments of the second reviewer. We appreciate the editor's help in improving the manuscript, as well as the editorial support and suggestions. According to the proposed comments, we carefully revised the manuscript. The responses to the comments of the second reviewer are listed point-by-point in the attached file "Response to reviewers", the revisions are annotated **red** through the manuscript (in the version of track changes). The manuscript is co-authored by Sergei Katsev, Quanyou Liu, Gleb S. Pokrovski and Zhijun Jin. We kindly ask you to consider it for publication in "*Science of the Total Environment*".

In the revised manuscript, we used total organic carbon content, iron speciation, organic carbon isotope ( $\delta^{13}\text{C}_{\text{org}}$ ), and pyrite sulfur isotope ( $\delta^{34}\text{S}_{\text{py}}$ ) data to establish relationships between organic carbon preservation and anoxic conditions in fine-grained sediments from the middle Eocene lacustrine depositional environments of the Jiyang Depression, Bohai Bay Basin, eastern China. Our results identified that despite potential inputs of S into the paleolake by volcanism, hydrothermal fluids, or transgression, bacterial sulfate reduction depleted the sulfate pool sufficiently to have created ferruginous geochemistry water conditions for the effectively preservation of organic carbon in sediments of Shahejie Formation. This is a direct link between lacustrine organic carbon burial and its controlling factors among multivariate geological events.

We believe that the revised manuscript will be of interest to the readership of researchers and professionals working on lacustrine environments. This manuscript has not been published or presented elsewhere in part or in entirety and is not under consideration by another journal. We have read and understood your journal's policies, and we believe that neither the manuscript nor the study violates any of these. There are no conflicts of interest to declare.

Thank you very much for your time and consideration. I look forward to hearing from you.

Sincerely,

Xinping Liang

Institute of Energy, Peking University, Beijing, 100871, China;

xinping.liang@pku.edu.cn

1 Carbon, iron and sulfur record of lacustrine paleo-environments  
2  
3 during the middle Eocene in eastern China  
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9 Xinping Liang<sup>a,c</sup>, Sergei Katsev<sup>b</sup>, Quanyou Liu<sup>a\*</sup>, Gleb S. Pokrovski<sup>c</sup>,  
10  
11 Zhijun Jin<sup>a,d\*</sup>  
12

13  
14 a. State Key Laboratory of Shale Oil and Gas Enrichment Mechanisms and Effective  
15  
16 Development, Institute of Energy, Peking University, Beijing 100871, China;  
17

18  
19 b. Large Lakes Observatory and Department of Physics, University of Minnesota  
20  
21 Duluth, 2205 E 5th St, Duluth, MN 55812, USA;  
22

23  
24 c. Géosciences Environnement Toulouse, Université Toulouse III – Paul Sabatier,  
25  
26 CNRS, IRD, CNES, OMP, 14 avenue Edouard Belin, F-31400 Toulouse, France;  
27

28  
29 d. Sinopec Petroleum Exploration and Production Research Institute, Beijing, 100083,  
30  
31 China  
32  
33

34  
35 \*Corresponding author: [liuqy@pku.edu.cn](mailto:liuqy@pku.edu.cn) or [qyouliu@sohu.com](mailto:qyouliu@sohu.com) (QY.L.) and  
36  
37 [jinzj1957@pku.edu.cn](mailto:jinzj1957@pku.edu.cn) (Z.J.J)  
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**Dear Editor Wei Ouyang and dear reviewers,**

We gratefully appreciate your help in improving the manuscript, as well as the editorial support and suggestions. Thank you for the positive evaluation of our work and we agree with the minor revisions. According to the proposed constructive comments, we carefully revised the manuscript and needed figures. The revisions are annotated red through the manuscript in the version of track changes. The manuscript is co-authored by Xinping Liang, Sergei Katsev, Quanyou Liu, Gleb S. Pokrovski and Zhijun Jin. We kindly ask you to consider it for publication in “*Science of the Total Environment*”.

**1. Followed by the editor’s suggestions, we submitted:**

- 1) Cover Letter;
  - 2) revised manuscript with changes marked red;
  - 3) revised manuscript with no changes marked;
  - 4) Graphical Abstract;
  - 5) Figures and Tables as separate files (Table 1 as separate file in Word format);
  - 6) 3 points of Highlights (maximum 85 characters, including spaces, per bullet point);
  - 7) response to Reviewers point-by-point;
- and we REMOVED the original version of our submission.

**2. Here are the responses to the comments of Reviewer #2.****Comments:**

After reviewing the manuscript, I recommend minor revisions before acceptance.

The carbon isotopes of organic matter and the sulfur isotopes of pyrite are influenced by sedimentary environment evolution and sediment dynamics, which should be considered.

The iron speciation is affected by the sedimentary environment and redox conditions, with the contents of ferrous carbonate and pyrite competing with each other. I suggest the authors consider some modern sedimentary environment studies to enhance their discussion of the marine transgression in the study area. Relevant references for consideration include: Liu et al., 2023, SB; Zhang et al., 2024, 3P; Kong et al., 2024, MG; Zhang et al., CG, 2024.

**Response:**

We are grateful for this kind suggestion and the references. We agree with the reviewer’s point that the influencing factors of carbon isotopes of organic matter ( $\delta^{13}\text{C}_{\text{org}}$ ), the sulfur isotopes of pyrite ( $\delta^{34}\text{S}_{\text{py}}$ ) and the iron speciation should be considered when these indicators are applied in the interpretation of paleoenvironments. As our samples are all fine-grained sediments in the semi-deep to deep lake, the TOC values vary between 1% and 10% (average 4%), and in the detailed core observations of the FY1 well, no strong storms, floods or fragments of higher plants were observed over a total length of 403.6 m, so we considered there was very few the terrestrial occasional effect, and the  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{34}\text{S}_{\text{py}}$  could be used for most cases. Here we did not use the high C/S ratios to distinguish between marine and terrestrial sediments here because the sulfur content increasing can also be caused by volcanic or hydrothermal activities, neither does the pyrite content.

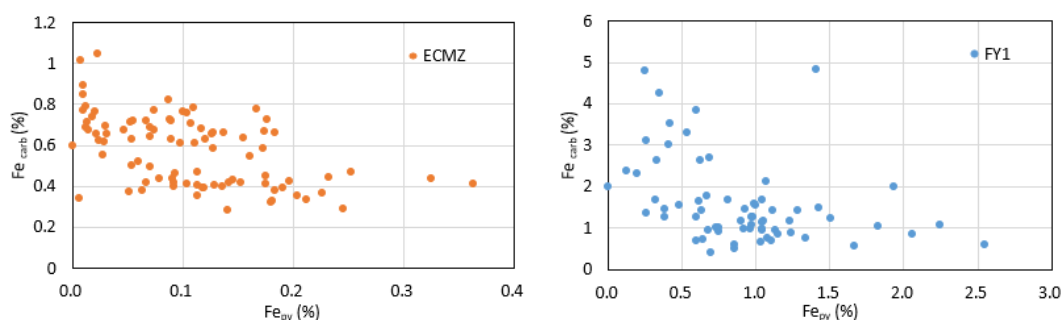
We agree with the reviewer’s comment that the iron speciation is applied to interpret the sedimentary environment and redox conditions. Here as our magnetite content ( $\text{Fe}_{\text{mag}}$ ) is low (< 0.13%), pointing to the absence of intense diagenetic transformation, so the iron speciation can be used to constrain the redox conditions of Shahejie Formation. As the oxidized Fe ( $\text{Fe}_{\text{ox}}$ ) is low, with

a maximum of 0.4%, so the contents of ferrous carbonate and pyrite compete with each other. This conclusion is also consistent with Liu et al.'s (2023, SB) viewpoint (Fig1.A, B). The difference between the samples of the two study areas is their total content, the total contents of ferrous carbonate and pyrite is lower than ~2% and ~6% respectively (Fig1.C), indicating the ferruginous to euxinic water conditions during Shahejie Formation.

As the TOC and  $\delta^{13}\text{C}_{\text{org}}$  values shows different sources of organic matter (Fig1.D) between ECMZ core of modern sedimentary environment (Kong et al., 2024, 3P) and FY-1 Well core of Shahejie Formation, we compared the values of highly reactive iron between 91 samples of ECMZ core and 66 samples of FY-1 Well core of Shahejie Formation, to try to enhance the discussion of the marine transgression during middle Eocene (Fig1.E, F). Here in core ECMZ, authigenic minerals such as framboid pyrite aggregates can document the seawater intrusion in East China Sea, and continuous and slight decrease in the contents of magnetite and haematite illustrates that the sea level continued to rise (Liu et al., 2023, SB). However, this could happen after volcanic and hydrothermal activities during Shahejie Formation in Jiyang Lake. For example, as volcanic activity brings large amounts of nutrients and trace metals to the surface water, the positive feedback can increase paleoproductivity, accelerate the reducing bottom water conditions, and formed the high content of authigenic minerals such as framboid pyrite.

Therefore, we combined  $\delta^{13}\text{C}_{\text{org}}$  to distinguish volcanism and transgressions because volcanism can cause negative  $\delta^{13}\text{C}_{\text{org}}$  excursions, whereas marine transgressions usually happen in warmer climates and cause positive  $\delta^{13}\text{C}_{\text{org}}$  excursions. Also, we propose that the precipitation of calcium carbonate in organic-rich shale is the result of increased pH due to strong photosynthesis by algae in the warm climate during marine transgression in the Jiyang calcareous lake. This may also be the difference between shallow marine and terrestrial deposits. Our mineral analyses show that the carbonate content in the study interval was generally high, with average calcite and dolomite contents of 37% and 10%, respectively. For example, the content of  $\text{Fe}_{\text{carb}}$  is higher than that of  $\text{Fe}_{\text{py}}$  from 3225 to 3200 m (Unit 5 in Fig.2), indicating that the sulfur isotope fractionation of pyrite in the paralic lakes during the sulfate reduction process was constrained by changes in the global sea level. The sea level increased in the warm and humid climate, brought large amounts of  $\text{Ca}^{2+}$  to form carbonates as well as high paleo-productivity promoted the deposition of organic-rich layers simultaneity. Thus formed the alternating carbonate and organic-rich shale layers, and after that the organic matter was degraded in a limited manner under ferruginous conditions and was well preserved. Saturated carbonate ions combined with iron and formed siderite, making its content higher in lacustrine sediments than that in modern sedimentary environments (Fig1.E).

This enhanced discussion of the marine transgression of the above explanation has been added in the manuscript. Please see lines 447-464.



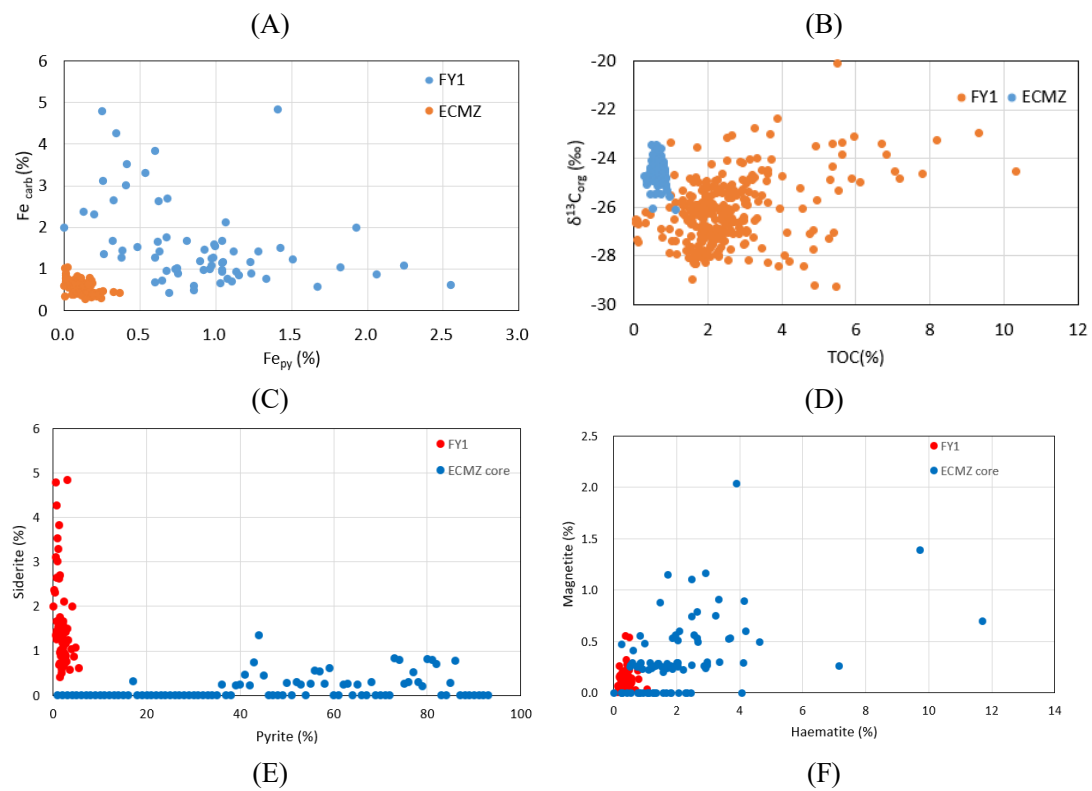


Fig.1. Comparison of the highly reactive iron values, TOC and  $\delta^{13}\text{C}_{\text{org}}$  between samples of CEMZ core from modern sedimentary environment (Liu et al., 2023, SB; Zhang et al., 2024, 3P) and samples of FY1 Well from Jiyang Lake.

Thank you for your time and consideration. I look forward to hearing from you.

Best wishes for the journal "Science of the Total Environment"!

Yours sincerely,

Xinping Liang on behalf of all authors

[xinping.liang@pku.edu.cn](mailto:xinping.liang@pku.edu.cn)

Institute of Energy, Peking University



1 Carbon, iron and sulfur **records** of lacustrine paleo-environments during the  
2 middle Eocene in eastern China

3

#### 4 **Abstract**

5 It is widely recognized that anoxic conditions facilitate the preservation of organic  
6 carbon in marine sediments. However, the specific geological factors that lead to the  
7 development of such conditions in paleo-lakes are less well understood. Owing to their  
8 smaller size, paleolakes could experience more frequent and stronger changes in  
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10 fluids, or ocean transgressions, can also strongly affect the lacustrine organic carbon  
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13 sulfur isotope ( $\delta^{34}\text{S}_{\text{py}}$ ) data to establish relationships between organic carbon  
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15 lacustrine depositional environments from the Shahejie Formation of the Jiyang  
16 Depression, Bohai Bay Basin, eastern China. The results reveal TOC between 1% and  
17 10%, highly-reactive iron to total iron ratios greater than 0.38, and most TOC to total  
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19 Shahejie Formation were formed as a result of high primary productivity during the  
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21 organic matter in anoxic bottom waters. Negative  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{34}\text{S}_{\text{py}}$  excursions  
22 recorded in the Shahejie Formation indicate water column conditions to have been  
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24 excursions may have been caused by hydrothermal fluids input whereas  $\delta^{34}\text{S}_{\text{py}}$  values  
25 approaching 20‰ suggest frequent marine transgressions. In particular, despite  
26 potential inputs of S into the paleolake by volcanism, hydrothermal fluids, or marine  
27 transgressions, bacterial sulfate reduction efficiently depleted the sulfate pool to have  
28 created ferruginous geochemistry water conditions for the effective preservation of  
29 organic carbon in sediments. Our results establish a direct link between lacustrine shale  
30 geochemical signatures and geological phenomena that impact its sedimentation.

31

32 **Key words:** organic carbon burial; ferruginous conditions; volcanism; transgression;  
33 paralic lacustrine shale; middle Eocene

34

## 35 **1. Introduction**

36 Anoxic conditions facilitate burial and preservation of organic carbon by slowing  
37 down microbial degradation, primarily in marine sediments (Shen Y. et al., 2003;  
38 Planavsky et al., 2011; Clarkson et al., 2014, 2016; Guilbaud et al., 2015; Raiswell et  
39 al., 2018), whilst factors that cause such conditions in lakes have not been sufficiently  
40 investigated. Multiple geologic events, such as volcanism, subsurface hydrothermal  
41 activity, and marine water incursion, can substantially affect sediment diagenesis and  
42 the burial of organic matter in both marine and lacustrine basins. Volcanic ash layers,  
43 for example, are prevalent in organic-rich deposits (organic carbon content greater than  
44 2.0%) such as the Bazhenov Formation (western Siberia, Russia), the Eagle Ford  
45 Formation (Gulf Coast Basin, USA), the Wufeng-Longmaxi Formation (Sichuan Basin,  
46 China), the Fengcheng and Lucaogou Formations (Junggar Basin, China) (Ruebsam et

47 al., 2020; Liang et al., 2020; Liu et al., 2021, 2024). Volcanic activity may increase  
48 biological productivity in the photic zone by supplying nutrients and affect aquatic  
49 environments and their sedimentary records by providing fluxes of heat, dissolved  
50 carbon dioxide, and methane (Duggen et al., 2010; Langmann et al., 2010; Liu et al.,  
51 2019). Enhanced preservation of organic material in sediments can lead to the  
52 formation of organic-rich shales (Kim et al., 2015; LaRowe et al., 2020). Hydrothermal  
53 and volcanic inputs, recorded by high concentrations of metals and heterogeneous tuff  
54 in shales, are correlated with changes in paleo-productivity, anoxia, and organic matter  
55 burial (Magnall et al., 2016; He et al., 2020). However, the mechanisms by which  
56 geological events affect formation and preservation of organic matter in lacustrine  
57 environments are much less constrained than in marine environments.

58 Like the modern counterparts, ancient lakes were important sinks of organic  
59 carbon (Sklarew, 1979; Layton-Matthews et al., 2013; Swanner et al., 2020). Being  
60 much smaller than oceans, lakes are more sensitive to environmental changes and can  
61 record geologic events on shorter time scales. Paralic lakes, in particular, can be  
62 affected by volcanic activity, hydrothermal discharges, marine transgressions or other  
63 geological events (Malumián and Ramos, 1984; Duggen et al., 2010; Lee et al., 2018;  
64 Zeng et al., 2018; Zhang et al., 2018; Liu et al., 2024), so the controlling factors for the  
65 burial of lacustrine organic carbon are more complicated. For example, the Kabuno  
66 Bay (East Africa) is ferruginous, whereas Lake Kivu is sulfidic even though they both  
67 receive iron through hydrothermal sub-lacustrine springs (Bhattarai et al., 2012; Ross  
68 et al., 2014; Swanner et al. 2020). Studying variations in lacustrine conditions of  
69 sedimentation may help understand the analogous marine processes on their

70 correspondingly longer time scales.

71 In this regard, ancient lakes of the Jiyang Depression (Fig.1) in the Bohai Bay  
72 Basin, eastern China offer an excellent natural environment to investigate in detail the  
73 continental sedimentary record of the middle Eocene. A series of successive lacustrine  
74 shale sediments 150–300 m thick were deposited between the upper sub-member of  
75 Member 4 and the lower sub-member of Member 3 of the Shahejie Formation ( $Es_4^1$   
76 and  $Es_3^3$ ) (Chen et al., 2008; Liang C. et al., 2018; Shi et al., 2019). This depositional  
77 period corresponds to a global increase in the atmospheric  $CO_2$  during the Middle  
78 Eocene Climate Warming (MECO) (Fig.1, A; Lourens et al., 2005; Jovane et al., 2007;  
79 Zachos et al., 2008; Bijl et al., 2010). Therefore, this study combines total organic  
80 carbon contents (TOC) and total sulfur (TS) values of the Fanye-1 well (FY1, Fig. 1,  
81 B), with the vertical variation in Fe speciation, organic carbon isotope ( $\delta^{13}C_{org}$ ), and  
82 pyrite sulfur isotope ( $\delta^{34}S_{py}$ ) data, to establish a direct link between organic carbon  
83 preservation and anoxic conditions, and the factors that affect organic carbon burial in  
84 lacustrine basins during middle Eocene.

85

## 86 2. Geological Setting

87 The Bohai Bay Basin is a large Cenozoic sedimentary basin, which was formed  
88 at the intersection of three major tectonic regions that included the ancient Asian,  
89 Tethys and Pacific Oceans (Fig. 1, B). The subduction of the West Pacific plate under  
90 the North China Craton was the controlling factor in the tectonic evolution rate and  
91 orientation of the Bohai Bay Basin (Chen et al., 2008). Between the Late Paleocene  
92 and Eocene, subduction of the Pacific Plate decreased to its lowest rate of about 40

93 mm/a at 43 Ma, and the orientation changed from north-north-west to north-west-west.  
94 The rate gradually increased to 60 mm/a from 43 to 32 Ma, making the entire Asia  
95 continent an extended tectonic domain. This spreading reached its faulting limit at  
96 about 23 Ma in the Oligocene leading to the formation of the Late Mesozoic-Paleogene  
97 Bohai Bay Basin, which is divided into seven depressions and three uplifts (Chen et al.,  
98 2008).

99 Among them, the Jiyang Depression is the largest sedimentation center of the  
100 basin, spanning latitudes from 35 to 40°N. The depression is about 200 km long from  
101 east to west and 120 km wide from north to south, with a total area of 26,000 km<sup>2</sup> (Song  
102 et al., 2020). Cenozoic deposition during Es<sub>4</sub><sup>1</sup> and Es<sub>3</sub><sup>3</sup> sub-members in the Bohai Bay  
103 Basin coincided with an intensive fault depression, resulting in the formation of the  
104 Jiyang Lake whose estimated ancient depth was 190–290 m (Fig. 1., C) with the  
105 deepest area likely reaching 600 m (Chen et al., 2008). The lake has existed in the basin  
106 for about 4 million years and was connected to the west Pacific paleo-ocean during  
107 multiple periods, lasting for several thousand years each (Song et al., 2020). Between  
108 these episodes, the lake basin likely remained closed (Chen et al., 2008).

109 During Es<sub>4</sub><sup>1</sup> time, as the basin subsided, the lake experienced high salinities  
110 affected by different geological processes. During the Es<sub>3</sub><sup>3</sup> period of humid climate, as  
111 the lake basin widened and subsidence increased, the lake connected to the ocean, thus  
112 increasing accommodation space. Abundant semi-deep to deep waters (10–60 m depth)  
113 provided favorable conditions for deposition of fine-grained sedimentary rocks such as  
114 black shale. The rocks were predominantly argillitic with extensive layers of both  
115 massive and lamellar textures and with veins of sparry limestone, limy mudstone, and

116 dolomite (Chen et al., 2008; Liang C. et al., 2018; Song et al., 2020).

117

### 118 **3. Materials and Methods**

119 Core analysis shows that the high-quality source rocks of Es<sub>4</sub><sup>1</sup> and Es<sub>3</sub><sup>3</sup> (to ~1000  
120 m) were widely distributed in semi-deep or deep lacustrine facies, intercalated with  
121 mm-to-cm thick layers of volcanic ash in Jiyang Depression. Here a length of 403.6 m  
122 of whole-core was taken from the FY1 well (Shi et al., 2019; Song et al., 2020). Black  
123 and gray-black, layered, grainy, muddy shale dominates the Es<sub>4</sub><sup>1</sup> and Es<sub>3</sub><sup>3</sup> lithologies.  
124 A total of 270 core samples was obtained at a spacing of 1.0–1.5 m and these were  
125 analyzed for TOC, TS,  $\delta^{13}\text{C}_{\text{org}}$  and major element analyses. A subset of 70 samples at  
126 an interval of 5–6 m was subjected to iron speciation and  $\delta^{34}\text{S}_{\text{py}}$  analyses.

127 The concentrations of TOC and TS were determined using an Eltra infrared (IR)  
128 C/S analyzer from the discrepancy between the total carbon (or sulfur) determined by  
129 combustion and the total inorganic carbon (or sulfur) determined by acidification.  
130 Ultrapure 6 N HCl was added in a silver cup to dissolve inorganic carbon and sulfur  
131 (mostly carbonate and sulfide minerals) from weighed portions of powdered samples.  
132 Analyses of  $\delta^{13}\text{C}_{\text{org}}$  were performed using a Costech<sup>TM</sup> 4010 coupled with a Thermo  
133 Finnigan MAT 253 via an open-split interface Conflo IV, with a reproducibility better  
134 than  $\pm 0.1\%$  as based on the international standard IAEA-600 (caffeine,  $\delta^{13}\text{C}_{\text{org}} = -$   
135  $27.77\%$ ).

136 For major element concentrations (Fe, Al), 300 mg of powdered samples were  
137 burnt at 600 °C for 12 h in a muffle furnace to remove volatiles compounds, followed  
138 by a standard multi-acid (HF-HCl-HNO<sub>3</sub>) digestion protocol designed for dissolution

139 in a Teflon bomb. An Agilent 7700 inductively coupled plasma mass spectrometer  
140 (ICP-MS) was used for the solution analyses, with an analytical precision of better than  
141  $\pm 5\%$  ( $1\sigma$ ) established using USGS standards (BHVO-2 and BCR-2).

142 Iron speciation and pyrite sulfur isotope analyses (in terms of  $\delta^{34}\text{S}_{\text{py}}$ ) were  
143 performed for a total of 70 samples at the State Key Laboratory of Biogeology and  
144 Environmental Geology, China University of Geosciences (Wuhan). Iron as pyrite  
145 ( $\text{Fe}_{\text{py}}$ ) was extracted using the chromium reduction method and iron speciation was  
146 determined by the sequential extraction method (Poulton and Canfield, 2005). Sulfur  
147 in pyrite ( $\text{S}_{\text{py}}$ ) was extracted as  $\text{H}_2\text{S}$  using a hot  $\text{CrCl}_2$  distillation for 2 h, trapped as  
148 silver sulfide ( $\text{Ag}_2\text{S}$ ), which was then quantified gravimetrically. The  $\text{Fe}_{\text{py}}$  content in  
149 each sample was then calculated assuming the ideal pyrite stoichiometry ( $\text{FeS}_2$ ). Iron  
150 from carbonate minerals ( $\text{Fe}_{\text{carb}}$ ) was extracted by dissolution for 24 h in cold 10 wt%  
151 HCl. Then ferric Fe (oxyhydroxides,  $\text{Fe}_{\text{ox}}$ ) was liberated from the residue of each  
152 sample, treated for 2 h with a sodium dithionite solution (50 g/L) buffered to a pH of  
153  $\sim 5$  with acetic acid and sodium citrate. Finally, Fe bound in magnetite ( $\text{Fe}_{\text{mag}}$ ) was  
154 extracted for 6 h using a 0.2 M ammonium oxalate and 0.17 M oxalic acid solution (pH  
155  $\sim 3$ ). After diluting the extracts by a factor of 100 in 2 wt%  $\text{HNO}_3$  (suprapure), an  
156 Agilent 7500ce ICP-MS was used to analyze each sequential extract. To increase  
157 precision, samples underwent processing in conjunction with internal calibration  
158 standards and blanks, by analyzing in duplicate each 10<sup>th</sup> sample per batch. The  
159 analytical precision was better than 5% of the value.

160 Sulfur isotope ratios ( $^{34}\text{S}/^{32}\text{S}$ ) were determined using a Thermo Fisher Scientific  
161 Delta V Plus isotope-ratio mass spectrometer coupled with a flash EA. The results are

162 expressed as  $\delta^{34}\text{S}_{\text{py}}$  following the standard delta notation as per mil deviations relative  
163 to the Vienna Cañon Diablo Troilite (Li et al., 2021). An analytical uncertainty of 0.2‰  
164 ( $1\sigma$ ) for pyrite  $\delta^{34}\text{S}$  was determined from replicate analyses of the International Atomic  
165 Energy Agency (IAEA) standards: S1 ( $\delta^{34}\text{S} = -0.3\text{‰}$ ), IAEA S2 ( $\delta^{34}\text{S} = +22.65\text{‰}$ ), and  
166 IAEA S3 ( $\delta^{34}\text{S} = -32.5\text{‰}$ ).

167

## 168 **4. Results**

169 The results of geochemical analyses of FY1 section are summarized in Table 1.  
170 The variation in chemical and isotopic composition of TOC,  $\delta^{13}\text{C}_{\text{org}}$ , TS,  $\delta^{34}\text{S}_{\text{py}}$  and Fe  
171 redox as a function of depth is presented in Fig. 2. The study interval was divided into  
172 7 units according to the changes in  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{34}\text{S}_{\text{py}}$  values.

### 173 **4.1. Organic carbon systematics**

174 TOC values of the 270 samples vary from about 1 to 10 % with an average value  
175 close to 4%, and with maximum enrichment in Units 1 and 5 (Fig. 2), but without  
176 systematic differences between  $\text{Es}_3^3$  and  $\text{Es}_4^1$ . The  $\delta^{13}\text{C}_{\text{org}}$  values for samples of  $\text{Es}_4^1$   
177 vary within a relatively narrow range of about -29‰ to -20‰ with an average of  $\sim -$   
178 26‰, whereas those from  $\text{Es}_3^3$  vary within even narrower range of about -28‰ to -23‰  
179 with a mean value -26‰ (Table 1). Samples with positive excursions of  $\delta^{13}\text{C}_{\text{org}}$  values  
180 ( $> -24\text{‰}$ ) are more frequent in  $\text{Es}_4^1$ , and are characterized by elevated TOC contents ( $>$   
181 4%). Samples showing more negative  $\delta^{13}\text{C}_{\text{org}}$  ( $\leq -26\text{‰}$ ) are also predominantly found  
182 in the  $\text{Es}_4^1$  sub-member (Fig. 2A, B).

183

### 184 **4.2. Iron systematics**



185 In the lacustrine samples of Es<sub>4</sub><sup>1</sup> and Es<sub>3</sub><sup>4</sup>, Fe<sub>T</sub> values range between 1.4 and 8.0%,  
186 with an average close to 3% and are generally dominated by highly reactive iron (Fe<sub>HR</sub>,  
187 including pyrite and carbonate iron, oxidized and magnetite iron) fraction (> 90% of  
188 Fe<sub>T</sub> on average). Pyrite iron (Fe<sub>py</sub>) ranges from 0.1 to 4% with an average of ~1%,  
189 which is slightly less than or comparable to carbonate iron (Fe<sub>carb</sub>) content varying from  
190 0.5 to 4 (average 1.5%). Oxidized iron (Fe<sub>ox</sub>) is low, with a maximum of 0.4%. The  
191 Fe/Al ratios are systematically higher than 0.44 (with a single sample exception of 0.18  
192 at 3346.9 m). Magnetite content (Fe<sub>mag</sub>) is low (< 0.13%), pointing to the absence of  
193 diagenesis; as a result, the iron speciation can be used to constrain the redox conditions.  
194 All Fe<sub>HR</sub>/Fe<sub>T</sub> values exceed 0.38, and almost all Fe<sub>py</sub>/Fe<sub>HR</sub> ratios are lower than 0.6,  
195 which is mostly due to the relatively high Fe<sub>carb</sub> content.

196 Iron speciation is a widely used proxy for water column redox conditions, and can  
197 differentiate between oxic and anoxic (ferruginous or euxinic) environments (Poulton  
198 and Canfield, 2005, 2011). For anoxic conditions, Fe<sub>py</sub>/Fe<sub>HR</sub> ratios are used to  
199 distinguish ferruginous (typically < 0.7) and euxinic (typically > 0.8) conditions;  
200 however, more recent work suggested values above 0.6 as evidence of euxinia (Poulton,  
201 2021). Under anoxic conditions, either diagenetic transformation of Fe<sub>HR</sub> minerals into  
202 Fe-rich clay, or the swift sedimentation of deposits lacking iron, can lower Fe<sub>HR</sub>  
203 concentrations. Total Fe/Al ratios provide complementary information on water  
204 column redox conditions. Indeed, although oxidative weathering or diagenesis of  
205 samples could obscure Fe<sub>py</sub> systematics, it would not significantly alter the Fe/Al ratios  
206 that are systematically lower than 0.44 in oxic marine sediments (Lyons and  
207 Severmann, 2006; Clarkson et al., 2014, 2016; Raiswell et al., 2018). Therefore, the

208 Fe/Al proxy in carbonate-rich sediments is relatively robust, provided  $Fe_T > 0.5$  wt%  
209 (Raiswell et al., 2018). For  $Fe_T < 0.5$  wt%, carbonate samples have a greater potential  
210 to be enriched in  $Fe_{HR}$  due to processes other than water column processes that arise  
211 under anoxic conditions (e.g., post sedimentary diagenesis).

212 Overall, TOC values higher than 0.5%, with total iron  $> 0.5$  wt%,  $Fe_{HR}/Fe_T$  ratios  $>$   
213 0.38 and  $Fe_{HR}/Fe_T$  ratios  $< 0.8$  throughout the succession (Fig. 2, A, E, F) collectively  
214 demonstrate predominantly anoxic ferruginous during the depositional period, despite  
215 evidence of pyrite enrichment of considerable spatial and temporal variability that  
216 cannot exclude local intermittent euxinic conditions in the basin.

217

### 218 **4.3. Sulfur systematics**

219 Total sulfur (TS) concentrations vary from about 0.2 to 11%, with an average of  
220  $\sim 1.4\%$  across the two main intervals (Table 1, Fig. 2). Most samples (231) have  
221 TOC/TS weight ratios above 2, with only a few (36) having TOC/TS  $< 2$  (Fig. 2A, C).  
222 According to Berner and Raiswell's (1984) analysis of modern sediments, TOC/TS  
223 values of  $< 2$  would correspond to euxinic conditions, those between 2 and 3.6  
224 represent "normal" marine conditions, those of 3.6 to 10 reflect freshwater and  
225 seawater transition zones, and those  $> 10$  correspond to freshwater sediments.  
226 Therefore, most of our samples from the study interval would indicate freshwater or  
227 marine transitional conditions, with only rare instances of euxinia (Fig.3).

228 Values of  $\delta^{34}S_{py}$  exhibit large variations within the studied section (Fig. 2D),  
229 ranging from 9‰ to 36‰ with an average of  $\sim 20\%$  with no significant differences  
230 between  $Es_3^3$  and  $Es_4^1$  (Table 1). As sulfur isotope values in marine sulfates were  $\sim 22\%$

231 during middle Eocene (Payton et al., 1998) and elevated  $\delta^{34}\text{S}_{\text{py}}$  values ( $> 20\text{‰}$ ) are  
232 consistent with the low levels of sulfate in the euxinic water column (Shen et al., 2003),  
233 our large  $\delta^{34}\text{S}_{\text{py}}$  variations (Fig. 2D) indicate that redox conditions fluctuated  
234 considerably over time. However, despite the large environmental fluctuations in  
235 Jiyang Lake during the middle Eocene, fine-grained sediments were formed during the  
236 early stage of diagenesis in a closed system and were almost unaffected by late  
237 diagenesis, which was consistent with very limited influence of weathering and  
238 metamorphism that could affect such sediments (Liang C. et al., 2018). This viewpoint  
239 is supported by the fact that interbedded carbonates and mudstones have consistently  
240 yielded similar redox interpretations across all instances of rock samples (Raiswell et  
241 al., 2018). Generally, the unusually high dolomite content in fine-grained sediments  
242 should indicate rather atypical lacustrine chemistry due to volcanism, hydrothermal  
243 fluids, or transgressions that may affected variability in calcium carbonate saturation  
244 leading to dolomite rather than calcite precipitation (Zhang et al., 2018; Liu et al., 2021).

245

## 246 **5. Discussion**

### 247 **5.1. High primary productivity in middle Eocene greenhouse**

248 Compared to the unmineralized fraction in deep sediments of modern large lakes  
249 and marine sediments (Galazzo et al., 2013; Liu et al., 2019, 2021), our high TOC  
250 values (average 4%) may indicate that the primary productivity of the lake over the  
251 entire interval ( $\text{Es}_4^1$  to  $\text{Es}_3^3$ ) was indeed higher than that during other MECO intervals  
252 (1–3% TOC; Galazzo et al., 2013). Algae-rich sediments worldwide are well-known  
253 to be a product of high primary productivity (Meyers, 1997). In Jiyang paleolakes,

254 algae-rich sedimentary layers, formed by alternating blooms of coccolithophytes and  
255 dinoflagellates, were a major feature of the Paleogene oil source rocks in the Bohai  
256 Bay Basin for more than 1 Ma (Xie et al., 2016; Song et al., 2020; Shi et al., 2021).  
257 These algal blooms are well recognized in the middle Eocene warming period of the  
258 Cenozoic (Bijl et al., 2010; Zachos et al., 2008; Pearson, 2010), which occurred  
259 41.4–39.2 Ma ago (Shi et al., 2019). During this time, a warm climate and associated  
260 high productivity were favorable for oxygen consumption beneath the photic zone. The  
261 water column became anoxic, thereby leading to enhanced preservation and burial of  
262 organic matter. High productivity can be supported by systematically elevated  
263 concentrations of both TOC and barium (Zeng et al., 2018). TOC values above 6% are  
264 recorded here over 11 intervals across the depth range 3343.47 to 3102.67 m, with two  
265 intervals having TOC values as high as 8.4% and 10.4% at 3176.51 m and 3192.90 m,  
266 respectively (Fig.2). The average Ba concentrations in Es<sub>4</sub><sup>1</sup> and Es<sub>3</sub><sup>3</sup> are 470 and 560  
267 ppm, respectively. Over the entire section in the Jiyang Depression, Ba values in  
268 samples positively correlate with the corresponding TOC values (Supplementary Table  
269 2). For comparison, in a similar high paleoproductivity Lake Malawi (East Africa), the  
270 TOC concentrations are ~ 6 % in the sediments from the anoxic deep parts of the lake  
271 (Li et al., 2018).

272         Meanwhile, high primary productivity can also be confirmed by organic carbon  
273 isotope values. Most samples show  $\delta^{13}\text{C}_{\text{org}}$  values between -29‰ and -25‰, indicating  
274 a source of lacustrine organic matter from exogenous terrestrial plants, authigenic  
275 phytoplankton photosynthesis, as well as possible allochthones (Meyers, 1997).  
276 Terrestrial C<sub>4</sub> plants were very rare in the Jiyang Depression during the middle Eocene

277 as they are usually found in dry environments and have the  $\delta^{13}\text{C}_{\text{org}}$  values higher than  
278 -20‰. However, there might have been some C3 plants in the lake, because small  
279 fragments of higher plants (including leaves) can be windblown and floating debris  
280 could sink, although some of the compounds of terrestrial origin may have been  
281 subsequently degraded by diagenesis. In the detailed core observations of the FY1 well,  
282 over a total length of 403.6 m, no fragments of higher plants were observed. Generally,  
283 there is no direct relationship between the concentration of biomarkers and the source  
284 of organic matter because many biomarkers can be detected at very low concentrations.  
285 There was probably some retene, oleanene, or  $\beta$ -carotene (Xu et al., 2020); however,  
286 the contribution of higher plants to the preserved organic matter is expected to be small.  
287 For another, the relative content of the biomarkers may also change further with  
288 diagenesis. For example, Xu et al. (2020) also proposed an existing algae source of  
289 retene, oleanene, or  $\beta$ -carotene during organic-rich shale formation. To sum up, the  
290 contribution of organic matter of terrestrial origin from higher plants depends on the  
291 lake size and sedimentation process. In a very large paralic lake continental runoff input  
292 can be significant only due to strong storms, floods or other events from land. As there  
293 were no land events in the Jiyang Depression with a total area of 26,000 km<sup>2</sup>, the  
294 detected compounds of higher plants do not mean that the terrestrial organic input is  
295 significant in this offshore lake.

296 Combined with the sedimentary characteristics of modern lakes, we propose that  
297 in the center of the paralic Jiyang lake like FY-1 Well, the organic matter may mainly  
298 come from lacustrine authigenesis, the input of terrigenous organic matter, such as  
299 plants, may only have occurred in brief periods. Of the studied 270 samples, only a few

300 (25 in Es<sub>3</sub><sup>3</sup> and 27 in Es<sub>4</sub><sup>1</sup>) showed  $\delta^{13}\text{C}_{\text{org}}$  values above -25‰, with an average TOC of  
301 5% (Fig.2), indicating that during this period organic matter may have been  
302 occasionally derived from very limited amount of terrestrial plants. Thus, most of the  
303 organic matter enrichment in the source rocks of the Shahejie Formation likely resulted  
304 from native algal and bacterial production coupled with favorable preservation  
305 conditions. Due to a globally significant increase of greenhouse gases in the MECO  
306 atmosphere (Bijl et al., 2010), photosynthetic carbon fixation could lead to carbon  
307 isotope ratios as low as -29‰ (Hodell and Schelske, 1998). Therefore, we propose that  
308 the negative excursions of  $\delta^{13}\text{C}_{\text{org}}$  corresponded to high primary productivity during  
309 warm and humid climate caused by periods of elevated atmospheric  $p\text{CO}_2$ . Under these  
310 elevated  $p\text{CO}_2$ ,  $\text{CO}_2$  was predominantly transported into lacustrine systems via  
311 photosynthesis, and was reduced by biological processes into organic matter with  
312 enrichment in the lighter isotope ( $^{12}\text{C}$ ), thereby yielding negative excursions of  $\delta^{13}\text{C}$   
313 values.

314

## 315 **5.2. Ferruginous/euxinic water conditions**

316 Lallier-Verges et al. (1993) quantified the degree of bacterial sulfate reduction  
317 (BSR) using the sulfate reduction index (SRI), which is defined as the ratio of primary  
318 organic carbon to residual organic carbon. Primary organic carbon encompasses both  
319 the organic carbon depleted via sulfate reduction, and the residual total organic carbon  
320 (TOC (wt.%) at present). Organic carbon loss ( $\text{C}_{\text{loss}}$ ) by degradation coupled with  
321 sulfate reduction may be assessed from the stoichiometry of the sulfate reduction  
322 equation proposed by Berner and Raiswell (1984):

323 
$$\text{SRI} = (\text{TOC} + C_{\text{loss}})/\text{TOC} \quad (1)$$

324 where  $C_{\text{loss}} = \text{TS}/1.33 \quad (2)$

325 Substituting (2) into (1) yields:

326 
$$\text{SRI} = (\text{TOC} + \text{TS}/1.33)/\text{TOC} = 1 + 0.75 \times \text{TS}/\text{TOC} \quad (3)$$

327 The SRI is regarded as the lowest degradation consumption index for total organic  
328 carbon. The higher the BSR activity, the higher the SRI value, and the greater the  
329 organic matter consumption. For  $\text{SRI} < 1.375$ , the BSR intensity can be limited by total  
330 sulfate and the amount of undegraded TOC may increase substantially. For  $\text{SRI} > 1.375$ ,  
331 the BSR intensity increases, and the overall TOC value is relatively low (Liu et al.,  
332 2021). The relationship between the sulfate reduction strength and the organic carbon  
333 content (SRI/TOC) in the study interval shows that most of the SRI values in the  
334 ferruginous water column are less than 1.375 (Fig. 4 (D)), indicating a weak sulfate  
335 reduction, which may have been conducive to organic matter preservation and burial.  
336 In contrast, euxinic waters with strong BSR may result both in organic preservation  
337 and consumption. It can be seen in Fig. 3 and 4 (D) that in the euxinic zone, most  
338 samples with  $\text{TOC} < 2\%$  have SRI values  $> 1.375$ .

339 Several mechanisms may have created ferruginous conditions at the bottom of the  
340 Jiyang lake. A combination of volcanism, hydrothermal fluids, and transgression may  
341 have brought reactive iron and maintained anoxic conditions, while the primary  
342 productivity was high. For example, volcanism could have increased nutrient influxes  
343 (Liu et al., 2019, 2024), and productivity, and stimulated oxygen consumption below  
344 the photic zone. Meanwhile, the isotopically “light” sulfur ( $\delta^{34}\text{S}_{\text{py}}$  of 0 ‰) from a  
345 volcanic source was preferentially utilized by BSR, resulting in low  $\delta^{34}\text{S}_{\text{py}}$  values.

346 However, intermittent sulfidization events in a ferruginous Jiyang Lake may not have  
347 led to elevated  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  ratios compared to typical marine values of 0.7, because such  
348 an increase may be obscured by the high carbonate ( $\text{Fe}_{\text{carb}}$ ) content largely dominating  
349 over  $\text{Fe}_{\text{py}}$  (Fig. 2, Unit 2, 3, 5). For all the samples, there are only two  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  values  
350 above 0.7, with the corresponding  $\delta^{34}\text{S}_{\text{py}}$  values of 24–25‰ (Fig. 4 A, C). The two  
351  $\delta^{34}\text{S}_{\text{py}}$  values, higher than those in the lower adjacent interval (~13 ‰), indicate that  
352 the basin became relatively closed and euxinic after a period of volcanism or  
353 hydrothermal activity. The positive  $\delta^{34}\text{S}_{\text{py}}$  values (> 20‰) are higher than the sulfate  
354  $^{34}\text{S}$  from seawater during middle Eocene, indicating the depletion of the light sulfur  
355 isotopes in sulfate under strong BSR. Meanwhile, the TOC values for these two  
356 samples are 3.4 and 2.8% at 3332.39 and 3226.24 m, respectively (Fig. 2), which are  
357 less than the average value (4.0%) of the study interval, indicating that BSR consumed  
358 the primary organic matter and converted sulfate to  $\text{H}_2\text{S}$ , and promoted pyrite formation.  
359 A rough positive covariation between the  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  ratios and TOC also supports the  
360 BSR occurrence (Fig. 4 A, B). However, the high TOC/TS ratios (> 2.0) and low sulfate  
361 reduction index (SRI) (< 1.375) suggest that it was sulfate availability, rather than  
362 organic matter supply, that constrained BSR in deep waters (Fig. 4 (D)).

363 For Jiyang Lake, there may have been occasional euxinic conditions as the  
364 TOC/TS values are less than 2 (in 36 samples from 270). Euxinia in the photic zone  
365 (from biomarker data) and deeper water (based on framboid size distributions) has been  
366 identified in Silurian, Devonian, Permian and Eocene oceans (Racka et al., 2010;  
367 Marynowski et al., 2012; Liu et al., 2019; Xu et al., 2020; Percival et al., 2022). Euxinia  
368 is prevalent in anoxic marine environments where sulfate is abundant. Modern



369 meromictic lakes develop euxinia when sulfate concentrations exceed 100  $\mu\text{M}$ , while  
370 below that threshold their monimolimnia (the deep stagnant layers) tend to be  
371 ferruginous. [Xu et al. \(2020\)](#) demonstrated that there were different euxinic water  
372 conditions during the deposition of the Shahejie Formation, evidenced by variations in  
373 the aryl isoprenoid ratio, relative amount of isorenieratane, long-chain n-alkane carbon  
374 isotopic composition and other molecular indicators, which indicated different  
375 intensity of bacterial sulfate reaction (BSR). In Jiyang Lake, potential sources for extra  
376 sulfate could have been episodic (for 5–10 ka) marine transgressions (Unit 2 and Unit  
377 5), volcanism (Unit 1, 2, 3 of  $\text{Es}_4^1$ , and Unit 5 of  $\text{Es}_3^3$ ) or hydrothermal fluids (Unit 4  
378 of  $\text{Es}_3^3$ ) ([Fig. 2](#)). Outside these episodes, sulfate would become depleted by BSR,  
379  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  values were mostly  $< 0.6$  and  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  values  $> 0.38$  ([Fig.4 A](#)), which also  
380 suggests that the deep-water column throughout the middle Eocene was predominantly  
381 ferruginous. Meanwhile, there might also be very occasional oxic episodes identified  
382 by the presence of bioturbation in anoxic brackish water ([Song et al., 2020](#)). Although  
383 Fe shuttling could potentially create local enrichments of  $\text{Fe}_{\text{carb}}$  ([Fig.4 \(B\)](#)) or  $\text{Fe}_{\text{ox}}$ ,  
384 resulting in high  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  and low  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  ratios, the deep lake was probably anoxic  
385 and ferruginous during most of the depositional period. The reduced Fe transported  
386 from the anoxic water column could have led to  $\text{Fe}_{\text{carb}}$  enrichments in bioturbated  
387 sediments. As anoxic ferruginous conditions expanded and contracted over time,  
388 reactive iron enrichment could form in even deeper settings.

389 In summary, the  $\text{Fe}_{\text{HR}}$  values between 1.2% and 6.6% generally show the same  
390 evolution trend as the total of  $\text{Fe}_{\text{py}}$  and  $\text{Fe}_{\text{carb}}$ , while  $\text{Fe}_{\text{ox}}$  and  $\text{Fe}_{\text{mag}}$  have little correlation  
391 with the  $\text{Fe}_{\text{HR}}$  content trend. Thus, organic matter enrichment was primarily created by

392 both enhanced preservation under ferruginous water conditions and high paleo-  
393 productivity with limited dilution of the shale by terrigenous clastic materials (Xie et  
394 al., 2016; Song et al., 2020).

### 395 **5.3. Impacts of geological events on organic carbon burial**

396 Our core analyses demonstrate that volcanism, hydrothermal activity, and marine  
397 transgressions affected the study area. Only few investigations of carbon and pyrite  
398 sulfur isotopic variations focused on lacustrine sedimentary intervals during the MECO.  
399 Our study uses different covariations between  $\delta^{34}\text{S}_{\text{py}}$  and  $\delta^{13}\text{C}_{\text{org}}$  values (Fig. 2B, D) to  
400 establish a relationship between geological events, biological productivity, and water  
401 redox conditions. It has been shown that a negative excursion of 2 to 6‰ in  $\delta^{13}\text{C}_{\text{org}}$  of  
402 both carbonate and organic carbon is linked to global volcanism (Lee et al., 2018; Liu  
403 et al., 2019; Longman et al., 2019; Shen J. et al., 2019b; Li Y. et al., 2021). Indeed, in  
404 the study intervals, volcanism effects are evident in nine prominent negative excursions  
405 in  $\delta^{13}\text{C}_{\text{org}}$  (Fig. 2B), which are correlated with tuff interlayers (Fig. 5). The pyroclastic  
406 interlayers in the shales are predominantly vitreous and crystalline debris of andesite  
407 (Fig. 5 (C, D)), in which microfractures were developed and ostracod fragments were  
408 deposited. Such negative excursions in  $\delta^{13}\text{C}_{\text{org}}$  values are typically associated with  
409 increases in primary productivity, which can be brought about by the increased delivery  
410 of nutrients following the volcanic events.

411 The same layers with highly negative  $\delta^{13}\text{C}_{\text{org}}$  are also associated with negative  
412 shifts in  $\delta^{34}\text{S}_{\text{py}}$  (as low as 8.9‰; Fig. 2D). The water column in the deep lake was  
413 usually closed when there were no geological events. In this case, the  $\text{SO}_4^{2-}$  reservoir  
414 is limited and could not be replenished. With the continuing exhaustion of the sulfate

415 reservoir (enriched in  $^{34}\text{S}$ ) by sulfur reduction through dissimilation,  $^{34}\text{S}_{\text{py}}$  gradually  
416 increased and approached that of the initial sulfate. In contrast to open marine  
417 sediments,  $^{34}\text{S}_{\text{py}}$  values in an almost infinite sea water sulfate reservoir, are usually  
418 below 0‰ (Li et al., 2021). Volcanic and hydrothermal activity generate sulfur with  
419  $\delta^{34}\text{S}$  of 0 to 5‰ (Huston, 1999), which is substantially below the values of water  
420 surface-sourced sulfate (~ 20‰ during study period). If sub-lacustrine eruptions of a  
421 volcano or associated geothermal fluids carried  $\text{H}_2^{32}\text{S}$ -enriched sulfide sulfur into a  
422 closed lake, its reaction with highly reactive iron could form isotopically equivalent  
423  $\text{Fe}^{32}\text{S}_2$ -enriched pyrite within a quite short period of time (i.e. several years). This  
424 process caused the decrease in  $\delta^{34}\text{S}_{\text{py}}$  values along with the sulfate of the light sulfur  
425 isotope was consumed by BSR. As volcanic  $\text{H}_2^{32}\text{S}$  was quickly consumed by iron and  
426 the BSR began to reduce sulfate in a closed system, the resulting pyrite had lighter  $\delta^{34}\text{S}$   
427 values. Higher  $\delta^{34}\text{S}_{\text{py}}$  values then formed again at low sulfate concentrations at the end  
428 of sulfate reduction. If volcanic activities or deep fluids carried large amounts of  
429 oxidized volatiles, such as  $\text{SO}_2$ , BSR would have been enhanced and more  $^{32}\text{S}$   
430 consumed. As a result,  $^{34}\text{S}_{\text{py}}$  first decreased and then increased with an increased  
431 amount of sulfate consumption. Indeed, this trend could be identified especially in  
432 Units 1 and 3 of  $\text{Es}_4^1$  (Fig. 2D). Because the bottom waters of the paleolake seemed to  
433 have remained ferruginous, the iron input (as Fe (II); Isley and Abbott, 1999; Kump  
434 and Seyfried, 2005) during these volcanic or hydrothermal activities must have  
435 exceeded the inputs of sulfur into the lake.

436 The presence of marine ostracods (Fig 5 (A)), elevated  $\delta^{34}\text{S}_{\text{py}}$  values (~20 ‰) and  
437 high carbonate content ( $\text{Fe}_{\text{carb}}$  to ~5%) collectively indicate marine transgressions,

438 which is consistent with the interpretation of the strata using the method of  
439 astronomical cycles (Ma et al., 2023). During middle Eocene warming, marine  
440 transgressions increased the lake water depth and supplied  $^{34}\text{S}$ -enriched sulfate,  
441 causing the  $\delta^{34}\text{S}_{\text{py}}$  value of pyrite to approach that of seawater. The  $\delta^{34}\text{S}_{\text{py}}$  values vary  
442 between 9 and 36 ‰, being both lower and higher than those of the marine sulfates  
443 identified during the MECO ( $20.9 \pm 0.5\text{‰}$ ; Longinelli, 1989; Kampschulte et al., 2001).  
444 Marine transgressions may have occurred roughly every 1,000 years over a period of  
445 5,000 years (Fig. 2, Units 2 and 5). As BSR generates isotopically light sulfide, the  
446 heavier  $\delta^{34}\text{S}_{\text{py}}$  values can be attributed to the consumption of sulfate sulfur after staged  
447 transgression when the lake system closed again. Mineral analyses show that the total  
448 content of  $\text{Fe}_{\text{mag}}$  and  $\text{Fe}_{\text{ox}}$  is low, with a maximum of 0.37%, so the contents of ferrous  
449 carbonate and pyrite compete with each other. This is consistent with most sediments  
450 in modern paralic environment (Liu et al., 2023; Zhang et al., 2024). Only the  
451 difference between the samples of the two study areas is the contents of ferrous  
452 carbonate, indicating the different water conditions during their sediment deposition.  
453 In Shahejie Formation, the carbonate content in the study interval was generally high,  
454 with average calcite and dolomite contents of 37% and 10%, respectively. For example,  
455 the content of  $\text{Fe}_{\text{carb}}$  is higher than that of  $\text{Fe}_{\text{py}}$  from 3225 to 3200 m in Unit 5 (Fig.2),  
456 indicating that the sulfur isotope fractionation of pyrite in the paralic lakes during the  
457 sulfate reduction process was constrained by changes in the global sea level. The sea  
458 level increased in the warm and humid climate, and transgression brought large  
459 amounts of  $\text{Ca}^{2+}$  to form carbonates. Meanwhile, high paleo-productivity also  
460 promoted the deposition of organic-rich layers. Therefore, the precipitation of calcium

461 carbonate and organic matter layers is the result of increased pH due to strong  
462 photosynthesis by algae in the warm climate during marine transgressions in the Jiyang  
463 calcareous lake. After that, the organic matter was degraded in a limited manner under  
464 ferruginous conditions and was well preserved.

465 The delicate equilibrium between ferruginous and euxinic chemical conditions  
466 could be influenced by the comparable rates of  $Fe_{HR}$  and sulfate input fluxes. On a  
467 global scale, continental sources stand out as the primary contributors to the potential  
468  $Fe_{HR}$  flux. At the regional scale, geological events, such as volcanic activity or ocean  
469 transgression, could also have liberated some reactive iron and sulfate into the lake,  
470 providing a conceivable mechanism for the transportation of ferrous iron and resulting  
471 in a disproportionate increase in the  $Fe_{HR}$  flux relative to that of sulfate. The interplay  
472 of all these processes have generated dominantly ferruginous environments during the  
473 middle Eocene in the Jiyang Depression.

474 On the basis of the aforementioned research, we propose that there was an  
475 extensive burial of lacustrine organic carbon in Eastern China during the warm and  
476 humid climate of the middle Eocene, which thereby created a positive feedback loop  
477 in the Earth's climate system. Frequent volcanic activity during the early stages of  $Es_4^1$   
478 might have brought aerosols to increase the albedo in the short-term cold climate  
479 (Fig.6B, maybe to 10 years). Most importantly, it released abundant  $CO_2$  into in the  
480 atmosphere and brought reactive iron and nutrients to create optimal environments for  
481 the growth and expansion of algae and plankton in the later stages (Fig.6A, to 1 million  
482 years) of the middle Eocene. As temperatures increased, the biological productivity in  
483 Jiyang Lake increased, leading to enhanced production of total organic carbon in

484 ferruginous water conditions. This positive feedback mechanism may have contributed  
485 to the sustained warmth of the middle Eocene climate. Based on this analysis, we  
486 highlight a combined effect on sedimentation of external events such as input of  
487 volcanic ash, intermittent hydrothermal fluids and marine transgressions during middle  
488 Eocene continental warming of western Pacific. These events could not only supply  
489 nutrients and catalytic elements to promote biological productivity and cause oxygen  
490 consumption, but they also enhanced the reactive iron input to form the dynamic anoxic  
491 ferruginous conditions that were conducive for the preservation of organic carbon.

492

## 493 **6. Conclusions**

494 The widespread terrestrial sedimentary and geochemical records of the middle  
495 Eocene in the Eastern China have been established using novel TOC, TS, iron  
496 speciation,  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{34}\text{S}_{\text{py}}$  data. These data, including the highly-reactive iron to total  
497 iron ratios ( $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}} > 0.38$ ), along with a wide range of total organic carbon content  
498 (TOC, from 1 to 10 %) exceeding that of total sulfur ( $\text{TOC}/\text{TS} > 2$ ), and low sulfate  
499 reduction indexes ( $\text{SRI} < 1.375$ ), collectively suggest widespread anoxic and  
500 ferruginous conditions that would have been favorable for burial of lacustrine organic  
501 carbon during the middle Eocene in the paralic lacustrine environments of the Jiyang  
502 Depression. The temporal stability of lacustrine ferruginous water conditions may have  
503 been due to the warm and humid climate during the middle Eocene, with high  
504 biological productivity and large oxygen consumption in the water column, leading to  
505 efficient burial of organic carbon in deep sediments.

506 Both  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{34}\text{S}_{\text{py}}$  values reveal transient geological events such as volcanism,

507 hydrothermal fluids, and transgressions. Negative  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{34}\text{S}_{\text{py}}$  excursions along  
508 the sedimentary column point to transient volcanic events, whereas positive  $\delta^{13}\text{C}_{\text{org}}$   
509 along with negative  $\delta^{34}\text{S}_{\text{py}}$  excursions indicate injection of associated hydrothermal  
510 fluids; in contrast, elevated  $\delta^{34}\text{S}_{\text{py}}$  (to  $\sim 20\text{‰}$ ) point to frequent marine transgressions.  
511 Despite potential inputs of sulfur into the paleolake as a result of these geological  
512 events, bacterial sulfate reduction efficiently consumed the sulfate pool, thereby  
513 creating ferruginous water conditions favorable for the efficient preservation of organic  
514 carbon.

515

## 516 **Acknowledgments**

517 We thank Yunqing Hao for assistance with microscopic slice analyses and for  
518 discussions, Prof. Chao Li and Prof. Yan'an Shen for help with the geochemical  
519 analyses, Prof. Bing Shen and Dr. Huiyuan Xu for discussions. This work was  
520 supported by the National Natural Science Foundation of China (Grants 42172151,  
521 41811530094, and 41625009), the China Postdoctoral Science Foundation (Grant  
522 2021M690204), and the National Key Research and Development Program (Grant  
523 2023YFF0806200). We thank the two reviewers and the editorial support for the  
524 constructive comments, which have greatly improved the quality of this paper.

525

## 526 **Research Data**

527 All of the processed data discussed has been uploaded in the supplementary tables.

528

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#### 734 [Table and Figure captions](#)

735

736 Table 1. Summary data of total organic carbon (TOC), organic carbon isotope  
737 composition ( $\delta^{13}\text{C}_{\text{org}}$ ), total sulfur (TS), pyrite sulfur isotope ( $\delta^{34}\text{S}_{\text{py}}$ ), Fe/Al ratio, and  
738 iron speciation of samples in the FY1 Well (data range, arithmetic average and number  
739 of samples, see [Supplementary Table 1](#) for data points).

740

741 Figure 1. (A) Map of sites with existing MECO records on a paleogeographic  
742 reconstruction for the middle Eocene at 40 Ma (modified from [Ploeg et al., 2023](#)). (B)  
743 Simplified geological map of Bohai Bay Basin in western Pacific, showing the core  
744 location of FY-1 Well in the Jiyang Depression in eastern China (modified from [Liang  
745 et al., 2016](#)). (C) Stratigraphic column of the study interval in the middle Eocene. The  
746 Es<sub>4</sub><sup>1</sup> and Es<sub>3</sub><sup>3</sup> sediments are deposited during the rifting stage over 38–50 Ma ago

747 (modified from Shi et al., 2019).

748

749 **Figure 2.** Iron speciation,  $\delta^{13}\text{C}_{\text{org}}$ , TOC, and  $\delta^{34}\text{S}_{\text{py}}$  values as a function of depth from  
750 the middle Eocene ( $\text{Es}_4^1$ – $\text{Es}_3^3$ ) black shales in the Jiyang Depression (geological  
751 timescale from Shi et al., 2019). (A) total organic carbon (TOC), (B)  $\delta^{13}\text{C}_{\text{org}}$ , (C) total  
752 sulfur content (TS), (D) pyrite sulfur isotope ( $\delta^{34}\text{S}_{\text{py}}$ ), (E) ratio of highly reactive Fe  
753 to total Fe ( $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ ), (F) ratio of pyrite iron to highly reactive iron ( $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ ), (G)  
754 content of pyrite iron, (H) content of carbonate iron. Note that  $\text{Fe}_{\text{HR}} =$   
755  $\text{Fe}_{\text{py}} + \text{Fe}_{\text{ox}} + \text{Fe}_{\text{mag}} + \text{Fe}_{\text{carb}}$ , the thresholds for oxic versus anoxic (0.22–0.38) and  
756 ferruginous versus euxinic conditions (0.6–0.8) are from Poulton et al. (2021); the  
757 units of the study interval are based on lithological and geochemical differences, as  
758 discussed in the text.

759

760 **Figure 3.** Plots of TOC vs TS, showing that the salinity of the most samples was similar  
761 to the salinity of seawater, corresponding to ferruginous water conditions.

762

763 **Figure 4.** Plots of (A)  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  vs  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ ; (B)  $\text{Fe}_{\text{carb}}$  vs  $\text{Fe}_{\text{py}}$ ; (C)  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  vs  $\delta^{34}\text{S}_{\text{py}}$ ;  
764 (D) TOC vs SRI.

765

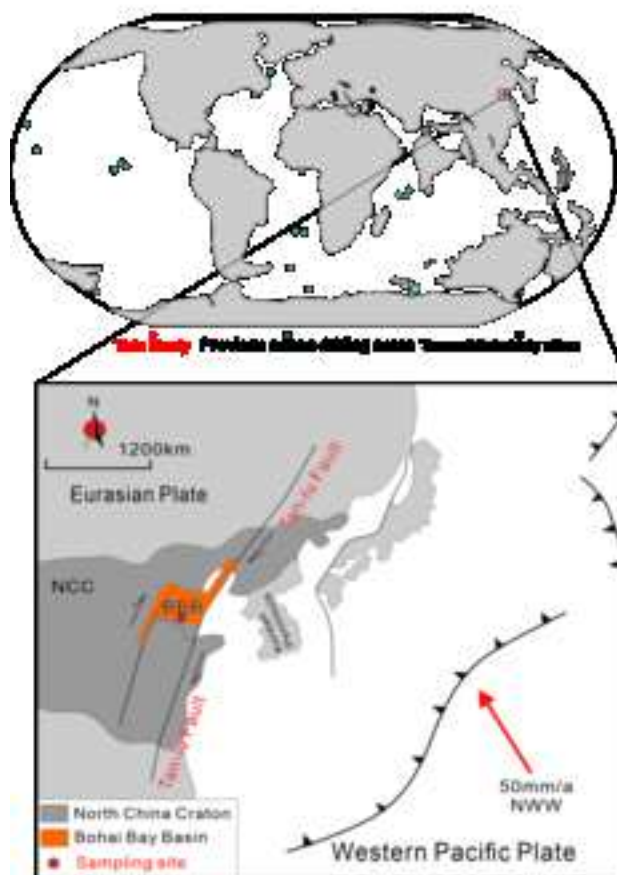
766 **Figure 5.** Microscopic features of volcanic ash in the Middle Eocene shale of the Jiyang  
767 Depression. (A) ostracod fragments in shales; (B) interbedded tuffs and shale; (C)  
768 interbedded tuffs and shale with micro fractures; (D) pyroclastic interlayer in shales.

769

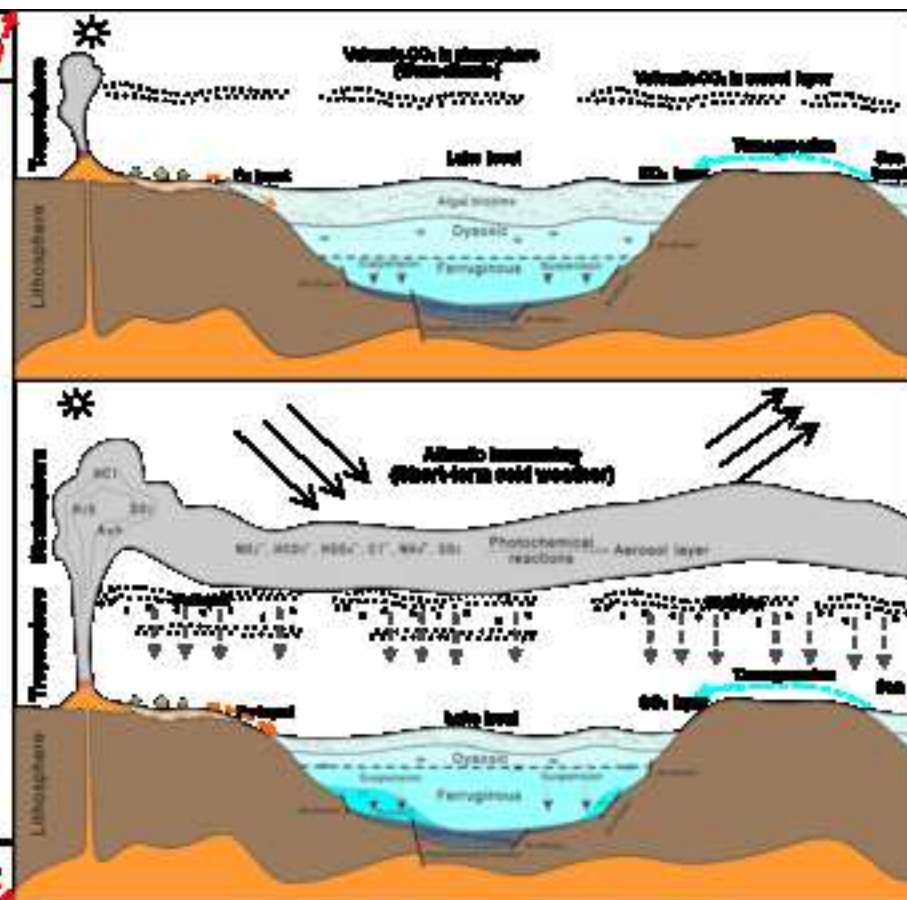
770 **Figure 6.** Sedimentary model of the paralic lake basin in the Jiyang Depression

771 developed in this study. (A) High primary productivity during middle Eocene long-  
772 time warmth. (B) Impacts of different geological events on organic carbon burial.  
773 During a short period of cooling caused by volcanism, despite potential external sulfur  
774 inputs, bacterial sulfate reduction sufficiently depleted the sulfate pool to have created  
775 ferruginous conditions.

776



Period	Stage	Thickens (m)	Lithology	Paleogene		Cretaceous		Jurassic		Triassic	
				Age	Stage	Age	Stage	Age	Stage	Age	Stage
Paleogene	Eocene	700-600	Lithology	700-600	700-600	Lithology	Lithology	Lithology	Lithology	Lithology	Lithology
		600-500		600-500							
		500-400		500-400							
	Oligocene	400-300		400-300							
		300-200		300-200							
		200-100		200-100							
	Cretaceous	Upper Cret.		100-120	100-120						
				120-140	120-140						
				140-160	140-160						
		Lower Cret.		160-180	160-180						
				180-200	180-200						
				200-220	200-220						
Jurassic	Middle Jurassic	220-240	220-240								
		240-260	240-260								
Triassic	Lower Triassic	260-280	260-280								
		280-300	280-300								



## Highlights

- The primary productivity was high during the Shahejie Formation in middle Eocene.
- Ferruginous conditions were predominant during lacustrine OC preservation.
- Multivariate geological events enhanced OC burial in paralic paleoenvironments.



1 Carbon, iron and sulfur records of lacustrine paleo-environments during the  
2 middle Eocene in eastern China

3

4 **Abstract**

5 It is widely recognized that anoxic conditions facilitate the preservation of organic  
6 carbon in marine sediments. However, the specific geological factors that lead to the  
7 development of such conditions in paleo-lakes are less well understood. Owing to their  
8 smaller size, paleolakes could experience more frequent and stronger changes in  
9 geochemical conditions than oceans. Such changes, such as volcanism, hydrothermal  
10 fluids, or ocean transgressions, can also strongly affect the lacustrine organic carbon  
11 burial thereby complicating sediment diagenesis record. Here, we used total organic  
12 carbon content (TOC), organic carbon isotope ( $\delta^{13}\text{C}_{\text{org}}$ ), iron speciation, and pyrite  
13 sulfur isotope ( $\delta^{34}\text{S}_{\text{py}}$ ) data to establish relationships between organic carbon  
14 preservation and anoxic conditions in fine-grained sediments from the middle Eocene  
15 lacustrine depositional environments from the Shahejie Formation of the Jiyang  
16 Depression, Bohai Bay Basin, eastern China. The results reveal TOC between 1% and  
17 10%, highly-reactive iron to total iron ratios greater than 0.38, and most TOC to total  
18 sulfur ratios exceeding 2. These data indicate that the organic-rich shales of the  
19 Shahejie Formation were formed as a result of high primary productivity during the  
20 warm and humid middle Eocene period, coupled with the efficient preservation of  
21 organic matter in anoxic bottom waters. Negative  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{34}\text{S}_{\text{py}}$  excursions  
22 recorded in the Shahejie Formation indicate water column conditions to have been  
23 influenced by transient volcanic eruptions. Positive  $\delta^{13}\text{C}_{\text{org}}$  and negative  $\delta^{34}\text{S}_{\text{py}}$

24 excursions may have been caused by hydrothermal fluids input whereas  $\delta^{34}\text{S}_{\text{py}}$  values  
25 approaching 20‰ suggest frequent marine transgressions. In particular, despite  
26 potential inputs of S into the paleolake by volcanism, hydrothermal fluids, or marine  
27 transgressions, bacterial sulfate reduction efficiently depleted the sulfate pool to have  
28 created ferruginous geochemistry water conditions for the effective preservation of  
29 organic carbon in sediments. Our results establish a direct link between lacustrine shale  
30 geochemical signatures and geological phenomena that impact its sedimentation.

31

32 **Key words:** organic carbon burial; ferruginous conditions; volcanism; transgression;  
33 paralic lacustrine shale; middle Eocene

34

## 35 **1. Introduction**

36 Anoxic conditions facilitate burial and preservation of organic carbon by slowing  
37 down microbial degradation, primarily in marine sediments (Shen Y. et al., 2003;  
38 Planavsky et al., 2011; Clarkson et al., 2014, 2016; Guilbaud et al., 2015; Raiswell et  
39 al., 2018), whilst factors that cause such conditions in lakes have not been sufficiently  
40 investigated. Multiple geologic events, such as volcanism, subsurface hydrothermal  
41 activity, and marine water incursion, can substantially affect sediment diagenesis and  
42 the burial of organic matter in both marine and lacustrine basins. Volcanic ash layers,  
43 for example, are prevalent in organic-rich deposits (organic carbon content greater than  
44 2.0%) such as the Bazhenov Formation (western Siberia, Russia), the Eagle Ford  
45 Formation (Gulf Coast Basin, USA), the Wufeng-Longmaxi Formation (Sichuan Basin,  
46 China), the Fengcheng and Lucaogou Formations (Junggar Basin, China) (Ruebsam et

47 al., 2020; Liang et al., 2020; Liu et al., 2021, 2024). Volcanic activity may increase  
48 biological productivity in the photic zone by supplying nutrients and affect aquatic  
49 environments and their sedimentary records by providing fluxes of heat, dissolved  
50 carbon dioxide, and methane (Duggen et al., 2010; Langmann et al., 2010; Liu et al.,  
51 2019). Enhanced preservation of organic material in sediments can lead to the  
52 formation of organic-rich shales (Kim et al., 2015; LaRowe et al., 2020). Hydrothermal  
53 and volcanic inputs, recorded by high concentrations of metals and heterogeneous tuff  
54 in shales, are correlated with changes in paleo-productivity, anoxia, and organic matter  
55 burial (Magnall et al., 2016; He et al., 2020). However, the mechanisms by which  
56 geological events affect formation and preservation of organic matter in lacustrine  
57 environments are much less constrained than in marine environments.

58 Like the modern counterparts, ancient lakes were important sinks of organic  
59 carbon (Sklarew, 1979; Layton-Matthews et al., 2013; Swanner et al., 2020). Being  
60 much smaller than oceans, lakes are more sensitive to environmental changes and can  
61 record geologic events on shorter time scales. Paralic lakes, in particular, can be  
62 affected by volcanic activity, hydrothermal discharges, marine transgressions or other  
63 geological events (Malumián and Ramos, 1984; Duggen et al., 2010; Lee et al., 2018;  
64 Zeng et al., 2018; Zhang et al., 2018; Liu et al., 2024), so the controlling factors for the  
65 burial of lacustrine organic carbon are more complicated. For example, the Kabuno  
66 Bay (East Africa) is ferruginous, whereas Lake Kivu is sulfidic even though they both  
67 receive iron through hydrothermal sub-lacustrine springs (Bhattarai et al., 2012; Ross  
68 et al., 2014; Swanner et al. 2020). Studying variations in lacustrine conditions of  
69 sedimentation may help understand the analogous marine processes on their

70 correspondingly longer time scales.

71 In this regard, ancient lakes of the Jiyang Depression (Fig.1) in the Bohai Bay  
72 Basin, eastern China offer an excellent natural environment to investigate in detail the  
73 continental sedimentary record of the middle Eocene. A series of successive lacustrine  
74 shale sediments 150–300 m thick were deposited between the upper sub-member of  
75 Member 4 and the lower sub-member of Member 3 of the Shahejie Formation ( $Es_4^1$   
76 and  $Es_3^3$ ) (Chen et al., 2008; Liang C. et al., 2018; Shi et al., 2019). This depositional  
77 period corresponds to a global increase in the atmospheric  $CO_2$  during the Middle  
78 Eocene Climate Warming (MECO) (Fig.1, A; Lourens et al., 2005; Jovane et al., 2007;  
79 Zachos et al., 2008; Bijl et al., 2010). Therefore, this study combines total organic  
80 carbon contents (TOC) and total sulfur (TS) values of the Fanye-1 well (FY1, Fig. 1,  
81 B), with the vertical variation in Fe speciation, organic carbon isotope ( $\delta^{13}C_{org}$ ), and  
82 pyrite sulfur isotope ( $\delta^{34}S_{py}$ ) data, to establish a direct link between organic carbon  
83 preservation and anoxic conditions, and the factors that affect organic carbon burial in  
84 lacustrine basins during middle Eocene.

85

## 86 **2. Geological Setting**

87 The Bohai Bay Basin is a large Cenozoic sedimentary basin, which was formed  
88 at the intersection of three major tectonic regions that included the ancient Asian,  
89 Tethys and Pacific Oceans (Fig. 1, B). The subduction of the West Pacific plate under  
90 the North China Craton was the controlling factor in the tectonic evolution rate and  
91 orientation of the Bohai Bay Basin (Chen et al., 2008). Between the Late Paleocene  
92 and Eocene, subduction of the Pacific Plate decreased to its lowest rate of about 40

93 mm/a at 43 Ma, and the orientation changed from north-north-west to north-west-west.  
94 The rate gradually increased to 60 mm/a from 43 to 32 Ma, making the entire Asia  
95 continent an extended tectonic domain. This spreading reached its faulting limit at  
96 about 23 Ma in the Oligocene leading to the formation of the Late Mesozoic-Paleogene  
97 Bohai Bay Basin, which is divided into seven depressions and three uplifts (Chen et al.,  
98 2008).

99 Among them, the Jiyang Depression is the largest sedimentation center of the  
100 basin, spanning latitudes from 35 to 40°N. The depression is about 200 km long from  
101 east to west and 120 km wide from north to south, with a total area of 26,000 km<sup>2</sup> (Song  
102 et al., 2020). Cenozoic deposition during Es<sub>4</sub><sup>1</sup> and Es<sub>3</sub><sup>3</sup> sub-members in the Bohai Bay  
103 Basin coincided with an intensive fault depression, resulting in the formation of the  
104 Jiyang Lake whose estimated ancient depth was 190–290 m (Fig. 1., C) with the  
105 deepest area likely reaching 600 m (Chen et al., 2008). The lake has existed in the basin  
106 for about 4 million years and was connected to the west Pacific paleo-ocean during  
107 multiple periods, lasting for several thousand years each (Song et al., 2020). Between  
108 these episodes, the lake basin likely remained closed (Chen et al., 2008).

109 During Es<sub>4</sub><sup>1</sup> time, as the basin subsided, the lake experienced high salinities  
110 affected by different geological processes. During the Es<sub>3</sub><sup>3</sup> period of humid climate, as  
111 the lake basin widened and subsidence increased, the lake connected to the ocean, thus  
112 increasing accommodation space. Abundant semi-deep to deep waters (10–60 m depth)  
113 provided favorable conditions for deposition of fine-grained sedimentary rocks such as  
114 black shale. The rocks were predominantly argillitic with extensive layers of both  
115 massive and lamellar textures and with veins of sparry limestone, limy mudstone, and

116 dolomite (Chen et al., 2008; Liang C. et al., 2018; Song et al., 2020).

117

### 118 **3. Materials and Methods**

119 Core analysis shows that the high-quality source rocks of Es<sub>4</sub><sup>1</sup> and Es<sub>3</sub><sup>3</sup> (to ~1000  
120 m) were widely distributed in semi-deep or deep lacustrine facies, intercalated with  
121 mm-to-cm thick layers of volcanic ash in Jiyang Depression. Here a length of 403.6 m  
122 of whole-core was taken from the FY1 well (Shi et al., 2019; Song et al., 2020). Black  
123 and gray-black, layered, grainy, muddy shale dominates the Es<sub>4</sub><sup>1</sup> and Es<sub>3</sub><sup>3</sup> lithologies.  
124 A total of 270 core samples was obtained at a spacing of 1.0–1.5 m and these were  
125 analyzed for TOC, TS,  $\delta^{13}\text{C}_{\text{org}}$  and major element analyses. A subset of 70 samples at  
126 an interval of 5–6 m was subjected to iron speciation and  $\delta^{34}\text{S}_{\text{py}}$  analyses.

127 The concentrations of TOC and TS were determined using an Eltra infrared (IR)  
128 C/S analyzer from the discrepancy between the total carbon (or sulfur) determined by  
129 combustion and the total inorganic carbon (or sulfur) determined by acidification.  
130 Ultrapure 6 N HCl was added in a silver cup to dissolve inorganic carbon and sulfur  
131 (mostly carbonate and sulfide minerals) from weighed portions of powdered samples.  
132 Analyses of  $\delta^{13}\text{C}_{\text{org}}$  were performed using a Costech<sup>TM</sup> 4010 coupled with a Thermo  
133 Finnigan MAT 253 via an open-split interface Conflo IV, with a reproducibility better  
134 than  $\pm 0.1\%$  as based on the international standard IAEA-600 (caffeine,  $\delta^{13}\text{C}_{\text{org}} = -$   
135  $27.77\%$ ).

136 For major element concentrations (Fe, Al), 300 mg of powdered samples were  
137 burnt at 600 °C for 12 h in a muffle furnace to remove volatiles compounds, followed  
138 by a standard multi-acid (HF-HCl-HNO<sub>3</sub>) digestion protocol designed for dissolution

139 in a Teflon bomb. An Agilent 7700 inductively coupled plasma mass spectrometer  
140 (ICP-MS) was used for the solution analyses, with an analytical precision of better than  
141  $\pm 5\%$  ( $1\sigma$ ) established using USGS standards (BHVO-2 and BCR-2).

142 Iron speciation and pyrite sulfur isotope analyses (in terms of  $\delta^{34}\text{S}_{\text{py}}$ ) were  
143 performed for a total of 70 samples at the State Key Laboratory of Biogeology and  
144 Environmental Geology, China University of Geosciences (Wuhan). Iron as pyrite  
145 ( $\text{Fe}_{\text{py}}$ ) was extracted using the chromium reduction method and iron speciation was  
146 determined by the sequential extraction method (Poulton and Canfield, 2005). Sulfur  
147 in pyrite ( $\text{S}_{\text{py}}$ ) was extracted as  $\text{H}_2\text{S}$  using a hot  $\text{CrCl}_2$  distillation for 2 h, trapped as  
148 silver sulfide ( $\text{Ag}_2\text{S}$ ), which was then quantified gravimetrically. The  $\text{Fe}_{\text{py}}$  content in  
149 each sample was then calculated assuming the ideal pyrite stoichiometry ( $\text{FeS}_2$ ). Iron  
150 from carbonate minerals ( $\text{Fe}_{\text{carb}}$ ) was extracted by dissolution for 24 h in cold 10 wt%  
151 HCl. Then ferric Fe (oxyhydroxides,  $\text{Fe}_{\text{ox}}$ ) was liberated from the residue of each  
152 sample, treated for 2 h with a sodium dithionite solution (50 g/L) buffered to a pH of  
153  $\sim 5$  with acetic acid and sodium citrate. Finally, Fe bound in magnetite ( $\text{Fe}_{\text{mag}}$ ) was  
154 extracted for 6 h using a 0.2 M ammonium oxalate and 0.17 M oxalic acid solution (pH  
155  $\sim 3$ ). After diluting the extracts by a factor of 100 in 2 wt%  $\text{HNO}_3$  (suprapure), an  
156 Agilent 7500ce ICP-MS was used to analyze each sequential extract. To increase  
157 precision, samples underwent processing in conjunction with internal calibration  
158 standards and blanks, by analyzing in duplicate each 10<sup>th</sup> sample per batch. The  
159 analytical precision was better than 5% of the value.

160 Sulfur isotope ratios ( $^{34}\text{S}/^{32}\text{S}$ ) were determined using a Thermo Fisher Scientific  
161 Delta V Plus isotope-ratio mass spectrometer coupled with a flash EA. The results are

162 expressed as  $\delta^{34}\text{S}_{\text{py}}$  following the standard delta notation as per mil deviations relative  
163 to the Vienna Cañon Diablo Troilite (Li et al., 2021). An analytical uncertainty of 0.2‰  
164 ( $1\sigma$ ) for pyrite  $\delta^{34}\text{S}$  was determined from replicate analyses of the International Atomic  
165 Energy Agency (IAEA) standards: S1 ( $\delta^{34}\text{S} = -0.3\text{‰}$ ), IAEA S2 ( $\delta^{34}\text{S} = +22.65\text{‰}$ ), and  
166 IAEA S3 ( $\delta^{34}\text{S} = -32.5\text{‰}$ ).

167

## 168 **4. Results**

169 The results of geochemical analyses of FY1 section are summarized in Table 1.  
170 The variation in chemical and isotopic composition of TOC,  $\delta^{13}\text{C}_{\text{org}}$ , TS,  $\delta^{34}\text{S}_{\text{py}}$  and Fe  
171 redox as a function of depth is presented in Fig. 2. The study interval was divided into  
172 7 units according to the changes in  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{34}\text{S}_{\text{py}}$  values.

### 173 **4.1. Organic carbon systematics**

174 TOC values of the 270 samples vary from about 1 to 10 % with an average value  
175 close to 4%, and with maximum enrichment in Units 1 and 5 (Fig. 2), but without  
176 systematic differences between  $\text{Es}_3^3$  and  $\text{Es}_4^1$ . The  $\delta^{13}\text{C}_{\text{org}}$  values for samples of  $\text{Es}_4^1$   
177 vary within a relatively narrow range of about -29‰ to -20‰ with an average of  $\sim -$   
178 26‰, whereas those from  $\text{Es}_3^3$  vary within even narrower range of about -28‰ to -23‰  
179 with a mean value -26‰ (Table 1). Samples with positive excursions of  $\delta^{13}\text{C}_{\text{org}}$  values  
180 ( $> -24\text{‰}$ ) are more frequent in  $\text{Es}_4^1$ , and are characterized by elevated TOC contents ( $>$   
181 4%). Samples showing more negative  $\delta^{13}\text{C}_{\text{org}}$  ( $\leq -26\text{‰}$ ) are also predominantly found  
182 in the  $\text{Es}_4^1$  sub-member (Fig. 2A, B).

183

### 184 **4.2. Iron systematics**



185 In the lacustrine samples of Es<sub>4</sub><sup>1</sup> and Es<sub>3</sub><sup>4</sup>, Fe<sub>T</sub> values range between 1.4 and 8.0%,  
186 with an average close to 3% and are generally dominated by highly reactive iron (Fe<sub>HR</sub>,  
187 including pyrite and carbonate iron, oxidized and magnetite iron) fraction (> 90% of  
188 Fe<sub>T</sub> on average). Pyrite iron (Fe<sub>py</sub>) ranges from 0.1 to 4% with an average of ~1%,  
189 which is slightly less than or comparable to carbonate iron (Fe<sub>carb</sub>) content varying from  
190 0.5 to 4 (average 1.5%). Oxidized iron (Fe<sub>ox</sub>) is low, with a maximum of 0.4%. The  
191 Fe/Al ratios are systematically higher than 0.44 (with a single sample exception of 0.18  
192 at 3346.9 m). Magnetite content (Fe<sub>mag</sub>) is low (< 0.13%), pointing to the absence of  
193 diagenesis; as a result, the iron speciation can be used to constrain the redox conditions.  
194 All Fe<sub>HR</sub>/Fe<sub>T</sub> values exceed 0.38, and almost all Fe<sub>py</sub>/Fe<sub>HR</sub> ratios are lower than 0.6,  
195 which is mostly due to the relatively high Fe<sub>carb</sub> content.

196 Iron speciation is a widely used proxy for water column redox conditions, and can  
197 differentiate between oxic and anoxic (ferruginous or euxinic) environments (Poulton  
198 and Canfield, 2005, 2011). For anoxic conditions, Fe<sub>py</sub>/Fe<sub>HR</sub> ratios are used to  
199 distinguish ferruginous (typically < 0.7) and euxinic (typically > 0.8) conditions;  
200 however, more recent work suggested values above 0.6 as evidence of euxinia (Poulton,  
201 2021). Under anoxic conditions, either diagenetic transformation of Fe<sub>HR</sub> minerals into  
202 Fe-rich clay, or the swift sedimentation of deposits lacking iron, can lower Fe<sub>HR</sub>  
203 concentrations. Total Fe/Al ratios provide complementary information on water  
204 column redox conditions. Indeed, although oxidative weathering or diagenesis of  
205 samples could obscure Fe<sub>py</sub> systematics, it would not significantly alter the Fe/Al ratios  
206 that are systematically lower than 0.44 in oxic marine sediments (Lyons and  
207 Severmann, 2006; Clarkson et al., 2014, 2016; Raiswell et al., 2018). Therefore, the

208 Fe/Al proxy in carbonate-rich sediments is relatively robust, provided  $Fe_T > 0.5$  wt%  
209 (Raiswell et al., 2018). For  $Fe_T < 0.5$  wt%, carbonate samples have a greater potential  
210 to be enriched in  $Fe_{HR}$  due to processes other than water column processes that arise  
211 under anoxic conditions (e.g., post sedimentary diagenesis).

212 Overall, TOC values higher than 0.5%, with total iron  $> 0.5$  wt%,  $Fe_{HR}/Fe_T$  ratios  $>$   
213 0.38 and  $Fe_{HR}/Fe_T$  ratios  $< 0.8$  throughout the succession (Fig. 2, A, E, F) collectively  
214 demonstrate predominantly anoxic ferruginous during the depositional period, despite  
215 evidence of pyrite enrichment of considerable spatial and temporal variability that  
216 cannot exclude local intermittent euxinic conditions in the basin.

217

### 218 **4.3. Sulfur systematics**

219 Total sulfur (TS) concentrations vary from about 0.2 to 11%, with an average of  
220  $\sim 1.4\%$  across the two main intervals (Table 1, Fig. 2). Most samples (231) have  
221 TOC/TS weight ratios above 2, with only a few (36) having TOC/TS  $< 2$  (Fig. 2A, C).  
222 According to Berner and Raiswell's (1984) analysis of modern sediments, TOC/TS  
223 values of  $< 2$  would correspond to euxinic conditions, those between 2 and 3.6  
224 represent "normal" marine conditions, those of 3.6 to 10 reflect freshwater and  
225 seawater transition zones, and those  $> 10$  correspond to freshwater sediments.  
226 Therefore, most of our samples from the study interval would indicate freshwater or  
227 marine transitional conditions, with only rare instances of euxinia (Fig.3).

228 Values of  $\delta^{34}S_{py}$  exhibit large variations within the studied section (Fig. 2D),  
229 ranging from 9‰ to 36‰ with an average of  $\sim 20\%$  with no significant differences  
230 between  $Es_3^3$  and  $Es_4^1$  (Table 1). As sulfur isotope values in marine sulfates were  $\sim 22\%$

231 during middle Eocene (Payton et al., 1998) and elevated  $\delta^{34}\text{S}_{\text{py}}$  values ( $> 20\text{‰}$ ) are  
232 consistent with the low levels of sulfate in the euxinic water column (Shen et al., 2003),  
233 our large  $\delta^{34}\text{S}_{\text{py}}$  variations (Fig. 2D) indicate that redox conditions fluctuated  
234 considerably over time. However, despite the large environmental fluctuations in  
235 Jiyang Lake during the middle Eocene, fine-grained sediments were formed during the  
236 early stage of diagenesis in a closed system and were almost unaffected by late  
237 diagenesis, which was consistent with very limited influence of weathering and  
238 metamorphism that could affect such sediments (Liang C. et al., 2018). This viewpoint  
239 is supported by the fact that interbedded carbonates and mudstones have consistently  
240 yielded similar redox interpretations across all instances of rock samples (Raiswell et  
241 al., 2018). Generally, the unusually high dolomite content in fine-grained sediments  
242 should indicate rather atypical lacustrine chemistry due to volcanism, hydrothermal  
243 fluids, or transgressions that may affected variability in calcium carbonate saturation  
244 leading to dolomite rather than calcite precipitation (Zhang et al., 2018; Liu et al., 2021).

245

## 246 **5. Discussion**

### 247 **5.1. High primary productivity in middle Eocene greenhouse**

248 Compared to the unmineralized fraction in deep sediments of modern large lakes  
249 and marine sediments (Galazzo et al., 2013; Liu et al., 2019, 2021), our high TOC  
250 values (average 4%) may indicate that the primary productivity of the lake over the  
251 entire interval ( $\text{Es}_4^1$  to  $\text{Es}_3^3$ ) was indeed higher than that during other MECO intervals  
252 (1–3% TOC; Galazzo et al., 2013). Algae-rich sediments worldwide are well-known  
253 to be a product of high primary productivity (Meyers, 1997). In Jiyang paleolakes,

254 algae-rich sedimentary layers, formed by alternating blooms of coccolithophytes and  
255 dinoflagellates, were a major feature of the Paleogene oil source rocks in the Bohai  
256 Bay Basin for more than 1 Ma (Xie et al., 2016; Song et al., 2020; Shi et al., 2021).  
257 These algal blooms are well recognized in the middle Eocene warming period of the  
258 Cenozoic (Bijl et al., 2010; Zachos et al., 2008; Pearson, 2010), which occurred  
259 41.4–39.2 Ma ago (Shi et al., 2019). During this time, a warm climate and associated  
260 high productivity were favorable for oxygen consumption beneath the photic zone. The  
261 water column became anoxic, thereby leading to enhanced preservation and burial of  
262 organic matter. High productivity can be supported by systematically elevated  
263 concentrations of both TOC and barium (Zeng et al., 2018). TOC values above 6% are  
264 recorded here over 11 intervals across the depth range 3343.47 to 3102.67 m, with two  
265 intervals having TOC values as high as 8.4% and 10.4% at 3176.51 m and 3192.90 m,  
266 respectively (Fig.2). The average Ba concentrations in Es<sub>4</sub><sup>1</sup> and Es<sub>3</sub><sup>3</sup> are 470 and 560  
267 ppm, respectively. Over the entire section in the Jiyang Depression, Ba values in  
268 samples positively correlate with the corresponding TOC values (Supplementary Table  
269 2). For comparison, in a similar high paleoproductivity Lake Malawi (East Africa), the  
270 TOC concentrations are ~ 6 % in the sediments from the anoxic deep parts of the lake  
271 (Li et al., 2018).

272         Meanwhile, high primary productivity can also be confirmed by organic carbon  
273 isotope values. Most samples show  $\delta^{13}\text{C}_{\text{org}}$  values between -29‰ and -25‰, indicating  
274 a source of lacustrine organic matter from exogenous terrestrial plants, authigenic  
275 phytoplankton photosynthesis, as well as possible allochthones (Meyers, 1997).  
276 Terrestrial C<sub>4</sub> plants were very rare in the Jiyang Depression during the middle Eocene

277 as they are usually found in dry environments and have the  $\delta^{13}\text{C}_{\text{org}}$  values higher than  
278 -20‰. However, there might have been some C3 plants in the lake, because small  
279 fragments of higher plants (including leaves) can be windblown and floating debris  
280 could sink, although some of the compounds of terrestrial origin may have been  
281 subsequently degraded by diagenesis. In the detailed core observations of the FY1 well,  
282 over a total length of 403.6 m, no fragments of higher plants were observed. Generally,  
283 there is no direct relationship between the concentration of biomarkers and the source  
284 of organic matter because many biomarkers can be detected at very low concentrations.  
285 There was probably some retene, oleanene, or  $\beta$ -carotene (Xu et al., 2020); however,  
286 the contribution of higher plants to the preserved organic matter is expected to be small.  
287 For another, the relative content of the biomarkers may also change further with  
288 diagenesis. For example, Xu et al. (2020) also proposed an existing algae source of  
289 retene, oleanene, or  $\beta$ -carotene during organic-rich shale formation. To sum up, the  
290 contribution of organic matter of terrestrial origin from higher plants depends on the  
291 lake size and sedimentation process. In a very large paralic lake continental runoff input  
292 can be significant only due to strong storms, floods or other events from land. As there  
293 were no land events in the Jiyang Depression with a total area of 26,000 km<sup>2</sup>, the  
294 detected compounds of higher plants do not mean that the terrestrial organic input is  
295 significant in this offshore lake.

296 Combined with the sedimentary characteristics of modern lakes, we propose that  
297 in the center of the paralic Jiyang lake like FY-1 Well, the organic matter may mainly  
298 come from lacustrine authigenesis, the input of terrigenous organic matter, such as  
299 plants, may only have occurred in brief periods. Of the studied 270 samples, only a few

300 (25 in Es<sub>3</sub><sup>3</sup> and 27 in Es<sub>4</sub><sup>1</sup>) showed  $\delta^{13}\text{C}_{\text{org}}$  values above -25‰, with an average TOC of  
301 5% (Fig.2), indicating that during this period organic matter may have been  
302 occasionally derived from very limited amount of terrestrial plants. Thus, most of the  
303 organic matter enrichment in the source rocks of the Shahejie Formation likely resulted  
304 from native algal and bacterial production coupled with favorable preservation  
305 conditions. Due to a globally significant increase of greenhouse gases in the MECO  
306 atmosphere (Bijl et al., 2010), photosynthetic carbon fixation could lead to carbon  
307 isotope ratios as low as -29‰ (Hodell and Schelske, 1998). Therefore, we propose that  
308 the negative excursions of  $\delta^{13}\text{C}_{\text{org}}$  corresponded to high primary productivity during  
309 warm and humid climate caused by periods of elevated atmospheric  $p\text{CO}_2$ . Under these  
310 elevated  $p\text{CO}_2$ ,  $\text{CO}_2$  was predominantly transported into lacustrine systems via  
311 photosynthesis, and was reduced by biological processes into organic matter with  
312 enrichment in the lighter isotope ( $^{12}\text{C}$ ), thereby yielding negative excursions of  $\delta^{13}\text{C}$   
313 values.

314

## 315 **5.2. Ferruginous/euxinic water conditions**

316 Lallier-Verges et al. (1993) quantified the degree of bacterial sulfate reduction  
317 (BSR) using the sulfate reduction index (SRI), which is defined as the ratio of primary  
318 organic carbon to residual organic carbon. Primary organic carbon encompasses both  
319 the organic carbon depleted via sulfate reduction, and the residual total organic carbon  
320 (TOC (wt.%) at present). Organic carbon loss ( $C_{\text{loss}}$ ) by degradation coupled with  
321 sulfate reduction may be assessed from the stoichiometry of the sulfate reduction  
322 equation proposed by Berner and Raiswell (1984):

323 
$$\text{SRI} = (\text{TOC} + C_{\text{loss}})/\text{TOC} \quad (1)$$

324 where  $C_{\text{loss}} = \text{TS}/1.33 \quad (2)$

325 Substituting (2) into (1) yields:

326 
$$\text{SRI} = (\text{TOC} + \text{TS}/1.33)/\text{TOC} = 1 + 0.75 \times \text{TS}/\text{TOC} \quad (3)$$

327 The SRI is regarded as the lowest degradation consumption index for total organic  
328 carbon. The higher the BSR activity, the higher the SRI value, and the greater the  
329 organic matter consumption. For  $\text{SRI} < 1.375$ , the BSR intensity can be limited by total  
330 sulfate and the amount of undegraded TOC may increase substantially. For  $\text{SRI} > 1.375$ ,  
331 the BSR intensity increases, and the overall TOC value is relatively low (Liu et al.,  
332 2021). The relationship between the sulfate reduction strength and the organic carbon  
333 content (SRI/TOC) in the study interval shows that most of the SRI values in the  
334 ferruginous water column are less than 1.375 (Fig. 4 (D)), indicating a weak sulfate  
335 reduction, which may have been conducive to organic matter preservation and burial.  
336 In contrast, euxinic waters with strong BSR may result both in organic preservation  
337 and consumption. It can be seen in Fig. 3 and 4 (D) that in the euxinic zone, most  
338 samples with  $\text{TOC} < 2\%$  have SRI values  $> 1.375$ .

339 Several mechanisms may have created ferruginous conditions at the bottom of the  
340 Jiyang lake. A combination of volcanism, hydrothermal fluids, and transgression may  
341 have brought reactive iron and maintained anoxic conditions, while the primary  
342 productivity was high. For example, volcanism could have increased nutrient influxes  
343 (Liu et al., 2019, 2024), and productivity, and stimulated oxygen consumption below  
344 the photic zone. Meanwhile, the isotopically “light” sulfur ( $\delta^{34}\text{S}_{\text{py}}$  of 0 ‰) from a  
345 volcanic source was preferentially utilized by BSR, resulting in low  $\delta^{34}\text{S}_{\text{py}}$  values.

346 However, intermittent sulfidization events in a ferruginous Jiyang Lake may not have  
347 led to elevated  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  ratios compared to typical marine values of 0.7, because such  
348 an increase may be obscured by the high carbonate ( $\text{Fe}_{\text{carb}}$ ) content largely dominating  
349 over  $\text{Fe}_{\text{py}}$  (Fig. 2, Unit 2, 3, 5). For all the samples, there are only two  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  values  
350 above 0.7, with the corresponding  $\delta^{34}\text{S}_{\text{py}}$  values of 24–25‰ (Fig. 4 A, C). The two  
351  $\delta^{34}\text{S}_{\text{py}}$  values, higher than those in the lower adjacent interval (~13 ‰), indicate that  
352 the basin became relatively closed and euxinic after a period of volcanism or  
353 hydrothermal activity. The positive  $\delta^{34}\text{S}_{\text{py}}$  values (> 20‰) are higher than the sulfate  
354  $^{34}\text{S}$  from seawater during middle Eocene, indicating the depletion of the light sulfur  
355 isotopes in sulfate under strong BSR. Meanwhile, the TOC values for these two  
356 samples are 3.4 and 2.8% at 3332.39 and 3226.24 m, respectively (Fig. 2), which are  
357 less than the average value (4.0%) of the study interval, indicating that BSR consumed  
358 the primary organic matter and converted sulfate to  $\text{H}_2\text{S}$ , and promoted pyrite formation.  
359 A rough positive covariation between the  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  ratios and TOC also supports the  
360 BSR occurrence (Fig. 4 A, B). However, the high TOC/TS ratios (> 2.0) and low sulfate  
361 reduction index (SRI) (< 1.375) suggest that it was sulfate availability, rather than  
362 organic matter supply, that constrained BSR in deep waters (Fig. 4 (D)).

363 For Jiyang Lake, there may have been occasional euxinic conditions as the  
364 TOC/TS values are less than 2 (in 36 samples from 270). Euxinia in the photic zone  
365 (from biomarker data) and deeper water (based on framboid size distributions) has been  
366 identified in Silurian, Devonian, Permian and Eocene oceans (Racka et al., 2010;  
367 Marynowski et al., 2012; Liu et al., 2019; Xu et al., 2020; Percival et al., 2022). Euxinia  
368 is prevalent in anoxic marine environments where sulfate is abundant. Modern



369 meromictic lakes develop euxinia when sulfate concentrations exceed 100  $\mu\text{M}$ , while  
370 below that threshold their monimolimnia (the deep stagnant layers) tend to be  
371 ferruginous. Xu et al. (2020) demonstrated that there were different euxinic water  
372 conditions during the deposition of the Shahejie Formation, evidenced by variations in  
373 the aryl isoprenoid ratio, relative amount of isorenieratane, long-chain n-alkane carbon  
374 isotopic composition and other molecular indicators, which indicated different  
375 intensity of bacterial sulfate reaction (BSR). In Jiyang Lake, potential sources for extra  
376 sulfate could have been episodic (for 5–10 ka) marine transgressions (Unit 2 and Unit  
377 5), volcanism (Unit 1, 2, 3 of  $\text{Es}_4^1$ , and Unit 5 of  $\text{Es}_3^3$ ) or hydrothermal fluids (Unit 4  
378 of  $\text{Es}_3^3$ ) (Fig. 2). Outside these episodes, sulfate would become depleted by BSR,  
379  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  values were mostly  $< 0.6$  and  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  values  $> 0.38$  (Fig.4 A), which also  
380 suggests that the deep-water column throughout the middle Eocene was predominantly  
381 ferruginous. Meanwhile, there might also be very occasional oxic episodes identified  
382 by the presence of bioturbation in anoxic brackish water (Song et al., 2020). Although  
383 Fe shuttling could potentially create local enrichments of  $\text{Fe}_{\text{carb}}$  (Fig.4 (B)) or  $\text{Fe}_{\text{ox}}$ ,  
384 resulting in high  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  and low  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  ratios, the deep lake was probably anoxic  
385 and ferruginous during most of the depositional period. The reduced Fe transported  
386 from the anoxic water column could have led to  $\text{Fe}_{\text{carb}}$  enrichments in bioturbated  
387 sediments. As anoxic ferruginous conditions expanded and contracted over time,  
388 reactive iron enrichment could form in even deeper settings.

389 In summary, the  $\text{Fe}_{\text{HR}}$  values between 1.2% and 6.6% generally show the same  
390 evolution trend as the total of  $\text{Fe}_{\text{py}}$  and  $\text{Fe}_{\text{carb}}$ , while  $\text{Fe}_{\text{ox}}$  and  $\text{Fe}_{\text{mag}}$  have little correlation  
391 with the  $\text{Fe}_{\text{HR}}$  content trend. Thus, organic matter enrichment was primarily created by

392 both enhanced preservation under ferruginous water conditions and high paleo-  
393 productivity with limited dilution of the shale by terrigenous clastic materials (Xie et  
394 al., 2016; Song et al., 2020).

### 395 **5.3. Impacts of geological events on organic carbon burial**

396 Our core analyses demonstrate that volcanism, hydrothermal activity, and marine  
397 transgressions affected the study area. Only few investigations of carbon and pyrite  
398 sulfur isotopic variations focused on lacustrine sedimentary intervals during the MECO.  
399 Our study uses different covariations between  $\delta^{34}\text{S}_{\text{py}}$  and  $\delta^{13}\text{C}_{\text{org}}$  values (Fig. 2B, D) to  
400 establish a relationship between geological events, biological productivity, and water  
401 redox conditions. It has been shown that a negative excursion of 2 to 6‰ in  $\delta^{13}\text{C}_{\text{org}}$  of  
402 both carbonate and organic carbon is linked to global volcanism (Lee et al., 2018; Liu  
403 et al., 2019; Longman et al., 2019; Shen J. et al., 2019b; Li Y. et al., 2021). Indeed, in  
404 the study intervals, volcanism effects are evident in nine prominent negative excursions  
405 in  $\delta^{13}\text{C}_{\text{org}}$  (Fig. 2B), which are correlated with tuff interlayers (Fig. 5). The pyroclastic  
406 interlayers in the shales are predominantly vitreous and crystalline debris of andesite  
407 (Fig. 5 (C, D)), in which microfractures were developed and ostracod fragments were  
408 deposited. Such negative excursions in  $\delta^{13}\text{C}_{\text{org}}$  values are typically associated with  
409 increases in primary productivity, which can be brought about by the increased delivery  
410 of nutrients following the volcanic events.

411 The same layers with highly negative  $\delta^{13}\text{C}_{\text{org}}$  are also associated with negative  
412 shifts in  $\delta^{34}\text{S}_{\text{py}}$  (as low as 8.9‰; Fig. 2D). The water column in the deep lake was  
413 usually closed when there were no geological events. In this case, the  $\text{SO}_4^{2-}$  reservoir  
414 is limited and could not be replenished. With the continuing exhaustion of the sulfate

415 reservoir (enriched in  $^{34}\text{S}$ ) by sulfur reduction through dissimilation,  $^{34}\text{S}_{\text{py}}$  gradually  
416 increased and approached that of the initial sulfate. In contrast to open marine  
417 sediments,  $^{34}\text{S}_{\text{py}}$  values in an almost infinite sea water sulfate reservoir, are usually  
418 below 0‰ (Li et al., 2021). Volcanic and hydrothermal activity generate sulfur with  
419  $\delta^{34}\text{S}$  of 0 to 5‰ (Huston, 1999), which is substantially below the values of water  
420 surface-sourced sulfate (~ 20‰ during study period). If sub-lacustrine eruptions of a  
421 volcano or associated geothermal fluids carried  $\text{H}_2^{32}\text{S}$ -enriched sulfide sulfur into a  
422 closed lake, its reaction with highly reactive iron could form isotopically equivalent  
423  $\text{Fe}^{32}\text{S}_2$ -enriched pyrite within a quite short period of time (i.e. several years). This  
424 process caused the decrease in  $\delta^{34}\text{S}_{\text{py}}$  values along with the sulfate of the light sulfur  
425 isotope was consumed by BSR. As volcanic  $\text{H}_2^{32}\text{S}$  was quickly consumed by iron and  
426 the BSR began to reduce sulfate in a closed system, the resulting pyrite had lighter  $\delta^{34}\text{S}$   
427 values. Higher  $\delta^{34}\text{S}_{\text{py}}$  values then formed again at low sulfate concentrations at the end  
428 of sulfate reduction. If volcanic activities or deep fluids carried large amounts of  
429 oxidized volatiles, such as  $\text{SO}_2$ , BSR would have been enhanced and more  $^{32}\text{S}$   
430 consumed. As a result,  $^{34}\text{S}_{\text{py}}$  first decreased and then increased with an increased  
431 amount of sulfate consumption. Indeed, this trend could be identified especially in  
432 Units 1 and 3 of  $\text{Es}_4^1$  (Fig. 2D). Because the bottom waters of the paleolake seemed to  
433 have remained ferruginous, the iron input (as Fe (II); Isley and Abbott, 1999; Kump  
434 and Seyfried, 2005) during these volcanic or hydrothermal activities must have  
435 exceeded the inputs of sulfur into the lake.

436 The presence of marine ostracods (Fig 5 (A)), elevated  $\delta^{34}\text{S}_{\text{py}}$  values (~20 ‰) and  
437 high carbonate content ( $\text{Fe}_{\text{carb}}$  to ~5%) collectively indicate marine transgressions,

438 which is consistent with the interpretation of the strata using the method of  
439 astronomical cycles (Ma et al., 2023). During middle Eocene warming, marine  
440 transgressions increased the lake water depth and supplied  $^{34}\text{S}$ -enriched sulfate,  
441 causing the  $\delta^{34}\text{S}_{\text{py}}$  value of pyrite to approach that of seawater. The  $\delta^{34}\text{S}_{\text{py}}$  values vary  
442 between 9 and 36 ‰, being both lower and higher than those of the marine sulfates  
443 identified during the MECO ( $20.9 \pm 0.5\text{‰}$ ; Longinelli, 1989; Kampschulte et al., 2001).  
444 Marine transgressions may have occurred roughly every 1,000 years over a period of  
445 5,000 years (Fig. 2, Units 2 and 5). As BSR generates isotopically light sulfide, the  
446 heavier  $\delta^{34}\text{S}_{\text{py}}$  values can be attributed to the consumption of sulfate sulfur after staged  
447 transgression when the lake system closed again. Mineral analyses show that the total  
448 content of  $\text{Fe}_{\text{mag}}$  and  $\text{Fe}_{\text{ox}}$  is low, with a maximum of 0.37%, so the contents of ferrous  
449 carbonate and pyrite compete with each other. This is consistent with most sediments  
450 in modern paralic environment (Liu et al., 2023; Zhang et al., 2024). Only the  
451 difference between the samples of the two study areas is the contents of ferrous  
452 carbonate, indicating the different water conditions during their sediment deposition.  
453 In Shahejie Formation, the carbonate content in the study interval was generally high,  
454 with average calcite and dolomite contents of 37% and 10%, respectively. For example,  
455 the content of  $\text{Fe}_{\text{carb}}$  is higher than that of  $\text{Fe}_{\text{py}}$  from 3225 to 3200 m in Unit 5 (Fig.2),  
456 indicating that the sulfur isotope fractionation of pyrite in the paralic lakes during the  
457 sulfate reduction process was constrained by changes in the global sea level. The sea  
458 level increased in the warm and humid climate, and transgression brought large  
459 amounts of  $\text{Ca}^{2+}$  to form carbonates. Meanwhile, high paleo-productivity also  
460 promoted the deposition of organic-rich layers. Therefore, the precipitation of calcium

461 carbonate and organic matter layers is the result of increased pH due to strong  
462 photosynthesis by algae in the warm climate during marine transgressions in the Jiyang  
463 calcareous lake. After that, the organic matter was degraded in a limited manner under  
464 ferruginous conditions and was well preserved.

465 The delicate equilibrium between ferruginous and euxinic chemical conditions  
466 could be influenced by the comparable rates of  $\text{Fe}_{\text{HR}}$  and sulfate input fluxes. On a  
467 global scale, continental sources stand out as the primary contributors to the potential  
468  $\text{Fe}_{\text{HR}}$  flux. At the regional scale, geological events, such as volcanic activity or ocean  
469 transgression, could also have liberated some reactive iron and sulfate into the lake,  
470 providing a conceivable mechanism for the transportation of ferrous iron and resulting  
471 in a disproportionate increase in the  $\text{Fe}_{\text{HR}}$  flux relative to that of sulfate. The interplay  
472 of all these processes have generated dominantly ferruginous environments during the  
473 middle Eocene in the Jiyang Depression.

474 On the basis of the aforementioned research, we propose that there was an  
475 extensive burial of lacustrine organic carbon in Eastern China during the warm and  
476 humid climate of the middle Eocene, which thereby created a positive feedback loop  
477 in the Earth's climate system. Frequent volcanic activity during the early stages of  $\text{Es}_4^1$   
478 might have brought aerosols to increase the albedo in the short-term cold climate  
479 (Fig.6B, maybe to 10 years). Most importantly, it released abundant  $\text{CO}_2$  into in the  
480 atmosphere and brought reactive iron and nutrients to create optimal environments for  
481 the growth and expansion of algae and plankton in the later stages (Fig.6A, to 1 million  
482 years) of the middle Eocene. As temperatures increased, the biological productivity in  
483 Jiyang Lake increased, leading to enhanced production of total organic carbon in

484 ferruginous water conditions. This positive feedback mechanism may have contributed  
485 to the sustained warmth of the middle Eocene climate. Based on this analysis, we  
486 highlight a combined effect on sedimentation of external events such as input of  
487 volcanic ash, intermittent hydrothermal fluids and marine transgressions during middle  
488 Eocene continental warming of western Pacific. These events could not only supply  
489 nutrients and catalytic elements to promote biological productivity and cause oxygen  
490 consumption, but they also enhanced the reactive iron input to form the dynamic anoxic  
491 ferruginous conditions that were conducive for the preservation of organic carbon.

492

## 493 **6. Conclusions**

494 The widespread terrestrial sedimentary and geochemical records of the middle  
495 Eocene in the Eastern China have been established using novel TOC, TS, iron  
496 speciation,  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{34}\text{S}_{\text{py}}$  data. These data, including the highly-reactive iron to total  
497 iron ratios ( $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}} > 0.38$ ), along with a wide range of total organic carbon content  
498 (TOC, from 1 to 10 %) exceeding that of total sulfur ( $\text{TOC}/\text{TS} > 2$ ), and low sulfate  
499 reduction indexes ( $\text{SRI} < 1.375$ ), collectively suggest widespread anoxic and  
500 ferruginous conditions that would have been favorable for burial of lacustrine organic  
501 carbon during the middle Eocene in the paralic lacustrine environments of the Jiyang  
502 Depression. The temporal stability of lacustrine ferruginous water conditions may have  
503 been due to the warm and humid climate during the middle Eocene, with high  
504 biological productivity and large oxygen consumption in the water column, leading to  
505 efficient burial of organic carbon in deep sediments.

506 Both  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{34}\text{S}_{\text{py}}$  values reveal transient geological events such as volcanism,

507 hydrothermal fluids, and transgressions. Negative  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{34}\text{S}_{\text{py}}$  excursions along  
508 the sedimentary column point to transient volcanic events, whereas positive  $\delta^{13}\text{C}_{\text{org}}$   
509 along with negative  $\delta^{34}\text{S}_{\text{py}}$  excursions indicate injection of associated hydrothermal  
510 fluids; in contrast, elevated  $\delta^{34}\text{S}_{\text{py}}$  (to  $\sim 20\text{‰}$ ) point to frequent marine transgressions.  
511 Despite potential inputs of sulfur into the paleolake as a result of these geological  
512 events, bacterial sulfate reduction efficiently consumed the sulfate pool, thereby  
513 creating ferruginous water conditions favorable for the efficient preservation of organic  
514 carbon.

515

## 516 **Acknowledgments**

517 We thank Yunqing Hao for assistance with microscopic slice analyses and for  
518 discussions, Prof. Chao Li and Prof. Yan'an Shen for help with the geochemical  
519 analyses, Prof. Bing Shen and Dr. Huiyuan Xu for discussions. This work was  
520 supported by the National Natural Science Foundation of China (Grants 42172151,  
521 41811530094, and 41625009), the China Postdoctoral Science Foundation (Grant  
522 2021M690204), and the National Key Research and Development Program (Grant  
523 2023YFF0806200). We thank the two reviewers and the editorial support for the  
524 constructive comments, which have greatly improved the quality of this paper.

525

## 526 **Research Data**

527 All of the processed data discussed has been uploaded in the supplementary tables.

528

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733

#### 734 Table and Figure captions

735

736 Table 1. Summary data of total organic carbon (TOC), organic carbon isotope  
737 composition ( $\delta^{13}\text{C}_{\text{org}}$ ), total sulfur (TS), pyrite sulfur isotope ( $\delta^{34}\text{S}_{\text{py}}$ ), Fe/Al ratio, and  
738 iron speciation of samples in the FY1 Well (data range, arithmetic average and number  
739 of samples, see Supplementary Table 1 for data points).

740

741 Figure 1. (A) Map of sites with existing MECO records on a paleogeographic  
742 reconstruction for the middle Eocene at 40 Ma (modified from Ploeg et al., 2023). (B)  
743 Simplified geological map of Bohai Bay Basin in western Pacific, showing the core  
744 location of FY-1 Well in the Jiyang Depression in eastern China (modified from Liang  
745 et al., 2016). (C) Stratigraphic column of the study interval in the middle Eocene. The  
746 Es<sub>4</sub><sup>1</sup> and Es<sub>3</sub><sup>3</sup> sediments are deposited during the rifting stage over 38–50 Ma ago

747 (modified from Shi et al., 2019).

748

749 Figure 2. Iron speciation,  $\delta^{13}\text{C}_{\text{org}}$ , TOC, and  $\delta^{34}\text{S}_{\text{py}}$  values as a function of depth from  
750 the middle Eocene ( $\text{Es}_4^1$ – $\text{Es}_3^3$ ) black shales in the Jiyang Depression (geological  
751 timescale from Shi et al., 2019). (A) total organic carbon (TOC), (B)  $\delta^{13}\text{C}_{\text{org}}$ , (C) total  
752 sulfur content (TS), (D) pyrite sulfur isotope ( $\delta^{34}\text{S}_{\text{py}}$ ), (E) ratio of highly reactive Fe  
753 to total Fe ( $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ ), (F) ratio of pyrite iron to highly reactive iron ( $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ ), (G)  
754 content of pyrite iron, (H) content of carbonate iron. Note that  $\text{Fe}_{\text{HR}} =$   
755  $\text{Fe}_{\text{py}} + \text{Fe}_{\text{ox}} + \text{Fe}_{\text{mag}} + \text{Fe}_{\text{carb}}$ , the thresholds for oxic versus anoxic (0.22–0.38) and  
756 ferruginous versus euxinic conditions (0.6–0.8) are from Poulton et al. (2021); the  
757 units of the study interval are based on lithological and geochemical differences, as  
758 discussed in the text.

759

760 Figure 3. Plots of TOC vs TS, showing that the salinity of the most samples was similar  
761 to the salinity of seawater, corresponding to ferruginous water conditions.

762

763 Figure 4. Plots of (A)  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  vs  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ ; (B)  $\text{Fe}_{\text{carb}}$  vs  $\text{Fe}_{\text{py}}$ ; (C)  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  vs  $\delta^{34}\text{S}_{\text{py}}$ ;  
764 (D) TOC vs SRI.

765

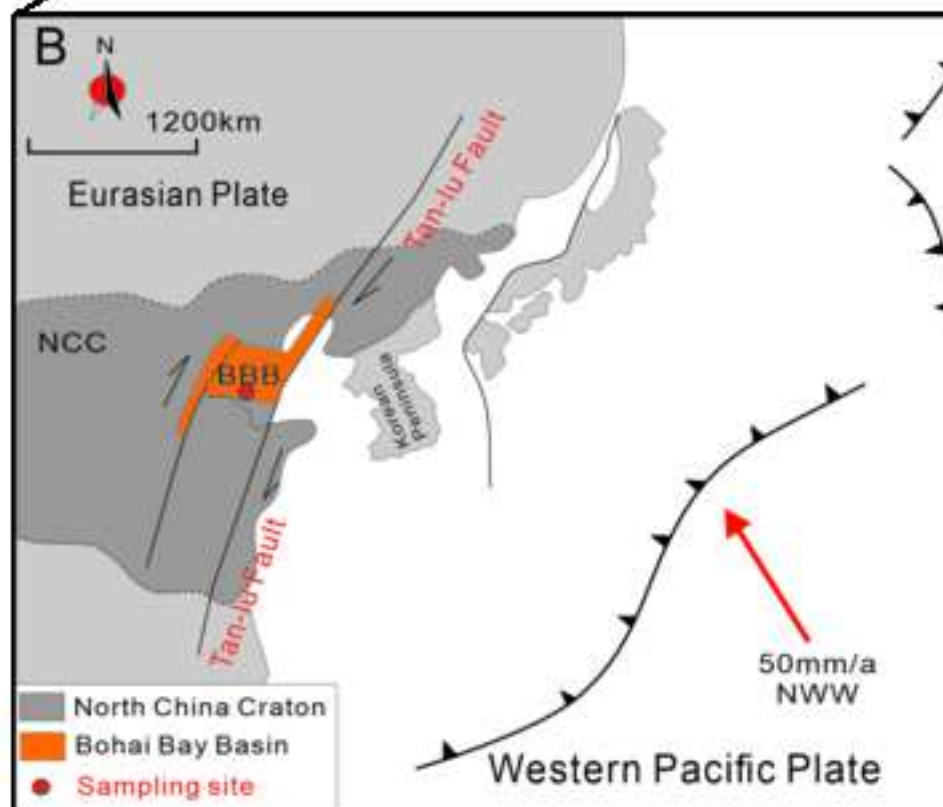
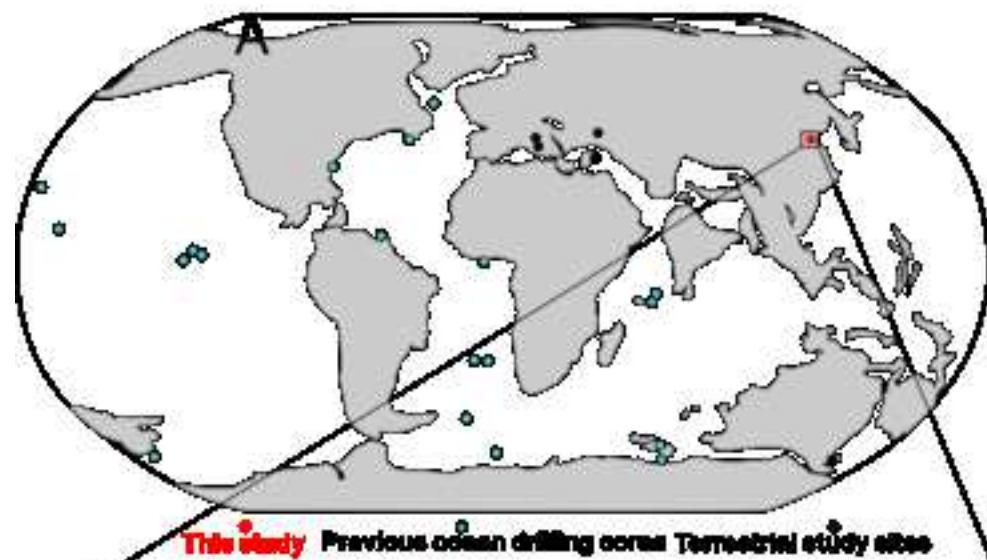
766 Figure 5. Microscopic features of volcanic ash in the Middle Eocene shale of the Jiyang  
767 Depression. (A) ostracod fragments in shales; (B) interbedded tuffs and shale; (C)  
768 interbedded tuffs and shale with micro fractures; (D) pyroclastic interlayer in shales.

769

770 Figure 6. Sedimentary model of the paralic lake basin in the Jiyang Depression

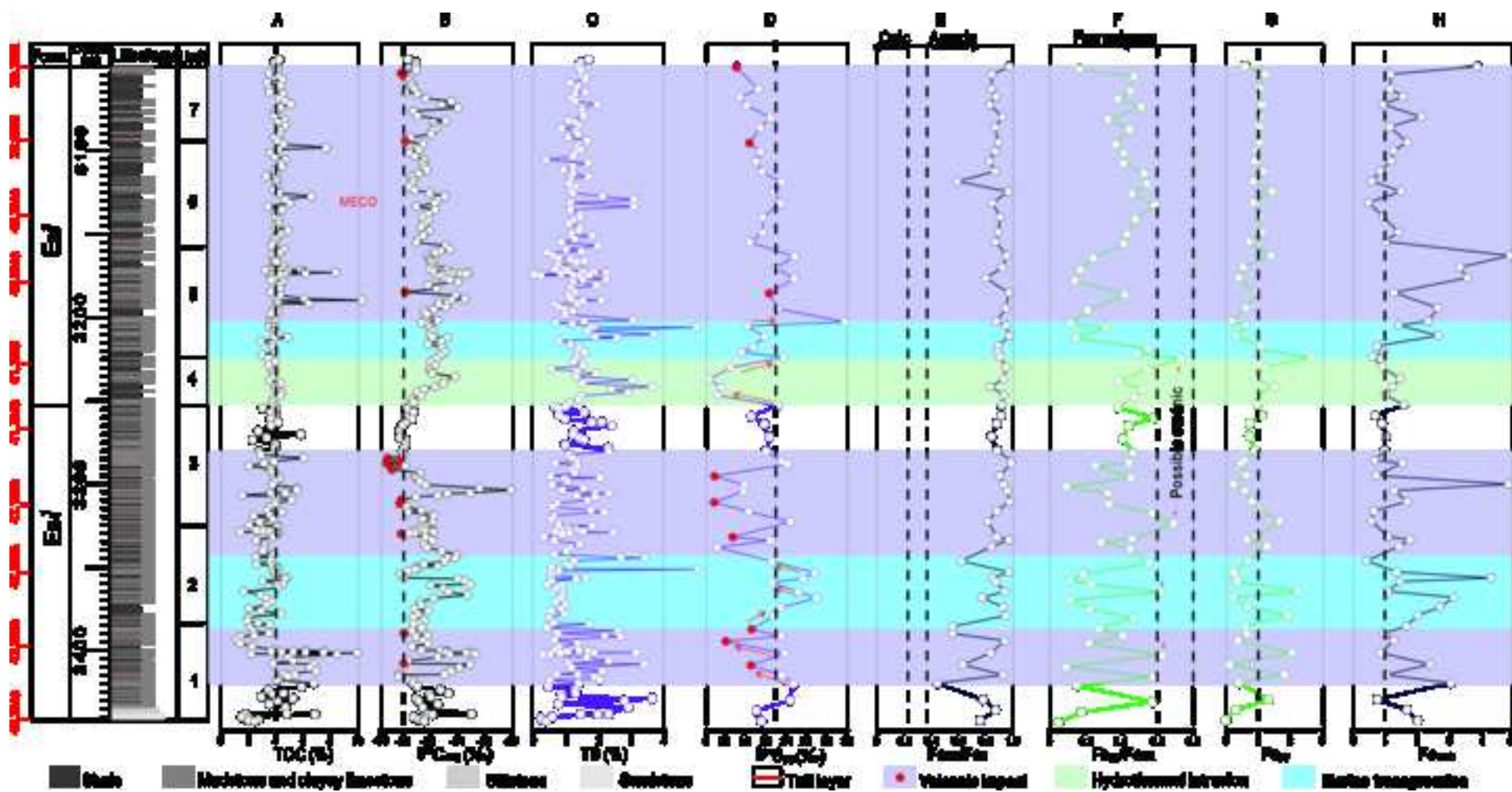
771 developed in this study. (A) High primary productivity during middle Eocene long-  
772 time warmth. (B) Impacts of different geological events on organic carbon burial.  
773 During a short period of cooling caused by volcanism, despite potential external sulfur  
774 inputs, bacterial sulfate reduction sufficiently depleted the sulfate pool to have created  
775 ferruginous conditions.

776

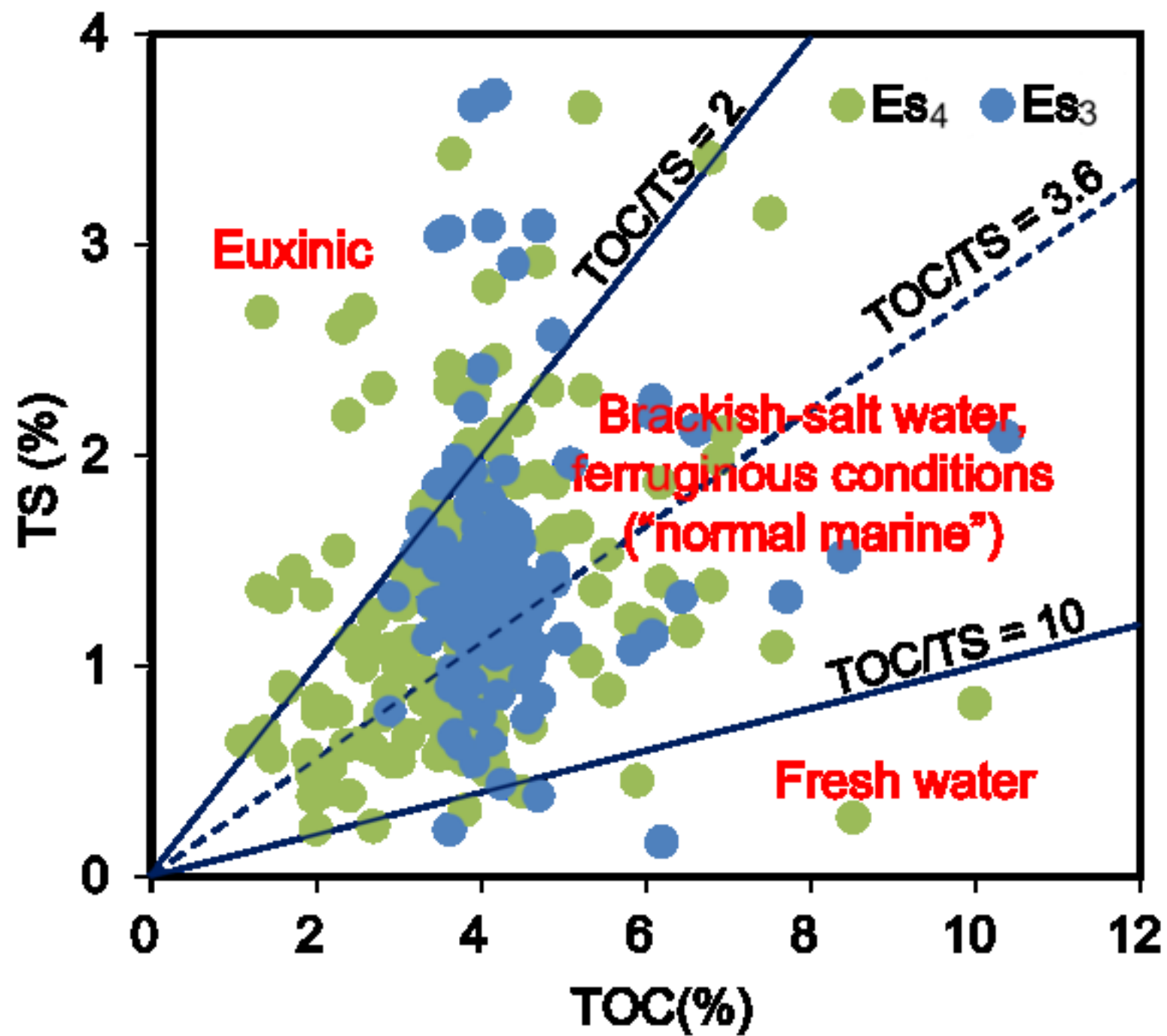


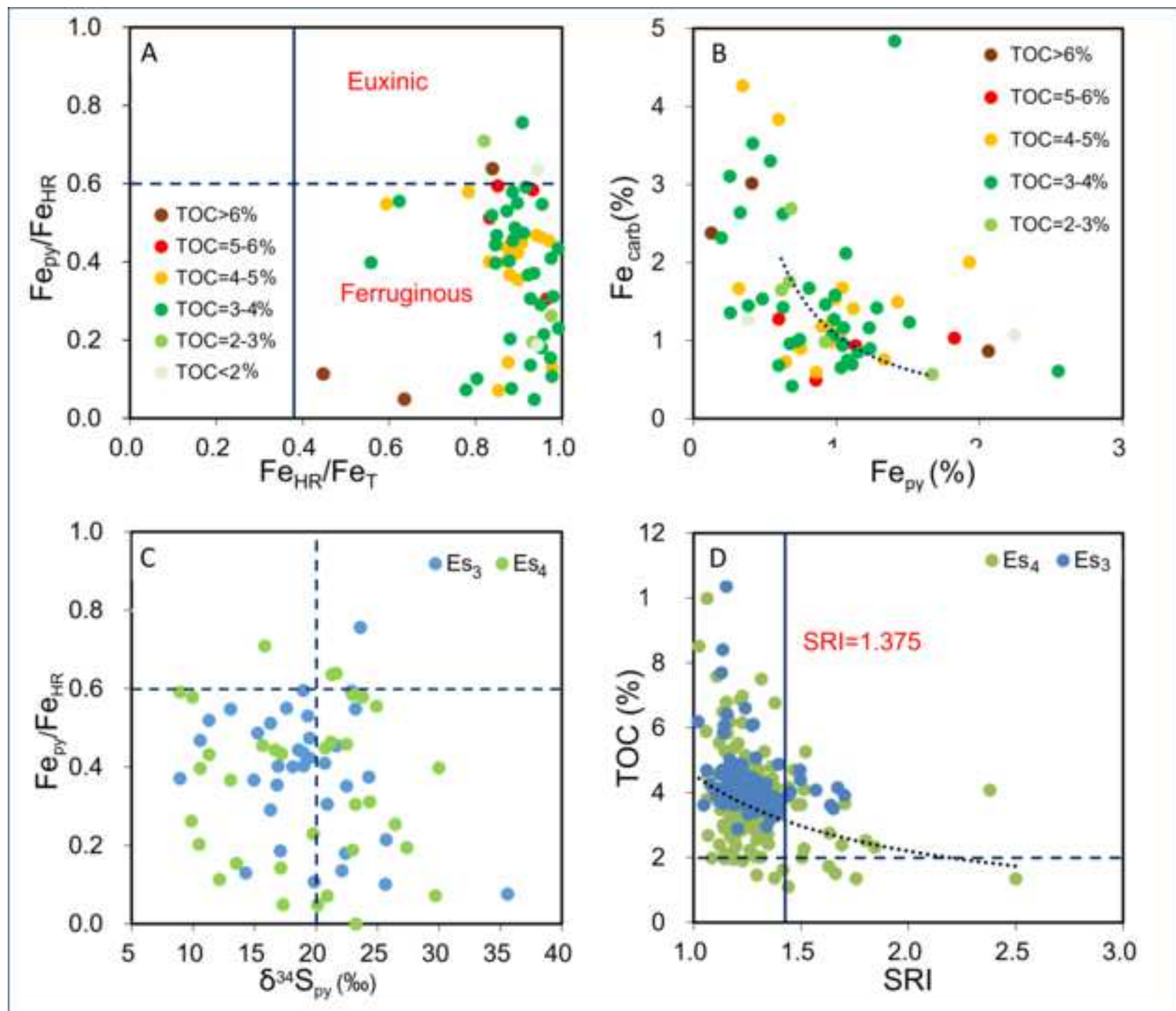
Period	Stage	Member	Thickness (m)	Lithology	
					Member
Neogene	Pliocene	Nm1	100-450	[Lithology]	
		Nm2			
	Miocene	Mg1	300-1250	[Lithology]	
		Mg2			
Paleogene	Oligocene	Ol1	100-500	[Lithology]	
		Ol2			
		Ol3			
		Eocene	Es1	0-450	[Lithology]
			Es2		
			Es3	0-350	[Lithology]
	Es4				
	Eocene	Shabelle (Es)	Es5	700-1200	[Lithology]
			Es6		
			Es7		
			Es8		
	Eocene	Kangdian (Es)	Es9	0-1500	[Lithology]
			Es10		
			Es11	0-90	[Lithology]
Es12					

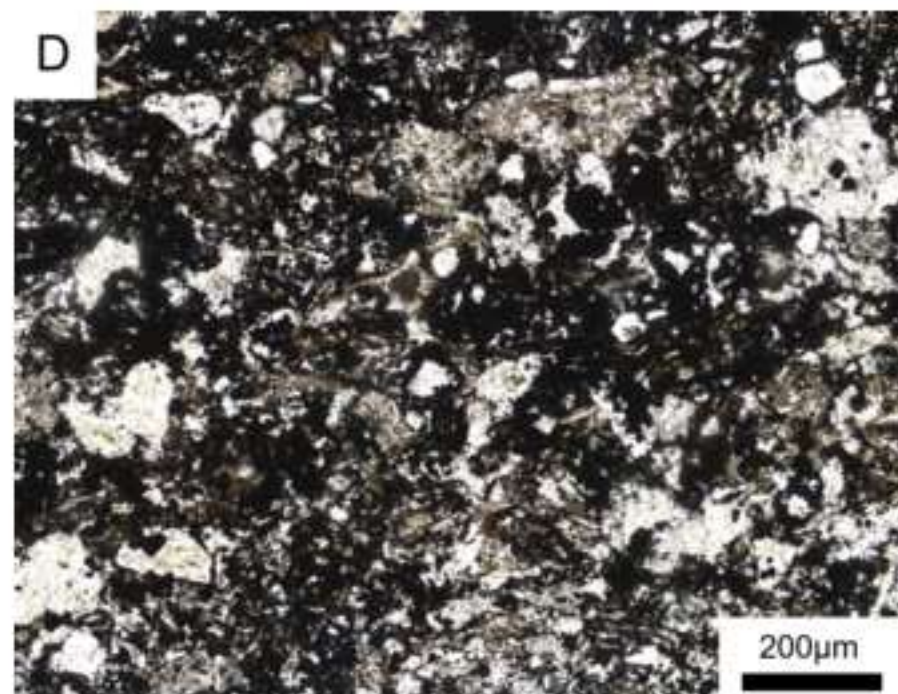
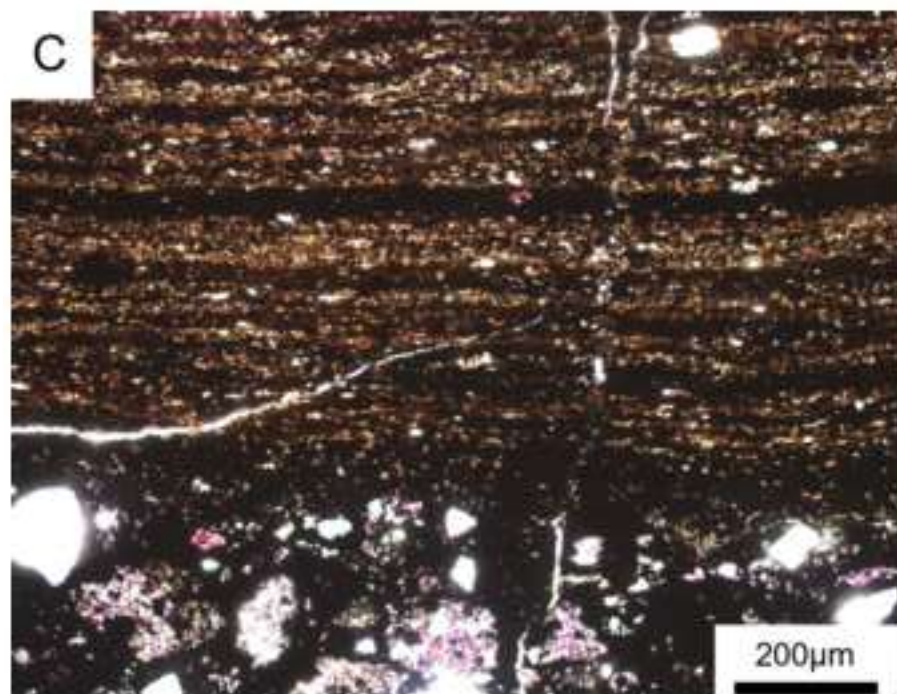
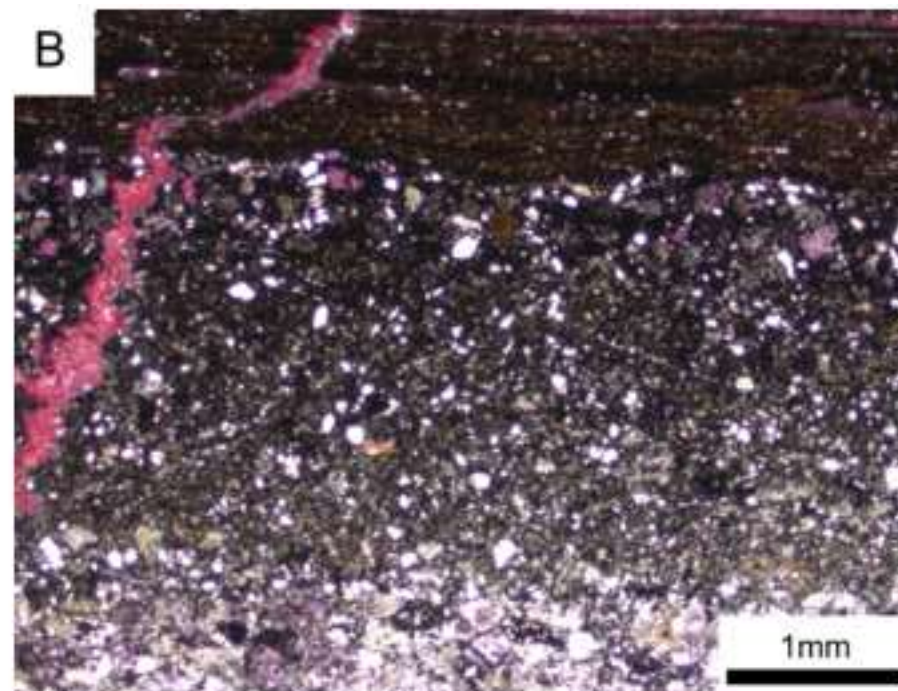
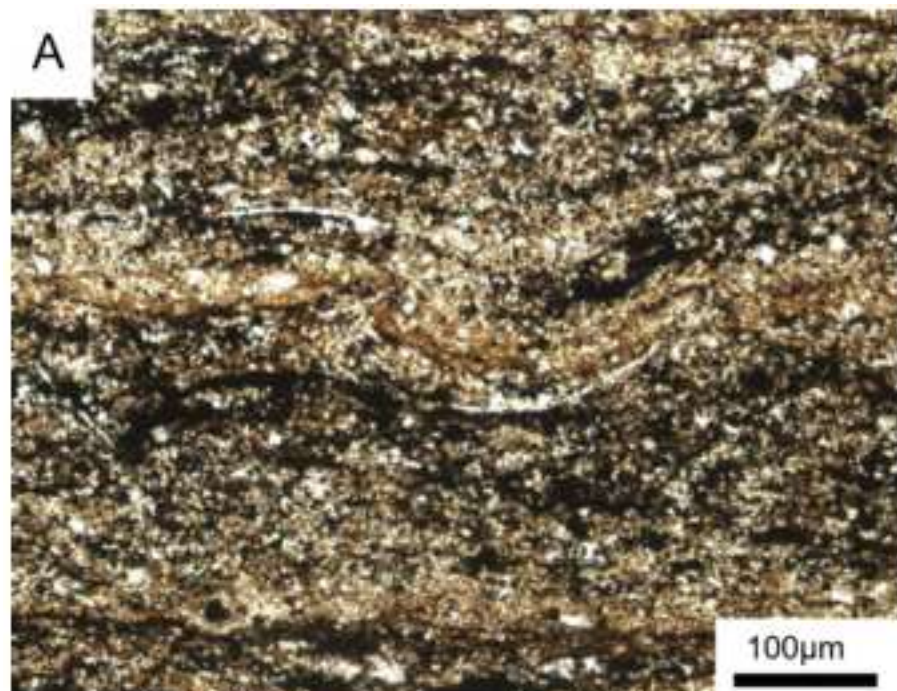


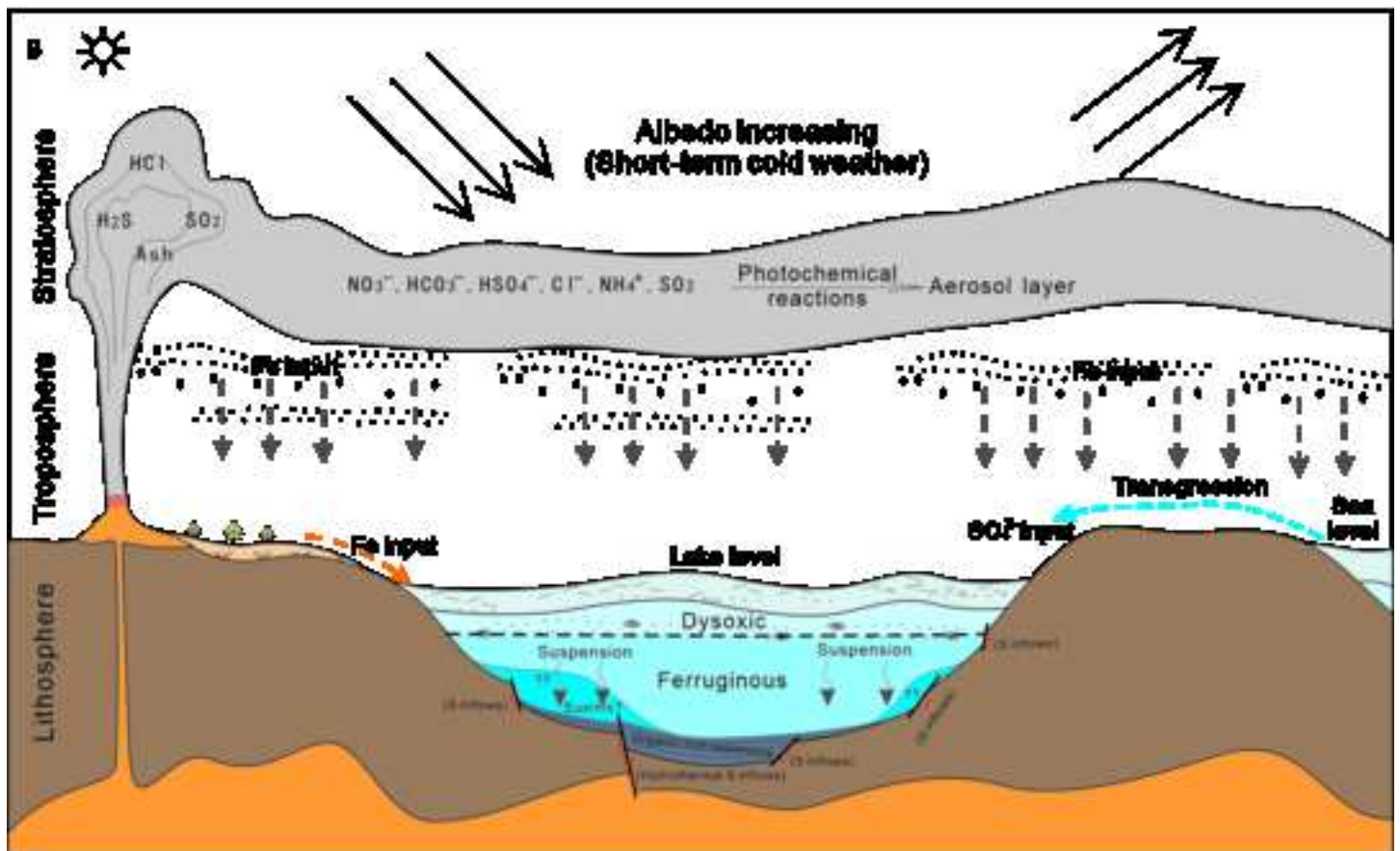
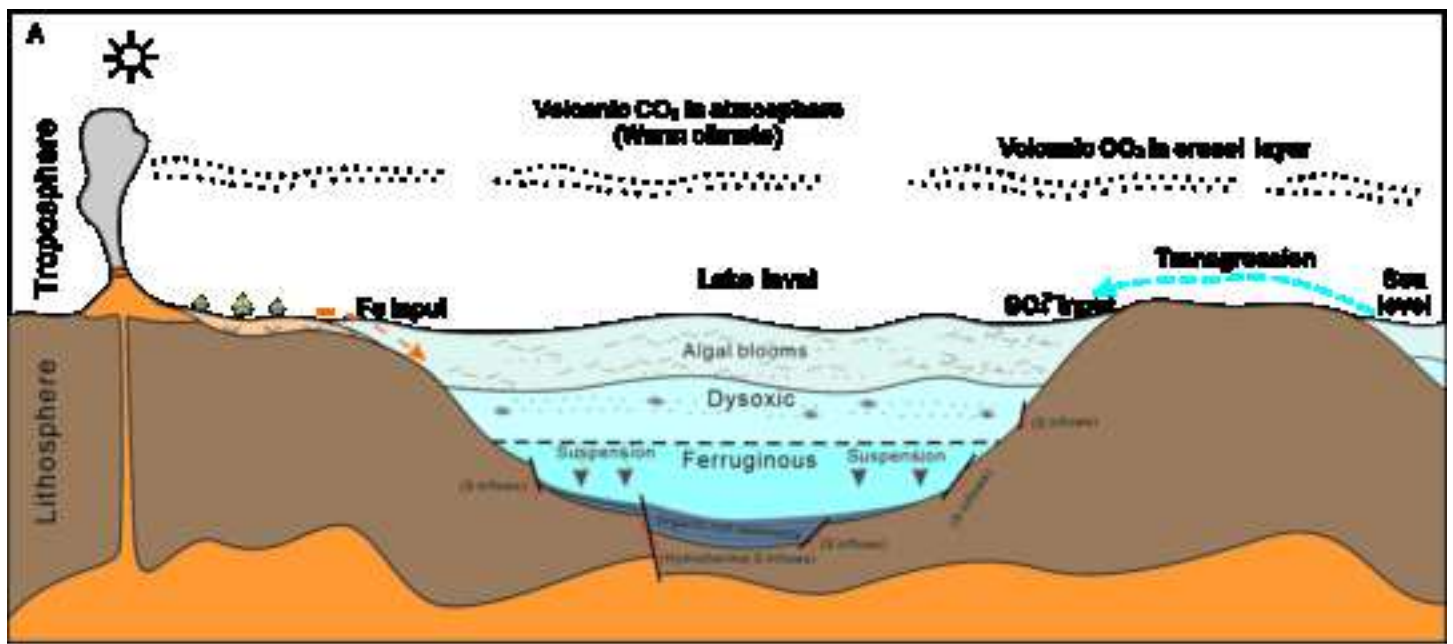






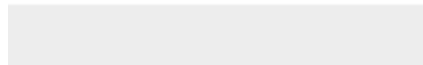








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**Supplementary Material**  
Supplementary Table 1+2.xlsx



**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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