Effects on global warming by microbial methanogenesis in alkaline lakes during the Late Paleozoic Ice Age (LPIA)

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Abstract

Methane (CH_4) is an important greenhouse gas, but its behavior and influencing factors over geological timescales are not sufficiently clear. This study investigated the Late Paleozoic Ice Age (LPIA), which is thought to have experienced an interval of rapid warming at *ca*. 304 Ma, that may have been analogous to modern warming. To explore possible causes of this warming event, we investigated ancient alkaline lakes in the Junggar Basin, northwestern China. Results show that microbial CH_4 cycling here was strong, as evidenced by $\delta^{13}C_{carb}$ values of >5‰, ~+0.6‰ offsets between pristane $\delta^{13}C$ ($\delta^{13}C_{Pr}$) and phytane $\delta^{13}C$ ($\delta^{13}C_{Ph}$) values, a 3β-methylhopane index of 9.5% ± 3.0%, and the highly negative $\delta^{13}C$ values of hopanes (–44‰ to –61‰). Low sulfate concentrations in the alkaline lakes made methanogenic archaea more competitive than sulfate-reducing bacteria, and the elevated levels of dissolved inorganic carbon promoted methanogenesis. Biogenic CH_4 emissions from alkaline lakes may have contributed to rapid climate warming in addition to CO_2.

INTRODUCTION

Atmospheric CH_4 is an important greenhouse gas (Hinrichs et al., 2003; Kirschke et al., 2013). The primary source of CH_4 to the atmosphere are methanogenic microorganisms, which account for ~74% of global CH_4 emissions (Vanwonterghem et al., 2016). Therefore, exploring conditions that are conducive to microbial CH_4 production is important for understanding global climate change (Orphan et al., 2001; Pancost et al., 2007). Wetlands have been identified as the major source of atmospheric CH_4 (~33%), but also contributions from lakes are important (~20%) (Bastviken et al., 2011). However, due to the relatively short timescale of modern observations and uncertainties in model boundary conditions, it is not clear how these sources contribute to global warming. Therefore, studies of the microbial CH_4 cycle and its climatic effects through geological history are important for understanding the current and future climatic trends (Kim and Zhang, 2022).

The Late Paleozoic Ice Age (LPIA; *ca*. 340–290 Ma) had similar atmospheric pCO_2 to that seen over the past few million years (Montañez et al., 2016; Foster et al., 2017; Richey et al., 2020). In addition, the LPIA likely had the highest atmospheric pCH_4 of the Phanerozoic (up to 10 ppmv) and thus is an important interval for understanding CH_4 cycling and its climatic effects in deep time. It has been suggested that greenhouse gases induced rapid warming in the middle LPIA (at *ca*. 304 Ma), evidenced by the increases of pCO_2 and sea-surface temperatures, marine transgression, and a major loss of continental ice volume

(Richey et al., 2020; Montañez, 2022; Fielding et al., 2023). However, the causes and interlinks of these events are unproven (Chen et al., 2022). One possible explanation for unusually high pCH$_4$ is an expansion of equatorial forests and coal deposits (Bartdorff et al., 2008). However, recently, several lines of evidence of microbial CH_4 activity were found in sediments of an ancient alkaline lake deposited during the LPIA in the Fengcheng (305–296 Ma) (Wang et al., 2020; Xia et al., 2021) and Lucaogou formations (292–288 Ma) (Sun et al., 2022), Junggar Basin, northwest China (Fig. 1). This is significant because modern alkaline lakes contain alkalophilic methanogenic archaea adapted to high-pH environments that can result in abnormally high CH_4 production (Fazi et al., 2021). Hence the CH_4 production of lacustrine settings could be an alternative explanation for the development of LPIA.

This study investigated the late Paleozoic, organic-rich, alkaline lacustrine sedimentary rocks of the Fengcheng Formation in the Mahu Sag, northwestern Junggar Basin. We also compared the early-stage alkaline lacustrine deposits of the Lucaogou Formation in the southeast. Details about the geological and environmental settings including the age constraints are provided in the Supplemental Material[1]. Based on a detailed description of the CH_4 cycle and its spatial–temporal variations, we discuss the possible controls on net CH_4 production, specifically including limits imposed by the sulfur cycle and dissolved inorganic carbon (DIC).

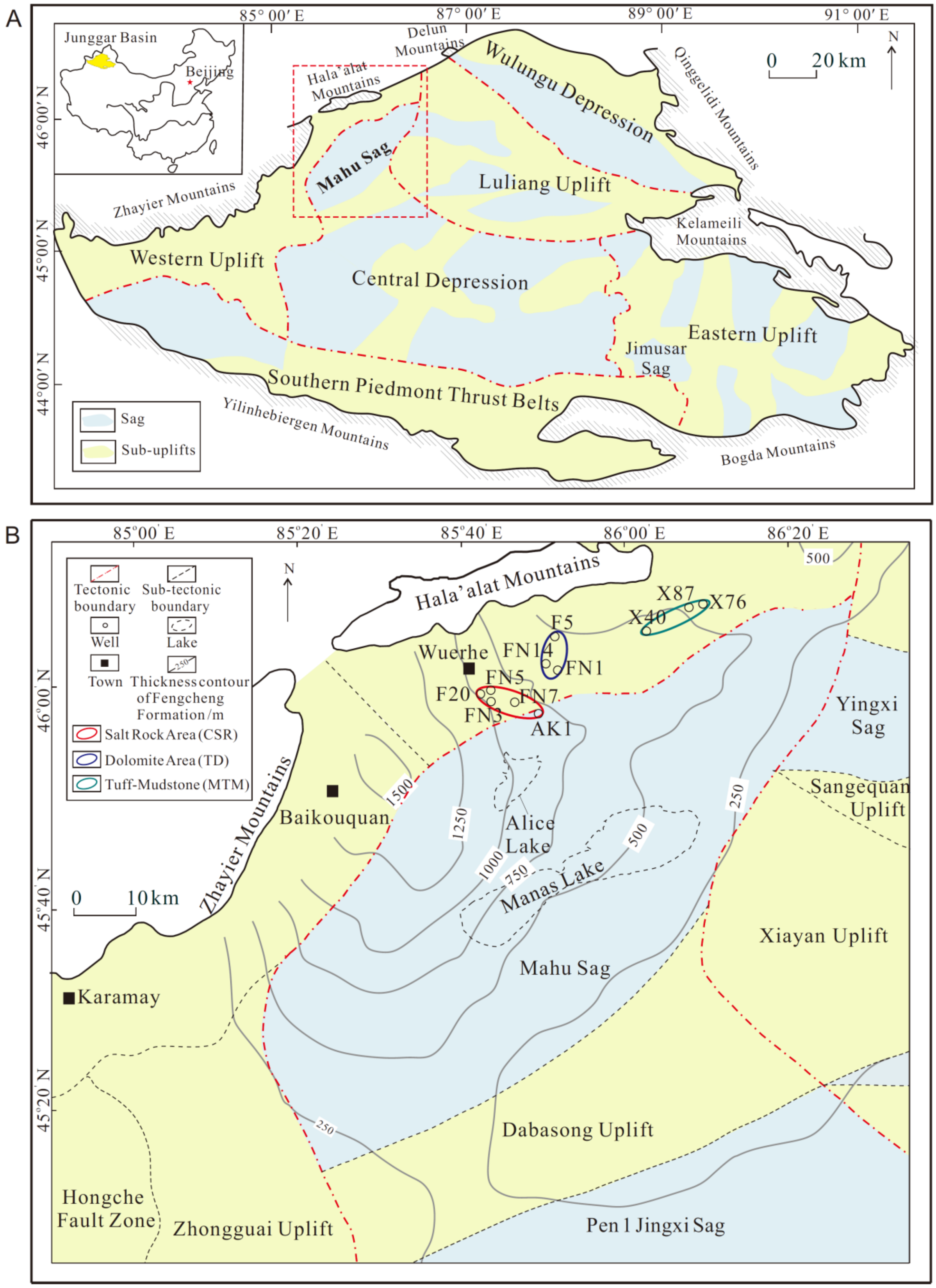

Fig. 1. Structural setting of the study area. (A) the Junggar Basin, northwestern China. Box shows area of B. (B) Mahu Sag.

RESULTS AND DISCUSSION

Evidences for microbial methane cycling in Late Paleozoic alkaline lakes

We identified several lines of evidence for methane cycling in the Fengcheng Formation, including (a) carbonate $\delta^{13}C$ ($\delta^{13}C_{carb}$) > 5‰ at the top in its depocenter (Xia et al., 2020), (b) ~+0.6‰ offsets between $\delta^{13}C_{pr}$ and $\delta^{13}C_{ph}$ (Fox et al., 2020), (c) 3β-methylhopane index (3β-MeHI) [=(C_{31} 3β-methylhopane/(C_{31} 3β-methylhopane + C_{30} αβ-hopane) × 100)] (Summons and Jahnke, 1990) varying between 2.3%–14.2% (Xia et al., 2021), and (d) extremely negative $\delta^{13}C$ values of regular hopanes (–44‰ to –61‰).

The extremely heavy $\delta^{13}C_{carb}$ values (usually 5‰–15‰) are indicative of heterotrophic methanogenic archaea, which convert biomass into isotopically light CH_4 and isotopically enriched CO_2 (Curtis et al., 1986). $\delta^{13}C_{carb}$ values of the Fengcheng Formation are –3.8‰ to 5.8‰, and the $\delta^{13}C_{carb}$ values at the top of F_3 (the third member) in the central salt rock (CSR) area are >5‰ (Fig. 2A). The main sources of general phytane are from chlorophylls *a* + *b* and methanogenic archaea, and *n*-alkyl lipids are depleted in ^{13}C compared to the isoprenoids in algae, whereas in heterotrophs, the opposite pattern is observed (Grice et al., 2005; Fox et al., 2020). The ~+0.9‰ isotopic offsets between *n*-alkanes (C_{17}–C_{19}) and isoprenoids (pristane and phytane) in our data, paired with the ~+0.6‰ offsets between $\delta^{13}C_{pr}$ and $\delta^{13}C_{ph}$ (Fig. 2A; Fig. S1), indicate a heterotrophic source. In light of the >5‰ $\delta^{13}C_{carb}$ values, the most conservative explanation is strong methanogenic activity (Curtis et al., 1986). The high 3β-MeHI, indicated by metastable reaction monitoring gas chromatography–mass spectrometry (MRM-GC-MS) analyses on mass charge ratio (*m/z*) 426-205, points to a high abundance of microaerophilic methanotrophic proteobacteria (Table S1; Fig. S2; Xia et al., 2021). C_{31} regular hopanes with extremely negative $\delta^{13}C$ values (–44‰ to –61‰; Fig. S1) were detected in the Fengcheng Formation, suggesting an active methanotrophic population (Freeman et al., 1990; Pancost et al., 2007). These lines of evidence collectively show that the ancient alkaline lake had the most active methane cycle during deposition of F_3 (Table S1; Fig. 2A).

An even more active methanogen population may have existed during deposition of the Lucaogou Formation in the southeastern Junggar Basin, where $\delta^{13}C_{carb}$ values are even higher (6.8‰–19.8‰) (Curtis et al., 1986). This conclusion is supported by findings of regular hopanes with very negative $\delta^{13}C$ values (–44.4‰ to –55.6‰) and high contents of 3β-methylhopanes in the Lucaogou Formation (Ding et al., 2020; Sun et al., 2022).

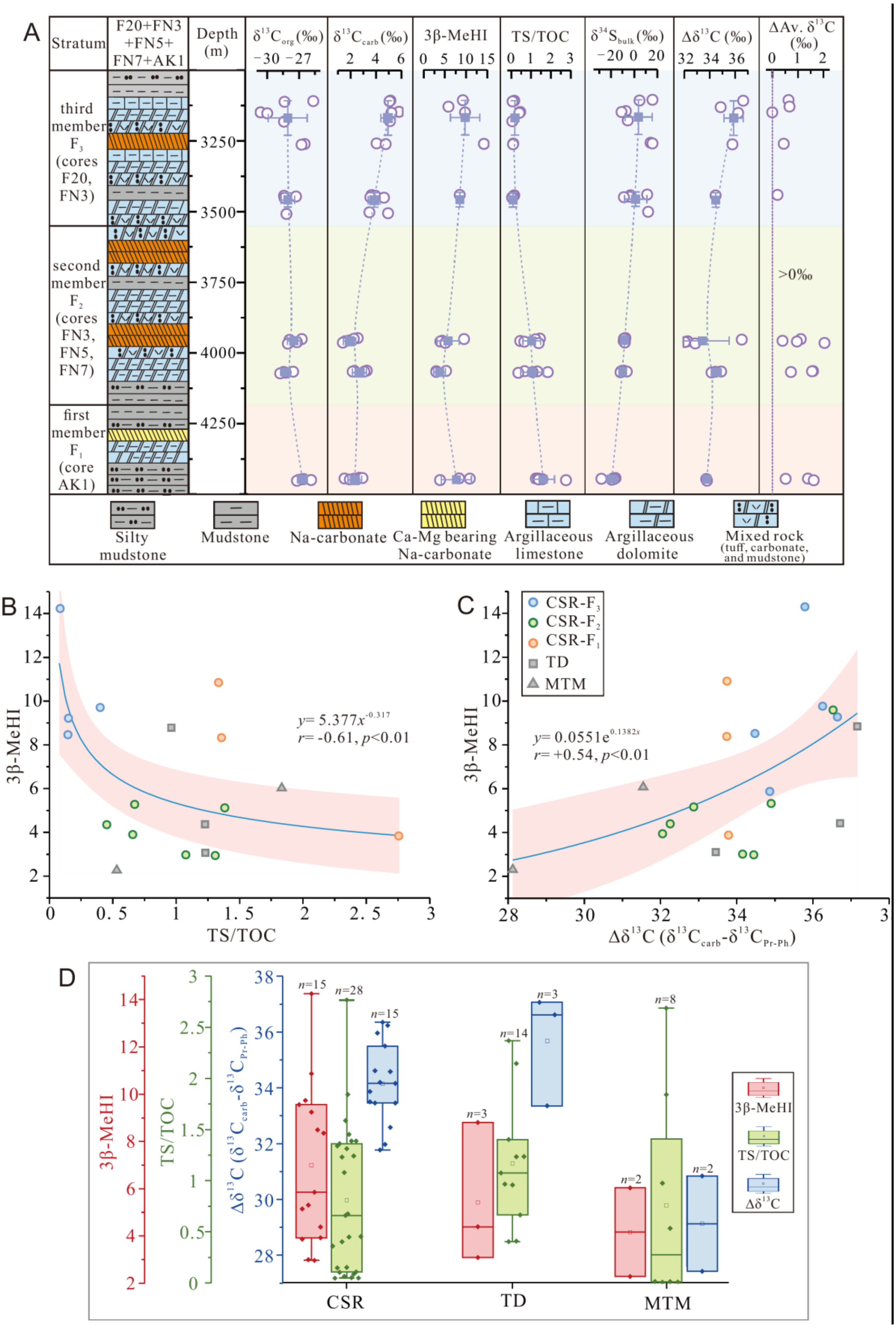

Fig. 2. Spatial and temporal variations of the proxies in the Fengcheng Formation in the study area. (A) Organic $\delta^{13}C$ ($\delta^{13}C_{org}$), carbonate $\delta^{13}C$ ($\delta^{13}C_{carb}$), 3β-methylhopane index (3β-MeHI), total S versus total

organic C (TS/TOC) ratios, $\delta^{34}S$ of decarbonated bulk rocks ($\delta^{34}S_{bulk}$), $\delta^{13}C_{carb}$ – $\delta^{13}C_{Pr\text{-}Ph}$ ($\Delta\delta^{13}C$), and average of $\delta^{13}C$ ($C_{17,18,19}$ *n*-alkanes) minus average of $\delta^{13}C$ (pristane, phytane) (ΔAv. $\delta^{13}C$) data plotted versus depth for the Fengcheng Formation. The trend lines are constructed from the mean values of samples with adjacent depths (solid square) (see sample numbers and data points for each well in Table S2 [see footnote 1]). The error bars represent the standard deviations of depths and proxies. $\delta^{13}C_{org}$, $\delta^{13}C_{carb}$, TS/TOC, and 3β-MeHI data are from Xia et al. (2020, 2021). Depths of samples from wells F20, FN3, FN7, and AK1 are converted into equivalent depths in well FN5 based on stratigraphic correlations. (B, C) Plots of TS/TOC ratios versus 3β-MeHI values (B) and $\Delta\delta^{13}C$ versus 3β-MeHI values (C). Trend lines were calculated with Origin 2023 software (http://cloud.originlab.com/) and show 95% confidence intervals (pink shaded areas), with all the p-values are <0.01. (D) Lateral variations of 3β-MeHI, TS/TOC, and $\Delta\delta^{13}C$ data. The filled diamond and open square symbols represent original sample values and statistical median values. CSR—central salt rock; TD—transitional dolomite; MTM—marginal tuff-mudstone (see Fig. 1B).

Mechanisms of strong methane cycling in Late Paleozoic alkaline lakes

Co-evolution of the methane and sulfur cycles: The microbial CH_4 cycle is commonly closely related to the microbial S cycle (Kuivila et al., 1989). For example, methanogenic archaea and sulfate-reducing bacteria compete for the same reductants such as acetate and H_2 for their metabolism, while the methanotrophic archaea and sulfate-reducing bacteria typically have a symbiotic relationship (Orphan et al., 2001).

In this study, total S/total organic C (TS/TOC) ratios and $\delta^{34}S$ values of decarbonated bulk rocks ($\delta^{34}S_{bulk}$) were used to further constrain the [SO_4^{2-}] in the alkaline lakes and its possible effects on microbial CH_4 production (see the supplement for details). Our results show that in the CSR, TS/TOC ratios decrease gradually from F_1 (the first Member) to F_3 of the Fengcheng Formation, and $\delta^{34}S_{bulk}$ values (approximately equivalent to $\delta^{34}S_{pyrite}$) increase gradually (Fig. 2A; Fig. S3). The TS/TOC ratios exhibit a strong negative correlation with $\delta^{34}S_{bulk}$ values (Fig. S3), which is consistent with a Rayleigh fractionation model for S isotopes during sulfate reduction in a closed system (Canfield, 2019). From F_1 to F_3, the sulfate in the ancient alkaline lake was gradually reduced to H_2S by sulfate-reducing bacteria, and pyrite was formed and preserved under anoxic conditions, which resulted in a gradual decrease in the [SO_4^{2-}] in the water mass. $\delta^{34}S_{bulk}$ variations in samples of F_1 and F_2 (the second Member) are relatively small, whereas $\delta^{34}S_{bulk}$ values of F_3 vary widely (Fig. 2), which further supports a diminishing sulfate reservoir of F_3 (Fike et al., 2015). Abundant Na carbonate minerals such as nahcolite have been identified in the Fengcheng Formation, whereas sulfate minerals are rare or absent, independently constraining the high pH of the lake in which it was deposited (Wang et al., 2020).

The co-evolution of the CH_4 and S cycles during deposition of the Fengcheng Formation is now further considered based on 3β-MeHI values and TS/TOC ratios. There is an obvious correlation between these two proxies up-section. It appears that F_1 and F_2 in the CSR had relatively higher sulfate concentrations and had a moderately intense CH_4 cycle, while F_3 had lower sulfate concentrations, possibly because conditions became more stagnant and sulfate was fully consumed by microbial sulfate reduction. There is a strong negative correlation between 3β-MeHI values and TS/TOC ratios (Fig. 2B; $r = -0.61$), suggesting that the alkaline lacustrine environment with a low sulfate concentration likely promoted microbial methanogenesis and methanotrophy.

In the Lucaogou Formation in the southeastern Junggar Basin, TS/TOC ratios are 0.005–0.05 (Xia et al., 2022), which are much lower than those of the Fengcheng Formation (TS/TOC = 0.05–5.9; mean = 1.1 ± 1.2; Table S1). This indicates that the sulfate concentrations of the Lucaogou lake water were even lower (Berner and Raiswell, 1984). Methanogenic archaea would thus have been more competitive than sulfate-reducing bacteria, which would explain the stronger CH_4 cycling in this setting.

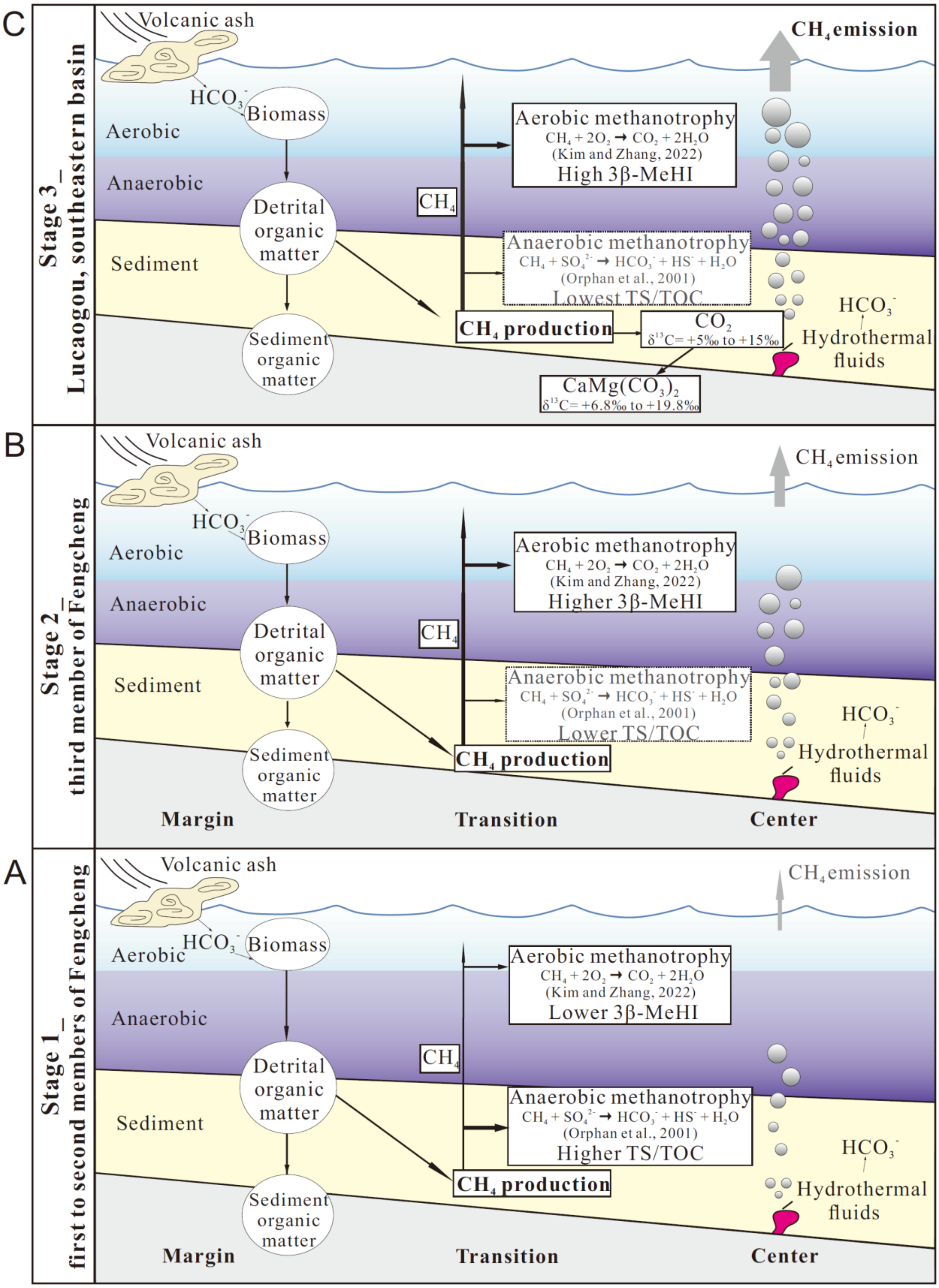

Fig. 3. Model of microbial CH_4 cycling in alkaline lakes during the LPIA. During deposition of (A) the first and second Members (F_1 and F_2) of Fengcheng Formation in the northwestern Junggar Basin; (B) the

third Member of Fengcheng Formation (F_3); (C) the Lucaogou Formation in the southeastern Junggar Basin. 3β-MeHI—3β-methylhopane index; TS/TOC—total S versus total organic C ratio.

High concentrations of DIC in alkaline lakes may promote microbial methane cycling: In addition to sulfate, high alkalinity can also stimulate methanogenesis. High concentrations of DIC may promote microbial methanogenesis directly or indirectly (Liu and Whitman, 2008). In this study, $\Delta\delta^{13}C$ values ($\delta^{13}C_{carb} - \delta^{13}C_{Pr\text{-}Ph}$, where $\delta^{13}C_{Pr\text{-}Ph}$ is the average carbon isotopes of pristane and phytane) were used to assess the [DIC] in the alkaline lake waters and its possible effects on microbial CH_4 production (see the supplement for details; Naafs et al., 2016). The $\Delta\delta^{13}C$ values of the Fengcheng Formation are 28‰–38‰, i.e., much higher than the $\Delta\delta^{13}C$ ($\delta^{13}C_{carb}$ - $\delta^{13}C_{Phytol}$, about 19–23‰) values of modern marine sediments deposited with atmospheric pCO_2 is similar to that of the late Paleozoic (Foster et al., 2017). This is consistent with a high-pH environment, where the [DIC] increases as more CO_2 is converted to HCO_3^- and CO_3^{2-}. Additional HCO_3^- may have been introduced by hydrothermal fluids in this ancient alkaline lake (Cao et al., 2020).

From the lake center to margin, the [DIC] indicated by the $\Delta\delta^{13}C$ values in the CSR and transitional dolomite (TD) areas were significantly higher than those in the marginal tuff–mudstone (MTM) area, which is consistent with the spatial variations of the intensity of CH_4 cycling indicated by the 3β-MeHI values (Fig. 2D). [DIC] during deposition of members F_1 and F_2 of the Fengcheng Formation in the CSR with a moderately intense CH_4 cycle was relatively low, whereas [DIC] during deposition of F_3 with stronger CH_4 cycling was significantly higher (Fig. 2A). There is a strong positive correlation between 3β-MeHI and $\Delta\delta^{13}C$ values in the Fengcheng Formation (Fig. 2C; r = +0.54). As such, the high [DIC] in the alkaline lake may have directly promoted microbial methanogenesis through the pathway of CO_2 reduction (Liu and Whitman, 2008), or indirectly by providing a nearly limitless C source to the primary producers, which facilitated the burial of organic C (Grant, 2006).

In comparison, the [DIC] of the lake waters during deposition of the Lucaogou Formation may have been higher than during deposition of the Fengcheng Formation, given that its $\delta^{13}C_{Ph}$ (–30.7‰ to –32.3‰) is similar to that of the Fengcheng Formation, and its $\delta^{13}C_{carb}$ is significantly higher (Sun et al., 2022). $\Delta\delta^{13}C$ values of the Lucaogou Formation are slightly higher, which corresponds to higher [DIC] and stronger microbial CH_4 cycling in the Fengcheng case.

Summary: The deep hydrothermal and volcanic activity during deposition of members F_1 and F_2 in the Fengcheng Formation provided abundant DIC (Cao et al., 2020; Xia et al., 2020), which likely promoted the activity of methanogenic archaea (Fig. 3A). However, there was still some dissolved sulfate during deposition of F_1 and F_2, as evidenced by the moderate TS/TOC ratios (1.6 ± 0.6 and 1.0 ± 0.5, respectively) and relatively negative $\delta^{34}S_{bulk}$ values (–19.3‰ ± 4.6‰ and –9.1‰ ± 1.7‰, respectively). This allowed sulfate-reducing bacteria to compete with anaerobic methanogenic archaea, thus limiting the amount of CH_4 and the activity of microaerophilic methanotrophs near the chemocline (Fig. 3A). During deposition of F_3, the [DIC] in the lake water increased further, [SO_4^{2-}] decreased gradually due to sulfate reduction and pyrite formation (low TS/TOC ratios of 0.2 ± 0.1), and $\delta^{34}S_{bulk}$ values became more positive (+20‰) due to Rayleigh fractionation acting on a shrinking sulfate reservoir. This intensified the activity of methanogenic archaea and increased the amount of CH_4 emitted from the lake surface (Fig. 3B). In the early-stage alkaline lake that is represented by the Lucaogou Formation, [SO_4^{2-}] was lower (TS/TOC = 0.02 ± 0.02) and [DIC] were higher than those in the Fengcheng Formation. As a result, microbial CH_4

production was very strong, and a large amount of biogenic CH_4 may have been emitted from the lake surface (Fig. 3C).

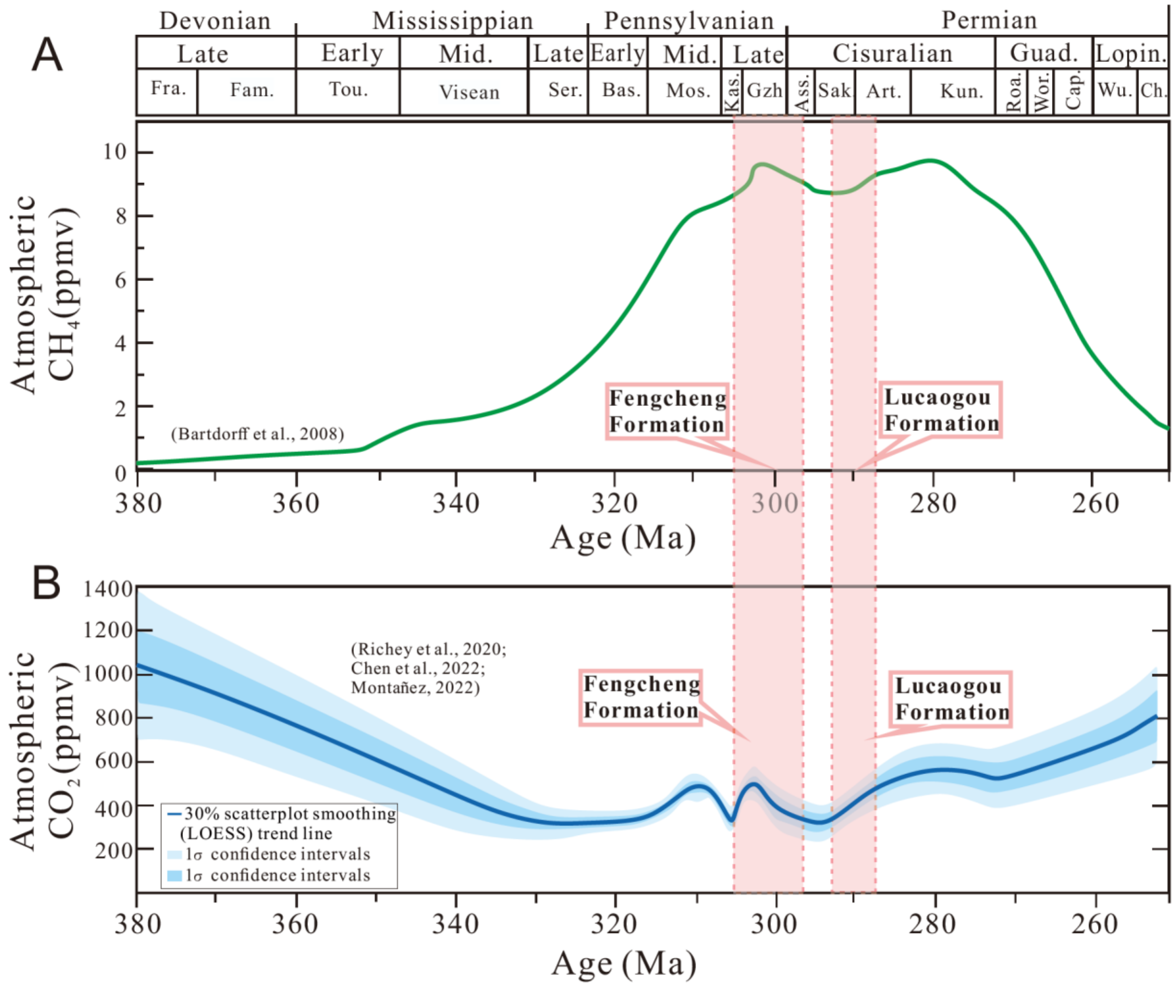

Fig. 4. Global pCH4 values (Bartdorff et al., 2008), and pCO2 values (Richey et al., 2020; Chen et al., 2022; Montañez, 2022) from 380–250 Ma. (A) Reconstruction of pCH_4. (B) Reconstruction of pCO_2.

Response of the microbial methane cycle in alkaline lakes to the LPIA

The temporal coincidence between strong CH_4 production in these alkaline lakes and strong rapid warming during the LPIA indicates that there may be a relationship between the two events (Fig. 4). According to Richey et al. (2020) and Montañez (2022), there may have been a rapid warming stage in the LPIA at *ca*. 304 Ma, and the Fengcheng Formation (305–296 Ma) includes this warming stage, which also corresponds to the highest atmospheric pCH_4 in the Phanerozoic (Fig. 4; Bartdorff et al., 2008). Compared with the Fengcheng Formation, the early alkaline lake in which the Lucaogou Formation was deposited from 292–288 Ma had higher microbial CH_4 production, which corresponds to the end of the LPIA (Fig. 4).

We performed a simple calculation of how much microbial CH_4 was emitted to the atmosphere, based on the formula $E_{CH4}=M_{OC} \times f_{MG} \times 1/2 \times (1-f_{MO})$, where E_{CH4}= mass of CH_4 emitted, M_{OC}= mass of organic carbon burial, f_{MG}= fraction of organic carbon degraded via methanogenesis, f_{MO}= fraction of methane oxidized (see the supplement for details). Our results suggest that the microbial CH_4 emission only from the Fengcheng Formation is considerable, as high as ~0.2–2.1 Gt. Expanding the Fengcheng Formation in the Mahu Sag to the total late Paleozoic lake of northwest China (~270,000 km^2; Carroll and Wartes, 2003), we estimate that ~10–109 Gt of CH_4 were emitted, equivalent to the greenhouse effect caused by ~690–7521 Gt of CO_2. Note that the estimation should be lower if they were several smaller lakes rather than one extensive lake. Considering the globally widespread swamplands, with water condition of low sulfate concentration and high content of organic matter like alkaline lakes, developed during the LPIA, the microbial CH_4 emission was an important factor that affected long-term global warming, although the CO_2 concentration could still have been the main factor of the LPIA evolution (Richey et al., 2020; Montañez, 2022).

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Author contributions:

Conceptualization: JC, ES, WH; Methodology: LX, JC, ES, XW, SY, DZ, YT, BX, WH; Investigation: LX, ES, JC; Visualization: LX, ES, JC; Writing—original draft: LX, JC; Writing—review & editing: LX, ES, JC.

Competing interests:

Authors declare that they have no competing interests.

Data availability:

All data are available in the main text or the Supplements.

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