Anaerobic oxidation of methane by Mn oxides in sulfate-poor environments

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ABSTRACT

Strongly 13C-depleted authigenic carbonates (e.g., δ13CVPDB < −30‰; VPDB—Vienna PeeDee belemnite) in nature are generally believed to form by sulfate-dependent anaerobic oxidation of methane (AOM). However, we demonstrate using geochemical data and thermodynamic calculation that such calcites are most likely derived from biogenic oxidation of methane in sulfate-poor, nonmarine environments during early diagenesis, as observed in the Triassic sandy conglomerates from the Junggar Basin, northwestern China. This process operated through preferential oxidation of 13C-depleted methane by Mn oxides in closed conditions, producing calcites with higher Mn contents and δ13C values in association with more 13C-enriched residual methane as a result of kinetic isotope fractionation. Thus, the Mn-rich and 13C-depleted carbonates are proposed as tracers of Mn-dependent AOM, which should have served as an important sink of greenhouse methane in low-sulfate early Earth’s oceans.

INTRODUCTION

Methane is a greenhouse gas that is closely related to the global carbon cycle and climate change (Etiöpe et al., 2008). The sulfate ion is commonly thought to be the dominant electron acceptor, with >90% of total CH4 production from modern marine sediments consumed through a biogeochemical process involving consortia of methanotrophic archaea and sulfate-reducing bacteria at the sulfate-methane transition zones (Boetius et al., 2000; Egger et al., 2016). Thus, 13C-depleted authigenic carbonate is commonly interpreted to result from SO42−-dependent anaerobic oxidation of methane (AOM; Drake et al., 2015). Such a process might not have been efficient in removing methane during the Precambrian, owing to low seawater sulfate concentration (Bristow and Grotzinger, 2013; Fakhraee et al., 2019). Nevertheless, various additional electron acceptors such as Fe and Mn oxides may have been involved in AOM, as reported from modern sediments and experimental simulations (Beal et al., 2009; Egger et al., 2016; Ettwig et al., 2016):

\[ \text{CH}_4 + 4\text{Mn}_2\text{O}_3 + 15\text{H}^+ \rightarrow \text{HCO}_3^- + 8\text{Mn}^{2+} + 9\text{H}_2\text{O}, \] (1)

\[ \text{CH}_4 + 4\text{MnO}_2 + 7\text{H}^+ \rightarrow \text{HCO}_3^- + 4\text{Mn}^{2+} + 5\text{H}_2\text{O}. \] (2)

Mn- and Fe-dependent AOM has been suggested to have the oxidative potential to oxidize a large amount of biogenic methane produced in the Proterozoic oceans (e.g., Beal et al., 2009). Yet, 13C- and Mn-rich carbonates in the rock records (e.g., Neoproterozoic and Mesoarchean Mn-rich rocks) were widely described to be a result of the organoclastic Mn-oxide reduction (Liu et al., 2006; Ossa Ossa et al., 2018) or of meteoric water diagenesis in nonmarine sandstones as seen in both the San Joaquin (California, USA) and Junggar (northwestern China) Basins (Hayes and Boles, 1993; Jin et al., 2008). Only one exception from the Jurassic Franciscan Complex, California Coast Ranges, was reported to directly relate to Mn-dependent AOM (Hein and Koski, 1987).

More recently, high-Mn calcites with δ13CVPDB (VPDB—relative to Vienna PeeDee belemnite) as low as −70‰ in the Mauh Sag (northwestern Junggar Basin in northwestern China), have been viewed to originate from thermochemical Mn reduction (TMnR) by thermogenetic methane at temperatures >95°C (Hu et al., 2018). The high temperatures were estimated with the assumption that the low-δ18O calcites were precipitated from evolved fresh water with δ18OVSMOW (VSMOW—relative to Vienna standard mean ocean water) of −4‰ to −6‰. Such low-δ18O calcites have been, however, reported from low-temperature carbonates worldwide, e.g., Ediacaran cap dolostones (Zhao and Zheng, 2015), challenging the link between low δ18O value in calcite and high-temperature conditions. A new technique of multiply substituted isotopologues in carbonates, or “clumped isotopes”, can be used as an independent tool to estimate paleotemperatures and reconstruct initial fluid δ18O values (Ghosh et al., 2006; Staudigel and Swart, 2019). However, anomalously low clumped isotope values (Δc) have been reported from modern seep authigenic carbonates, formed by AOM coupled with sulfate reduction, corresponding to temperatures as much as 50°C warmer than ambient temperatures (Loyd et al., 2016). Thus, in such cases, the maximum temperatures can be constrained using clumped isotopes.
We use clumped isotopic data, in situ $\delta^{13}C$ and $\delta^{18}O$ values, and Mn contents of calcites to investigate possible roles of Mn(III/IV) (oxidation states of Mn) in the formation of high-Mn calcites, and, potentially, in the removal of biogenic methane from early Earth’s oceans with low sulfate concentrations, where sulfate-dependent AOM may not have been efficient.

**GEOLOGICAL SETTING**

The Mahu Sag is located in the northwestern Junggar Basin, and petroleum is produced from the Lower Triassic Baikouquan Formation (unit T₁b, Fig. 1A). The Baikouquan Formation consists of alluvial fan-delta facies interlayered with massive, brown, silty mudstones and sandy to pebble conglomerates. The weathering of source mafic-ultramafic igneous rocks provided abundant high-valence Fe-Mn oxides to the basin, which were then deposited in the Baikouquan Formation.

![Geological map and cross section](http://pubs.geoscienceworld.org/gsa/geology/article-pdf/49/7/761/5337366/g48553.1.pdf)

Figure 1. (A) Geological map showing locations of the Mahu Sag and sampling wells, with inset showing the Junggar Basin in China. (B) Cross section AB showing petroleum migration to the Baikouquan Formation (unit T₁b) from unit Pₓf and Pₓw source rocks (Chen et al., 2016).
Formation (Hu et al., 2018). The Baikouquan Formation was buried to depths of 2500–5000 m and experienced compaction, two generations of calcite cementation, and dissolution of early calcite and feldspar (Zhang et al., 2018). Oil and the associated gas were charged from the Lower Permian unit P1f mudstones within the Baikouquan Formation during two periods: the Early Jurassic and Early Cretaceous (Fig. 1B; Cao et al., 2015; Qi et al., 2015).

**METHODS**

We examined thin sections of sandy conglomerates using transmitted-light and cathodoluminescence microscopes, a scanning electron microscope equipped with an energy-dispersive X-ray spectrometer, and an electron microprobe analyzer. Mineral identification and abundances were determined by powder X-ray diffraction. Iron oxides were identified by visible diffuse reflectance spectrum. Bulk-rock C-O isotopes and clumped isotopes were analyzed with a Thermo Finnigan MAT 253 mass spectrometer. We measured in situ carbon isotopes using a SHRIMP SI (sensitive high-resolution ion microprobe–stable isotope) secondary ion mass spectrometer (SIMS) with an error better than ±0.5‰. All δ13C and δ18O values are reported relative to VPDB and VSMOW, respectively. For detailed descriptions of the samples and methods, see the Supplemental Material1.

**RESULTS**

Petrolological observations indicate that the main diagenetic events include (1) compaction; (2) cementation of kaolinite, zeolite, and early calcite; followed by (3) dissolution of feldspar, volcanic detritus, zeolite, and early calcite; and finally (4) late calcite and quartz cementation (Fig. S1 in the Supplemental Material). The early calcites are 0%–15% in content and show poikilotopic features characteristic of less compaction due to shallow burial (Fig. 2A), and contain dissolution pores due to subsequent fluid influx. These calcites have MnO contents of 0.8 ± 0.01 wt% to 9.2 ± 0.01 wt% (1σ) with an average of 3.29 ± 2.72 wt% and a mean FeO/MnO ratio of 0.05 ± 0.03 (n = 40), and may have precipitated at temperatures <65°C as indicated by the clumped isotopes (n = 2; Fig. 3A; Table 1). Except for sample Ma154–3028.63, the remaining early calcites have in situ δ13C values ranging from −29.4%e ± 0.5%e to −58.1%e ± 0.5%e (1σ; n = 40; Table S1), showing a positive correlation with MnO contents (Fig. 3B). By comparison, late calcites, 0%–3% in MnO content, do not show dissolution but contain some oil fluid inclusions (Figs. 2B and 2C) and were precipitated at temperatures <142°C according to the clumped isotope data (n = 3; Table 1). These late calcites, which show higher FeO/MnO ratios compared to the early calcites, with an average of 0.23 ± 0.23 (n = 14), have much higher bulk δ13C, from −8.4%e ± 0.1%e to −6.0%e ± 0.1%e (1σ). Interestingly, iron oxides occur in both sandy conglomerate and interlayered mudstone, associated with detrital clay minerals (Figs. 2D and 2E), and have MnO/FeO ratios from 0.03 to 0.11 with an average of 0.04 ± 0.03 (n = 9; Table S2).

**DISCUSSION**

The presence of abundant iron oxides in the mudstones and conglomerates (Figs. 2D, 2E, and 2F) indicates an oxic lacustrine environment during deposition. Thus, the extremely δ13C-depleted carbonates enriched in Mn but depleted in other redox-sensitive elements are unlikely to have precipitated during the deposition (Wittkop et al., 2020). In contrast, such carbonates are generally viewed to form by AOM directly or indirectly coupled with Mn reduction of Fe oxide–hosted Mn oxides (Beal et al., 2009; Krylov et al., 2018). Indirectly, sulfate-dependent anaerobic oxidation of methane is coupled to oxidation of sulfide using Mn oxides, which can be active even at low sulfate concentrations and through cryptic sulfur cycling (Michaelis et al., 2002; Krylov et al., 2018). Specifically, sulfide produced through sulfate reduction can first react with Mn oxide to produce elemental sulfur:

\[
\text{MnO}_2(s) + \text{HS}^- + 3\text{H}^+ \rightarrow \text{Mn}^{2+} + S_2(s) + 2\text{H}_2\text{O}. \tag{3}
\]

where (s) is solid, and subscript “0” is zero valence.

The produced elemental sulfur can be further oxidized to sulfate, which then fuels the sulfate-driven AOM. By conducting a simple thermodynamic calculation, we assessed the viability of this pathway in oxidizing methane versus the direct methane oxidation using Mn oxides (Ettwig et al., 2016). Using Gibbs free energy values for Mn oxides, sulfide, Mn(II), and water, and considering a range of values for concentration of different compounds in the anoxic ancient oceans, our results indicate a higher favorability of the direct Mn oxidation in comparison with the indirect pathway using sulfide and elemental sulfur (Fig. S2; Table S3). More precisely, our estimation indicates that even at tens of micromolar of sulfide concentration, the energy available through direct oxidation of methane using Mn oxide is approximately three times higher than that provided by the indirect pathway (Fig. S2). While the sulfur-involved indirect pathway is thermodynamically less favorable, the kinetics of such a pathway might be faster (Beal et al., 2009).

For instance, previous experimental results indicate that despite the high energy available through direct Mn-driven AOM, the rate of sulfate-driven AOM is noticeably higher (Beal et al., 2009). Such a high rate, however, may have been substantially hampered at low sulfate concentrations, suggesting a less important role of the indirect pathway for methane oxidation. At the same time, in the studied area, sulfate reduction may have played only a minor role, if any, in the sedimentary sulfur cycle. This can be supported by two lines of evidence: (1) an absence of pyrite, as reported in Zhang et al. (2018) and Hu et al. (2018) as well as from all 15 conglomerate samples of this study, and (2) the fact that the calcites were precipitated earlier than the charge of oils (Fig. S1), and some of the calcites are not associated with oils. Taken together, by comparison with the direct methane oxidation using Mn oxides, the role of indirect oxidation of methane by Mn oxides using sulfur compounds under low sulfate conditions may have been insignificant, though it cannot be ruled out completely.

Our results further suggest that the iron-dependent oxidation of methane would have not been important in methane oxidation. More specifically, the calcites contain low FeO but high MnO contents, and thus were most likely generated from direct reduction of Mn(II/III) by methane, with only a minor contribution from Fe(III).

**Biogenic Oxidation of Methane by Mn Oxides**

It is crucial to determine whether biogenic oxidation of methane by Mn oxides occurred at low temperatures by microorganisms (Hein and Koski, 1987) or was thermochemical at slightly higher temperatures (Hu et al., 2018). Here, we present several lines of evidence for the occurrence of biogenic methane and its oxidation by Mn oxides at low temperatures to generate extremely 13C-depleted and Mn-rich calcites with high clumped isotope values (Δθ).

Triassic gas from the Mahu Sag has δ13C(C1,—methane) values from −39.3‰ to −46.9‰ (Cao et al., 2015). On the 1/n–δ13C diagram (n is carbon number of a gas molecule) of Chung et al. (1988), all the current δ13C values are significantly lower than for the co-generative, unaltered gas of the model for the Baikouquan Formation gas (Fig. S3). This implies that thermogenic gas must have mixed with biogenic methane (δ13C, <−50‰; Whiticar, 1999), and the biogenic methane was likely generated at <80°C during early Late Triassic (Fig. 1B; Fig. S1). Oxidation of such biogenic methane by Mn oxides is most likely to follow Equation 1 or 2 to generate CO2, resulting in a decrease in dryness coefficient (C1/C1,3) with increasing CO2/(C1,3+ CO2) or CH4 oxidation extents (Fig. 3C). This may have occurred in

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1Supplemental Material. Geological setting, analytical methods, and results in detail. Please visit https://doi.org/10.1130/GEOL.S.14079974 to access the supplemental material, and contact editing@geosociety.org with any questions.
a closed environment with limited amounts of methane supply from all pools. This hypothesis is in line with the extremely $\delta^{13}C$-depleted calcites with bulk $\delta^{13}C$ values as low as $-70\%e$ (Hu et al., 2018) and SIMS values as low as $-58\%e$ in this study (Fig. 3B; Table S1). The calcite $\delta^{13}C$ values are largely controlled by initial methane $\delta^{13}C_\text{m}$, carbon isotope fractionation, the oxidized methane–to–residual methane ratio, and the mixing proportion with inorganic $\text{CO}_2$ or $\text{HCO}_3^-$ (Machel et al., 1995; Whiticar, 1999). The extremely $\delta^{13}C$-depleted calcites ($<-58\%e$) are expected to have resulted from the oxidation of $\delta^{13}C$-enriched biogenic methane without significant contributions of inorganic $\text{CO}_2$ or $\text{HCO}_3^-$. With increasing CH$_4$ oxidation degree as reflected in the CO$_2/(\text{C}_1–5 + \text{CO}_2)$ ratio or MnO content, residual methane and thus newly generated calcite show progressively positive shifts in their $\delta^{13}C$ values (Figs. 3B and 3D).

The sample Ma15 calcite is the product of CH$_4$ oxidation to the highest degree, as indicated by the highest average MnO content (7 wt%; Table S1), and shows the highest bulk $\delta^{13}C$ value of $-31\%e$ (Table 1). This suggests that the calcite may have carbon derived either from complete oxidation of residual methane,
Table 1. Carbon and Oxygen and Clumped Isotopic Data of Baikouquan Formation (Unit T, b), Northwestern China, Calcite Cements

| Well  | Depth (m) | δ13C (‰ VPDB) | δ18O (‰ VSMOW) | δ13C (‰ VSMOW) | δ18O (‰ VSMOW) | Stdv | Δ13C CDES | Δ18O CDES | Temperature (°C) | Fluid δ13C (‰ VSMOW) | Origin |
|-------|-----------|---------------|----------------|----------------|----------------|------|-------------|-------------|------------------|---------------------|--------|
| Ma15  | 3069.99   | -30.55        | 0.79           | 5.86           | -24.3          | 0.26 | 0.611       | 0.014       | 0.008            | 59.13               | -16.1  |
| Ma154 | 3028.63   | -4.74         | 0.19           | 7.76           | -22.5          | 0.05 | 0.586       | 0.015       | 0.009            | 63.5                | -12.8  |
| Ma154 | 3031.05   | -6.58         | 0.02           | 8.12           | -22.1          | 0.10 | 0.500       | 0.025       | 0.014            | 115.54              | -5.9   |
| Ma154 | 3031.54   | -5.99         | 0.09           | 6.79           | -23.4          | 0.01 | 0.534       | 0.03        | 0.017            | 93.21               | -10.1  |
| Ma14  | 4105.4    | -8.37         | 0.02           | 12.94          | -17.4          | 0.02 | 0.484       | 0.037       | 0.022            | 141.65              | 1.83   |
| AH1   | 3863.4    | -35.5         | 0.10           | 13.61          | -16.8          | 0.15 | Biogenic    |             |                  |                     |
| AH2   | 3863.47   | -45.87        | 0.10           | 11.75          | -18.7          | 0.15 | Biogenic    |             |                  |                     |
| Ma6   | 3863.57   | -46.48        | 0.10           | 12.05          | -18.9          | 0.15 | Biogenic    |             |                  |                     |
| Ma6   | 3875.40   | -47.23        | 0.10           | 10.61          | -19.7          | 0.15 | Biogenic    |             |                  |                     |

Note: VPDB—Vienna PeeDee belemnite; VSMOW—Vienna Standard Mean Ocean Water; SD—standard deviation of the measurements; CDES—Carbon Dioxide Equilibrated Scale; SE—standard error of the Δ13C measurements; TMnR—Thermochemical manganese reduction.

CONCLUSION

In summary, we present a case showing direct oxidation of biogenic methane by Mn oxides in a sulfate-poor freshwater lacustrine environment during early diagenesis at <65 °C prior to oil and thermogenetic gas charge, producing Mn-rich and 13C-depleted calcites. Such an origin of carbonates may have occurred in Mesoarchean carbonates (Ossa et al., 2018). Much more Mn-dependent AOM in Earth’s history may have served as a significant sink of methane but has not yet been identified.
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