Thermochemical oxidation of methane induced by high-valence metal oxides in a sedimentary basin

Wen-Xuan Hu¹, Xun Kang¹, Jian Cao¹, Xiao-Lin Wang¹, Bin Fu² & Hai-Guang Wu¹

Thermochemical oxidation of methane (TOM) by high-valence metal oxides in geological systems and its potential role as a methane sink remain poorly understood. Here we present evidence of TOM induced by high-valence metal oxides in the Junggar Basin, located in northwestern China. During diagenesis, methane from deeper source strata is abiotically oxidized by high-valence Mn(Fe) oxides at 90 to 135 °C, releasing 13C-depleted CO₂, soluble Mn²⁺ and Fe²⁺. Mn generally plays the dominant role compared to Fe, due to its lower Gibbs free energy increment during oxidation. Both CO₂ and metal ions are then incorporated into authigenic calcites, which are characterized by extremely negative δ¹³C values (−70 to −22.5‰) and high Mn content (average MnO = 5 wt.%). We estimate that as much as 1224 Tg of methane could be oxidized in the study area. TOM is unfavorable for gas accumulation but may act as a major methane sink in the deep crustal carbon cycle.
Methane (\(\text{CH}_4\)) is an economically important fossil fuel, and by 2014 about \(4.3 \times 10^{14} \text{ m}^3\) or \(4.7 \times 10^8 \text{Tg}\) of proven natural gas reserves, including shale gas, had been identified in sedimentary basins worldwide\(^{1,2}\). However, methane is also a significant greenhouse gas, second only to \(\text{CO}_2\), in the contribution to the current global greenhouse effect\(^{3,4}\); during certain intervals of the geologic past, such as the Archean, it was perhaps the most significant greenhouse gas in the atmosphere\(^{5,6}\). Since the late Holocene pre-industrial era, the concentration of atmospheric methane had increased sharply from an average of 680 p.p.b.v. (parts per billion volume) during AD 800–1600 to 1799 p.p.b.v. by the year 2010\(^{4,7}\). Furthermore, the current emission flux of methane from sedimentary basins to the atmosphere is estimated to be 10 to 25 Tg yr\(^{-1}\), which is a key to understanding the global carbon cycle and climate change\(^{8,9}\).

Oxidation reactions are the key mechanism by which methane is consumed before emission into the atmosphere. Methane can theoretically be oxidized via two distinct geological processes. The first is anaerobic oxidation of methane (AOM), where methane oxidation is mediated by sulfate- or metal-reducing bacteria in an anoxic environment, typically resulting in the precipitation of authigenic carbonate\(^{10–12}\). The second is thermochemical oxidation of methane (TOM) at high temperatures by sulfate or high-valence metal oxides. Like the bacterially-mediated AOM reaction, this process typically results in the formation of authigenic carbonate\(^{13–16}\).

Natural gas reservoirs in sedimentary basins are typically buried to depths of several kilometers, and experience temperatures from 60 to 150 °C\(^{17}\), while the metabolism of the archaeal groups responsible for AOM are mainly active at temperatures below 80 °C\(^{18,19}\), limiting the depth at which archaea dominate the conversion of \(\text{CH}_4\) to \(\text{CO}_2\). Therefore, TOM is potentially the predominant methane oxidation process in the strata with high formation temperature (especially >80 °C) \(^{13–15,20}\).

Thermochemical sulfate reduction (TSR) consuming methane has been observed to occur in geological systems\(^{13–15,20}\). Its reaction conditions, as well as geological and geochemical responses, have been deeply explored\(^{13–15,20,21}\). In contrast, almost no geological evidence has been reported for the oxidation of methane with high-valence metal oxides, except for the oxidation of methane by Fe\(^{3+}\) in detrital biotite at temperatures above 270 °C during metamorphism\(^{16,22,23}\). To date, the process has only been simulated in the laboratory setting at high temperatures (350 to 650 °C) \(^{24–27}\). Thus, both the extent of TOM by high-valence metal oxides in geological systems and its role in the methane sink remain poorly understood.

The Junggar Basin is a major petroliferous basin in northwestern China, with an area of approximately \(1.3 \times 10^5 \text{ km}^2\) \(^{28}\). The Lower Triassic Baikouquan Formation (T\(_1\)b) is located on the western slope of the Mahu Sag, a structure forming part of the northwestern margin of the Junggar Basin (Fig. 1a). The Mahu Sag is the richest hydrocarbon reservoir in the Junggar Basin, with approximately two billion tons of proven crude oil reserves\(^{29}\). Continuous oil and gas reservoirs were recently discovered in the Baikouquan Formation (Fig. 1a), with the hydrocarbons believed to be derived largely from the dark, organic-rich mudstones of the underlying Lower Permian Fengcheng Formation (see Supplementary Note 1 and Supplementary Fig. 1 for detailed descriptions)\(^{28,30}\).

The Baikouquan Formation can be divided into three members, referred to as T\(_1\)b\(_1\), T\(_1\)b\(_2\), and T\(_1\)b\(_3\) in ascending stratigraphic order. The maximum burial depth of the unit from west to east across the Mahu Sag increases from 2850 m to 4300 m. The formation consists of interlayered mudstone and sandy conglomerate, deposited in a succession of alluvial fan-deltaic systems with abundant gravity flow deposits\(^{31,32}\). The brown or greyish-green conglomeratic layers contain pebble conglomerates, sandy gravel conglomerates, and sandstones, whereas the mudstone layers are dominated by massive brown silty mudstones with minor gray laminations (Fig. 1b). The abundance of brown mudstone increases up-section in three members, which is interpreted to reflect an arid-semiarid climate regime and oxic lacustrine environment during deposition\(^{33,35}\).

The T\(_1\)b\(_2\) sediments are derived from two provenances, i.e., the basement, comprising granite and mafic-ultramafic igneous rocks, and the sedimentary strata from the Carboniferous to the Permian\(^{36,37}\). The weathering of mafic-ultramafic rocks and tuffaceous components in sedimentary rocks forms abundant high-valence Fe-Mn oxides during T\(_1\)b deposition interval (see Supplementary Note 2 for provenance analysis)\(^{34}\).

In this study, we report the first geological evidence for extensive TOM induced by high-valence metal oxides in the Lower Triassic reservoir strata of the Junggar Basin. We find that methane was abiotically oxidized by high-valence Mn(Fe) oxides at high temperatures (90–135 °C) in the deep burial strata, ultimately yielding extremely \(\delta^{13}\text{C}\)-depleted authigenic calcites with high manganiferous contents. In the process thousands of Tg of \(\text{CH}_4\) were consumed, implying TOM may act as a major \(\text{CH}_4\) sink in the deep carbon cycles.

Results

**Distribution and geochemistry of calcite cements.** Authigenic calcite in the sandy conglomerates of the Baikouquan Formation occurs mainly as coarsely crystalline cement (Fig. 2a, b), sometimes within feldspar along cleavage (Fig. 2a). Based on microscopic observations, the total content of calcite cement in the sandy conglomerates ranges from 0 to 6% by area, with an average of ~2.5%. There are two stages of precipitation: the early-stage calcite occurs as xenomorphic crystals filling dissolved pores or poorly-connected interparticle pores (Fig. 2a), whereas the late-stage cements appear as coarse crystals, with well-developed crystal planes in the central portions of large interparticle pores (Fig. 2a, b).

Electron probe micro-analysis (EPMA) reveals that these authigenic calcites are enriched in manganese, with MnO content ranging from 0.79 to 14.67 wt.% (average = 5.05 wt.%; Fig. 3a). In detail, the MnO content of early-stage calcite cements is generally lower than 4.00 wt.%, while late-stage cements typically have MnO content greater than 5.00 wt.%, some up to 11.00–15.00 wt.% (Fig. 3a). In contrast, the FeO content of the calcite cements is very low, ranging from <0.01 to 0.79 wt.%, with an average of 0.12 wt.% (Fig. 3b).

Authigenic calcite cements in the T\(_1\)b reservoir rocks are very negative in \(\delta^{13}\text{C}\). Whole-rock carbonate \(\delta^{13}\text{C}\) values range from −69.8 to −22.5‰, though most samples fall within the −50.0 to −36.0‰ range (Fig. 4a). The calcite cements have \(\delta^{18}\text{O}\) values ranging from −22.6 to −12.8‰ (Fig. 4b).

In situ carbon isotope analyses reveal that the two generations of calcite cements have markedly different \(\delta^{13}\text{C}\) values, sometimes by 10‰ (Fig. 2c, d). In contrast, the difference in \(\delta^{18}\text{O}\) between the two generations of cement is relatively small, with a maximum offset of 1.9‰ (Supplementary Table 1). To better constrain the sources of the carbon and oxygen incorporated into calcite cements in the T\(_1\)b reservoir, we also measured the isotopic composition of calcite in the underlying reservoir rocks: −22.4 to −13.5‰ for \(\delta^{13}\text{C}\); and −18.5 to −12.8‰ for \(\delta^{18}\text{O}\).

**Geochemistry of hydrocarbons.** In most natural gas samples more than 95 mol. % hydrocarbons are light components, i.e., \(\text{C}_1–\text{C}_7\). \(\text{CH}_4\) is the most abundant hydrocarbon gas, with an aridity coefficient of 0.77–0.95. The non-hydrocarbon component...
consists mainly of N2, with minor CO2 and no detectable H2S. The extremely negative δ13C values in methane, ethane, propane, and butane are −39.3 to −46.8‰, −27.5 to −31.9‰, −27.2 to −30.2‰, and −26.0 to −28.8‰, respectively (Supplementary Table 2).

Gas chromatography of crude oil samples from T1b reveals a complete sequence of n-alkanes (Fig. 5), especially ~C8–C12, which are preferentially removed in the earliest stages of biodegradation19. This indicates that the hydrocarbons have not experienced microbial degradation. The absence of 25-norhopanes and other representative values of key parameters also show no evidence for biodegradation (Supplementary Table 3). Biomarker analyses are described in details in the Methods section.

**Discussion**

The extremely negative δ13C values of authigenic calcite can be interpreted to be derived from organic matter35,36. In organic matter-enriched geologic systems, both oxidation of organic matter and thermal decarboxylation of organic acids can generate significantly δ13C-depleted CO2, which may then be incorporated into authigenic calcite11,13,27,35. The δ13C value of authigenic calcite formed via the oxidation of hydrocarbons can be as low as −125‰11–13,36, whereas calcite precipitated from the decarboxylation of organic acids concentrates from −3 to −25‰, rarely yielding values below −25‰35,37. Authigenic calcite in the study area shows δ13C values falling mainly into the range of −50.0 to −36.0‰, with a minimum value of −69.8‰, consistent with the oxidation model for gaseous hydrocarbons11,12,36.

During the oxidation of gaseous hydrocarbons, 12C is preferentially oxidized to CO2, leaving the remaining hydrocarbon pool to become increasingly enriched in 13C as the reaction proceeds24,38,39. Figure 6 shows that the δ13C value of methane in T1b natural gas samples increases from around −45‰ to values above −40‰ as the CO2 contents of the gas increases; however, the isotopic composition of heavier hydrocarbon gases (C2−C4) remains comparatively stable. This result demonstrates that, within the T1b natural gas pool, abundant CH4 was oxidized during diagenesis. The δ13C values of the authigenic calcite in T1b are generally lower than those of the associated methane (−46.8 to 39.3‰; Fig. 7), further supporting our interpretation that the calcite is mainly derived from CO2 generated by methane oxidation11,12,36.

There are two mechanisms for oxidation of methane in sedimentary systems, i.e., AOM and TOM10,11,13–15. AOM has been observed mainly in modern marine sediments, especially near cold seeps on the seafloor, where the δ13C values of the associated authigenic carbonate can be as low as −125‰10,11,36. TOM can occur with or without TSR reactions. Methane is usually not the most active reductant in systems where TSR occurs compared with C2+ gaseous alkanes, so the minimum δ13C value of the associated calcite is not usually lower than −31‰13,15,39,40. TOM reactions induced by high-valence metal oxides instead of sulfate have never been reported in natural systems, though they have been simulated in the laboratory24–27.

All the three processes described above may have contributed to the precipitation of calcites in T1b. The range of measured δ13C values (−69.8 to −22.5‰) is compatible with calcite formed via AOM, but is also lower than the typical value of calcite formed via
methane-dominated TSR ($\delta^{13}$C = $-31\%$)\textsuperscript{13}. While there are no carbon isotope data reported for the carbonate associated with TOM induced by high-valence metal oxides in geological systems, the fractionation factors may be assumed to be similar to those in laboratory-simulated experiments. Thus, we cannot rule out the TOM process based on our isotopic measurements.

Anaerobic oxidation of methane by bacteria or archaea can be ruled out. Firstly, although archaeal groups such as ANME-1 and ANME-2 can anaerobically metabolize methane in the presence of oxidants such as MnO$\textsuperscript{2+}$, SO$_4^{2-}$, and Fe$^{3+}$ at temperatures < 80 °C\textsuperscript{10,18,19,41}, the high formation temperature (> 80 °C) does not favor the metabolism of these archaeal groups\textsuperscript{19}. The T$_1$ b reservoir strata were buried at depths of 2250–3200 m when they were firstly charged with methane in the Early Jurassic\textsuperscript{32}. Taking the geothermal gradient as 28–32 °C km$^{-1}$ and the surface temperature as 20 °C during the Early Jurassic\textsuperscript{42}, this corresponds to a formation temperature of 83–122 °C. The $\delta^{13}$C values of authigenic calcites also indicate precipitation of the cements at relatively high temperatures. A similar diagenetic condition was reported for the Brent Group of the North Sea with a burial depth of 2500–3500 m\textsuperscript{33,44}. The $\delta^{18}$O value of T$_1$ b pore water is likely to have increased by the same value (about 4‰) as the Brent Group from that of the initial meteoric water ($-10$ to $-8\%$) to $-6$ to $-4\%$\textsuperscript{44–46}. Using this $\delta^{18}$O value, we calculated that the temperature was greater than 90 °C during formation of more than 85% of the total calcite, with a background temperature range of 90–135 °C and an average of 109.6 °C (see Supplementary Data 2), consistent with the temperatures estimated from the geothermal gradient.

Secondly, T$_1$ b hydrocarbons show no evidence of biological degradation, indicating that archaea had negligible influence on the composition of oil and gas. The first manifestation of hydrocarbon biodegradation is typically the selective removal of C$_6$–C$_{12}$ normal alkanes\textsuperscript{19}. Light C$_2$–C$_6$ hydrocarbons exhibit a consistent degradation sequence: propane is the first compound to be altered, followed by butane, pentane, and C$_6$–C$_{11}$ hydrocarbons\textsuperscript{47}. The net effect of biodegradation is an overall decrease in wet gas components (C$_2$–C$_6$) and enrichment in methane\textsuperscript{19}. The crude oil hosted in the Baikouquan Formation shows a complete alkane series, with no obvious loss of C$_8$–C$_{12}$ alkanes, and no hump of unresolved complex mixtures (Fig. 5). Natural gas samples contain 5.14–22.68% wet gas (C$_2$–C$_6$) and 0.79–5.23% propane. Because AOM depends on the presence of biological mediators, and there is no evidence for biological modification, we can rule out this process of methane oxidation\textsuperscript{19,47}.

Thermochemical sulfate reduction can also be ruled out. There is very little SO$_4^{2-}$ in T$_1$ b formation waters\textsuperscript{38}, and no H$_2$S has been detected in T$_1$ b natural gas samples (Supplementary Table 2) or the associated crude oil in adjacent formations\textsuperscript{38,29}. Pyrite is also absent in T$_1$ b reservoir strata. The lack of both key
Manganese and iron contents in authigenic calcites. a Histogram of MnO content in early-stage and late-stage calcite cements from T1b sandy conglomerates. b Crossplot of MnO and FeO content in early-stage and late-stage calcite cements from T1b sandy conglomerates. The error bar (±SEM) is smaller than the symbol size. Source data are provided as Supplementary Data 1.

Fig. 4 Carbon and oxygen isotopic compositions in authigenic calcites. a Histogram of δ13C values of calcite cements in T1b reservoirs, and calcite veins in Pijw source rocks. b Crossplot of bulk rock δ13C and δ18O values in T1b calcite cements. The error bar (±SEM) is smaller than the symbol size. Source data can be seen in Supplementary Data 2.

reactants (i.e., sulfate) and characteristic products (sulfide in gaseous or mineral forms) strongly suggests that the TSR reaction did not occur in our study area. Thus, the highly negative δ13C values seen in the authigenic calcites cannot be attributed to methane oxidation by sulfate.

Therefore, we infer that the extremely negative δ13C observed in the study area results from methane oxidation by non-sulfate oxidants at high temperatures. It is shown that methane can serve as an electron acceptor for high-valence Mn and Fe oxides, leading to the formation of CO2 and the precipitation of calcite10. This process can be expressed with the following chemical formulas:

\[
\text{CH}_4 + 4\text{Mn}_2\text{O}_3 + 15\text{H}^+ \rightarrow \text{HCO}_3^- + 8\text{Mn}^{2+} + 9\text{H}_2\text{O} \\
\Delta G = -442 \text{ kJ/mol}
\]

\[
\text{CH}_4 + 4\text{MnO}_2 + 7\text{H}^+ \rightarrow \text{HCO}_3^- + 4\text{Mn}^{2+} + 5\text{H}_2\text{O} \\
\Delta G = -556 \text{ kJ/mol}
\]

\[
\text{CH}_4 + 8\text{Fe(OH)}_3 + 15\text{H}^+ \rightarrow \text{HCO}_3^- + 8\text{Fe}^{2+} + 21\text{H}_2\text{O} \\
\Delta G = -270.3 \text{ kJ/mol}
\]

\[
\text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^- \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O}
\]

The Gibbs free energy increment (ΔG) differs substantially between the first two reactions and the third one under the same conditions, with oxidation by MnO₃ or MnO₂ being approximately twice as energetically favorable as oxidation by Fe(OH)₃,10. In geological systems where high-valence Mn and Fe coexist, CH₄ can be preferentially oxidized by Mn rather than Fe. During the interval of T1b deposition, the northwestern margin of the Junggar Basin experienced an arid or semiarid climate31,33. Mafic-ultramafic rocks were weathered extensively from the provenance during the period of deposition and were ultimately deposited in the organic matter-depleted red layers of T1b (Supplementary Fig. 2). These red beds provided the material basis for subsequent methane oxidation by the high-valence Mn and Fe oxides49. XRF analysis shows that the Mn content of sandy conglomerates in T1b ranges from 0.07 to 0.48 wt.% (as MnO) in bulk rock, with an average of 0.17 wt.%; the Fe content ranges from 2.88 to 12.71 wt.% (as Fe₂O₃), with an average of 6.25 wt.% (Supplementary Table 4). Further XRD, FE-SEM, and EPMA analyses indicate that high-valence Mn(Fe) exists as hematite in the clastic rocks in T1b. Most of the hematite is disseminated in the clay-rich matrix, while minor occurrences as isolated amorphous aggregates are observed. The manganese generally occurs as the isomorphous Mn³⁺/⁴⁺ substitution in the hematite lattice structure50,51 at levels of 0.95–1.47 wt.% in the isolated hematite and 0.61–0.74 wt.% in the disseminated...
hematite in the form of Mn$_2$O$_3$ (see Supplementary Note 3 and Supplementary Fig. 3 for detailed descriptions).

The authigenic calcites in T$_1$b are generally enriched in manganese relative to whole rock samples, with MnO content ranging from 0.79 to 14.67 wt.% (average = 5.05 wt.%). However, the FeO content of the calcite cements is uniformly less than 1 wt.%, averaging at 0.12 wt.%. This reflects the energetic favorability of Mn as an oxidant relative to Fe. Thus, the precipitation of calcite was closely associated with methane oxidation by high-valence manganese.

It should be noted that C$_2$+ gaseous alkanes (especially ethane and propane) are usually preferentially oxidized during TSR reactions, whereas methane is the last to react$^{14,15,21,40}$. The oxidation of abundant methane in T$_1$b rocks has been influenced by several factors. One is the sufficient supply of Mn$^{3+/4+}$, which is present as hematite within brown clastic rocks and guarantees that almost all of the gaseous alkanes, including methane, will be consumed in the bleaching pathways$^{49}$. The other is that since methane is the main component of the T$_1$b natural gas, ultimately it will have dominated the thermochemical oxidation process. Moreover, the T$_1$b clastic strata are low-permeability due to their high clay content and complex grain composition$^{32}$. Consequently, gaseous alkanes mainly migrated by diffusion. Due to its higher initial concentration and higher diffusion coefficient, the quantity of methane reaching the matrix of reservoir rocks or mudstones at a distance from the oil-gas interface is much higher than that of C$_2$+, gaseous alkanes$^{52}$. Ultimately, as shown in Fig. 6, abundant methane was oxidized in the T$_1$b clastic rocks.

Microbial metabolism and high temperature can both serve to facilitate reactions (1) and (2). The former may reduce the energy threshold, while the latter can provide the activation energy necessary for the reaction to occur$^{10,24}$. Since microbial activity in the T$_1$b reservoir strata appears to have been minimal, heating would have been the only way to promote oxidation reactions. Considering the formation temperature (90–122 °C) during infiltration of natural gas and the main precipitation temperature (90–135 °C) of authigenic calcites, we can infer that methane oxidation in the study area mainly took place at 90–135 °C. Laboratory experiments have shown that reactions (1) and (2) do not occur at temperatures below 300 °C and 250 °C, respectively$^{24,27}$. However, during extended geological processes, long intervals of time can compensate for the slow rate of reactions at low temperatures. In the case of thermochemical sulfate reduction, experiments show that the reaction occurs at temperatures greater than 250 °C$^{53}$, though evidence for TSR has been observed in sedimentary basins at temperatures of ~100 °C$^{40}$. As another example, while the standard Rock Eval pyrolysis procedure shows the peak of hydrocarbon generation at 420–480 °C, in natural geological systems the peak of hydrocarbon generation typically occurs at 120–150 °C$^{54}$. This also appears to be the case for TOM.

**Fig. 5** Chromatogram and mass spectrogram of a representative T$_1$b crude oil sample (No. M18-O-1). a In the total ion chromatogram (TIC) Pr and Ph indicate pristane and phytane, respectively. b D represents demethylated hopanes in the m/z 177 mass spectrogram. c TT is tricyclic terpane and H is hopane in the m/z 191 mass spectrogram.
The long duration of geological time can compensate for a low reaction rate at relatively low temperatures. With the increasing burial depth of \( T_{1b} \), the formation temperature generally increased and reached 90 °C in the Middle Jurassic (~170 Ma, see Supplementary Note 4 and Supplementary Fig. 4 for thermal evolution). Since then, methane has been oxidized more efficiently.

Carbon isotope fractionation is expected to occur during thermal oxidation of methane, with the fractionation factor controlled by a number of factors, including the type of oxidant and the temperature\(^{24,27,53} \). In general, the residual methane is enriched in \(^{13}\)C as the reaction proceeds, while the generated CO\(_2\) is depleted, resulting in CO\(_2\) with a lower \( \delta^{13}C \) value than the initial methane pool (\( \delta^{13}C_{\text{CH}_4} \)). Taking the carbon isotope kinetic fractionation factor (\( \alpha \)) to be \( 10^3/(10^3 - \Delta) \) in reactions (1) and (2), where \( \Delta = \delta^{13}C_{\text{CH}_4} - \delta^{13}C_{\text{CO}_2} \), we calculate an \( \alpha \) value of 1.0175–1.0193 for Reaction (2) at 90–135 °C\(^{24} \). This value is close to that reported for the methane-dominated TSR in the East Sichuan Basin of China (1.0166) and the ethane-dominated TSR in the Jurassic Norphlet Formation of Mobile Bay (1.109)\(^{55} \). Then, a \( \Delta \) value of 17–19‰ for a closed system at 90–135 °C can be obtained. Carbon isotope fractionation also occurs during the calcite precipitation. At 90 to 135 °C, the \( \delta^{13}C \) of precipitated CaCO\(_3\) is expected to be 2 to 5‰ lower than that of the original gaseous CO\(_2\)\(^{56} \). Integrating the methane oxidation and calcite precipitation processes, the \( \delta^{13}C \) of authigenic calcite is expected
to be 19 to 24% lower than that of the residual methane. Thus, the expected $\delta^{13}C$ of authigenic calcite is $-70$ to $-59\%_o$. The extremely $^{13}C$-depleted calcites may also precipitate during the oxidation of primary microbial or kerogen-cracking-derived low $\delta^{13}C$ methane, although their relative quantities involved in the reaction remain ambiguous. The former is formed via bacterial methanogenesis at temperatures generally below 50–60 °C in the P1 source rock57, whereas the latter is generated as a concomitant of liquid oil expelled from low-maturity source rock19. In addition, it should be noted that the contributions of oxidation of minor C2⁺ and decarboxylation of organic acids from the source rock cannot be ruled out (Fig. 8). As shown in Fig. 7, the decarboxylation reaction can produce CO₂ with a $\delta^{13}C$ value of around $-25\%_o$. The addition of small amounts of CO₂ from C2⁺ oxidation and decarboxylation yields a range of potential $\delta^{13}C$ values in authigenic calcite from $-70$ to $-22.5\%_o$, consistent with our observations (Fig. 8).

Methane is generally believed to be stable in the crust, especially in sedimentary basins; oxidation is thought to occur mainly after the methane has reached the surface and been exposed to atmospheric oxygen8,9. The potentially important role of TOM as a methane sink in the deep strata of sedimentary basins has largely been neglected so far; methane oxidation in the deep crust has not been documented, and only a few relevant simulation experiments have been conducted to date24,27,53. In this study, we provide the first evidence for the occurrence of TOM in a clastic reservoir, and propose that TOM is an important CH₄ sink in the deep crustal carbon cycle.

In order to evaluate the extent to which TOM serves as a CH₄ sink, we made a series of semi-quantitative estimates based on the Mahu–Aihu2 oil producing area (highlighted in yellow in Fig. 1a), which contains a relatively dense concentration of exploration wells. Details of the calculations are described in the Methods section. Assuming an average authigenic calcite content of 2.5% in the relevant reservoir beds, we calculated a total authigenic calcite mass of 420 Tg. The calcite would require 57 Tg of CH₄ to be oxidized, assuming only 85% of the carbonate carbon is derived from methane oxidation. If only taking account of the total oil-charging area in the sag, a fairly conservative CH₄ consumption is 155 Tg. However, authigenic calcites are not restricted in the conglomerates and sandstones charged by liquid oil, they also occur in the wells far away from the oil-charging area. Extending these calculations to encompass the entire Mahu Sag (~5000 km²), we estimate that as much as 1224 Tg of CH₄ might be oxidized in the reservoir strata. The global submarine CH₄ flux to the atmosphere is only 8 to 65 Tg per year58, suggesting that TOM in sedimentary basins may play a geologically significant role in reducing CH₄ seepage to the surface. In other words, extensive TOM may be an important methane sink in sedimentary basins, while it is unfavorable for the accumulation of recoverable natural gas reserves.

This study reports geological evidence for widespread thermochemical oxidation of methane (TOM) induced by high-valence metal oxides in a natural environment, from the Junggar Basin in northwestern China. Methane was oxidized at high temperatures (90–135 °C) in the T₄ stratum, with high-valence metal oxides acting as the electron acceptor. This reaction resulted in the precipitation of authigenic calcite cements, characterized by extremely negative $\delta^{13}C$ values ($-70$ to $-22.5\%_o$) and high manganese contents (average MnO = 5 wt.%). While both Mn and Fe oxides served as methane oxidants, less Fe oxide was consumed due to the relatively higher Gibbs free energy increment of the reaction. Based on the abundance and distribution of authigenic calcite, we estimate that thousands of Tg of CH₄ were consumed by TOM in the Lower Triassic reservoir strata of the Mahu Sag. We further propose that the geologic importance of TOM has been underestimated to date, and that this critical methane sink should be a focus of future studies of the deep carbon cycle.

**Methods**

**Sampling.** A total of 103 rock samples were collected from T₄ reservoir beds in 11 wells from the western slope area of the Mahu Sag (Supplementary Table 5). In addition to rock samples, 9 crude oil and 12 natural gas samples were collected from the wells (Supplementary Table 6).

**Elemental analyses.** Backscattering electron (BSE) microprobe analyses were conducted on 38 sandy conglomerate samples, using a Japan Electron Optics Laboratory (JEOL) x-ray analyzer (JXA)-8800 electron microprobe operated at 15 kV, with a 10 nA beam current. The calcite cements in 14 sandy conglomerate samples were analyzed for their major element composition, using a 2 µm beam diameter and 10 s counting time. The major element compositions of whole-rock samples were measured on a Thermo Scientific ARL 9900 X-ray fluorescence (XRF) spectrometer. The relative standard deviation of measured major element

---

**Fig. 8** Schematic model of thermochemical methane oxidation in the clastic strata of petroliferous basins. R-COOH represents carboxylic acids. High-valence Mn (Fe) exists in hematite, which is generally found in the matrix of sandstone and conglomerate. Due to the high diffusivity of methane, minor high-valence Mn (Fe) in the brown-red mudstone adjacent to the reservoir rocks may also be reduced.
concentrations is around ±1% for elements with concentrations >1.0 wt% and about ±10% for the elements with concentrations <1.0 wt%, based on repeated measurements of Chinese national standard GBW 07103 (granite) and GBW 07105 (basalt). Both EPMA and XRF analyses were carried out at the State Key Laboratory for Mineral Deposits Research, Nanjing University.

Carbonate isotope analyses of bulk rock samples. The calcite cements in 50 Tj sandy conglomerate (i.e., reservoir rock) samples and 5 P.m mudstone (i.e., source rock) samples were analyzed for stable carbon and oxygen isotopes. Prior to analysis, each sample was broken into small pieces, and 1 g of calcite cement was manually selected under a binocular microscope. All samples were then crushed to a fine powder. Twenty milligrams of each powdered sample was reacted with 100% H3PO4 at 25 °C for more than 12 h, in a Kiel IV autosampler (ThermoFinnigan). The produced CO2 was then introduced into a Finnigan MAT 253 mass spectrometer for isotopic analysis. Carbon and oxygen isotope measurements were corrected using Chinese national standard GBW 04405 (δ13C = 0.57 ± 0.03%o VPDB; δ18O = −8.49 ± 0.13%o VPDB), an Ordovician carbonate from a site near Beijing. All analyses were performed at the Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences. The external precisions (1σ) of oxygen and carbon isotope analyses were ±0.08 and ±0.03‰, respectively.

SIMS δ34Sbulk analyses. Small pieces of polished thin sections of carbonate samples were mounted in Buehler EpoFix epoxy resin, together with carbonate reference materials: NBS-19 calcite, UWC-3 calcite (σλb = 0.28 ± 0.07‰, n = 5; cf. ref. 66) and Hammerfall dolomite (δ34SVPDB = −0.8 ± 0.07‰, n = 3; cf. ref. 60). Such small amount of Mn has less measurable matrix effects on SIMS measurements.

SIMS δ34Smineral analyses. The oxygen isotope composition of calcite was measured using the SHRIMP II microprobe at the RSES facility at ANU. Analytical methods were similar to those described by ref. 61. Sequences of sample analyses (typically three measurements) were bracketed by 1–2 analyses of standards. Corrected δ18O/Ho ratios are reported in standard δ18O notation, relative to Vienna Pee Dee Belemnite (VPDB). All δ18O values were calibrated against the UAM calcite standard (δ18O = −17.87‰, n = 0.03‰ of σ; cf. ref. 57). The spot-to-spot reproducibility (i.e., external precision) was typically better than ±0.30%o (1σ).

Composition and δ13C of natural gas. The composition of natural gas was determined using a Hewlett Packard 6890 II gas chromatograph (GC). Stable carbon isotope values were measured on an Optima isotope ratio mass spectrometer (IRMS) using a PDZ Europa 20-20 e isotope ratio mass spectrometer (IRMS) at the RSES facility at ANU. Analytical methods were similar to those described by ref. 63. Sequences of sample analyses (typically three measurements) were bracketed by 1–2 analyses of standards. Measured δ13C values were calibrated using the internal ‘calibrated black’ standard, with a value of −22.43%o relative to VPDB. All gas samples were analyzed in triplicate.

Biomarkers and δ13C in oil samples. The biomarker compositions of oil samples were analyzed on a Hewlett Packard 6890 II GC, using a Hewlett Packard PONA capillary column with dimensions of 50 m × 0.25 mm × 25 μm. Stable carbon isotope analyses of alkanes and arenes were performed on the same instrument, following the procedure described by ref. 63.

Estimating the methane sink capacity of the Mahu Sag. We first take the Mahu18-Aihu2 district, highlighted in blue dashed line in Fig. 1a, to be representative of the broader Mahu Sag. At least eight cores have been drilled in the 234 km² area, providing a good overview of the Tj reservoir strata. The combined thickness of these horizons with secondary cements ranges from 69 m to 48.3 m, with an average value of 28.7 m. Thus, the volume of rock containing secondary calcite can be estimated as: 234 × 10⁶ m² (area of the region of interest) × 28.7 m (average thickness of relevant horizons) = 6.7 × 10⁹ m³ of calcite cement-bearing strata. Multiplying by a typical sedimentary rock density of 2.5 × 10³ kg m⁻³ converts this volume to a total mass of 16.8 × 10¹² kg.

Based on the microscopic observations, the content of calcite cement in the relevant strata ranges from 1% to 5%, with the average value of 2.5%. Thus, we can calculate the total mass of authigenic calcite to be: 16.8 × 10¹² kg × 2.5% = 4.20 × 10¹² kg of calcite cement.

With the above estimate of the total mass of calcite cement in the Mahu18-Aihu2 district, we can calculate the mass of methane that would have been necessary to generate this cement. Due to its diffusion superiority of volatile natural gas relative to liquid oil, it can be approximately assumed that all carbon in the cement derived from natural gas. As the average relative content of CH₄ is 85% in the Tj bulk natural gas (Supplementary Table 2), the methane consumption can be estimated as: 420.0 × 10⁹ kg of CaCO₃ × 100.09 g mol⁻¹ × CaCO₃ × 16.06 g mol⁻¹ × 0.85 CH₄ = 57.3 × 10³ kg CH₄ (57.3 Tg of CH₄). Converting this mass to volume yields: 57.3 × 10³ kg CH₄ × 0.72 kg m⁻³ ÷ 7.96 × 10¹⁵ m³ of CH₄.

If only taking account of the oil-charging area, a fairly conservative methane consumption is 155 Tg, as the total discovered oil-charging area has reached 633 km² to the end of 2017 in the Mahu Sag (Fig. 1a). However, authigenic calcites are not restricted in the conglomerates and sandstones charged by oil, they also occur in the wells far away from the oil-charging area. The entire sag has an area of approximately 5000 km², which is roughly 20 times greater than the area of the Mahu18-Aihu2 district. Thus, we can estimate that the total mass of CH₄ abiotically oxidized by Fe-Mn oxides in the sag reaches 1.22 Tg.

The parameters used in the mass balance calculations are as follows: Mass₃CH₄ = 16.05 g mol⁻¹; Mass₃CCD = 100.09 g mol⁻¹; Density of CH₄ = 0.72 kg m⁻³ (defined at 273.15 K and 101.325 kPa); Density of rock = 2.50 × 10³ kg m⁻³.

Data availability All necessary data generated or analyzed during this study are included in this published article, and other auxiliary data are available from the corresponding authors on reasonable request.

Received: 20 June 2017 Accepted: 19 October 2018 Published online: 03 December 2018

References
1. U.S. Energy Information Administration. Annual Energy Outlook 2015 https://www.eia.gov/outlooks/aeo/pdf/0383(2015).pdf (EIA, 2015).
2. International Energy Agency. Natural Gas Information 2016 https://doi.org/10.1787/nat_gas-2016-en (IEA, 2016).
3. Wubbels, D. J. & Hayhoe, K. Atmospheric methane and global change. Earth Sci. Rev. 57, 177–210 (2002).
4. Hopcroft, P. O., Valdes, P. J., O’Connor, F. M., Kaplan, J. O. & Beering, D. J. Understanding the glacial methane cycle. Nat. Commun. 4, 14383 (2013).
5. Pavlov, A. A., Kasting, J. F., Brown, L. L., Rages, K. A. & Freedman, R. Greenhouse warming by CH₄ in the atmosphere of early Earth. J. Geophys. Res. 118, 19981–19990 (2013).
6. Jiang, G., Kennedy, M. J. & Christie-Blick, N. Stable isotope evidence for methane seeps in Neoproterozoic postglacial cap carbonates. Nature 426, 822–826 (2003).
7. Kirschke, S. et al. Three decades of global methane sources and sinks. Nat. Geosci. 6, 813–823 (2013).
8. Eitoque, G., Milkov, A. V. & Derbyshire, E. Did geologic emissions of methane play any role in Quaternary climate change? Glob. Planet. Chang. 61, 79–88 (2008).
9. Berbesi, L. A., di Primio, R., Anka, Z., Horsfield, B. & Wilkes, H. Methane leakage from evolving petroleum systems: Masses, rates and inferences for climate feedback. Earth Planet. Sci. Lett. 387, 219–228 (2014).
10. Beal, E. J., House, C. H. & Orphan, V. J. Manganese- and iron-dependent marine methane oxidation. Science 325, 184–187 (2009).
11. Michaelis, W. et al. Microbial reefs in the black sea fueled by anaerobic methane oxidation of methane. Science 297, 1013–1015 (2002).
12. Drake, H. et al. Extreme δ¹³C depletion of carbonates formed during oxidation of terrigenous methane in peridotitic granite. Nat. Commun. 6, 1–9 (2015).
13. Worden, R. H. & Smalley, P. C. H₂S-producing reactions in deep carbonate gas reservoirs: Khuff Formation, Abu Dhabi. Chem. Geol. 133, 157–171 (1996).
14. Cai, W., Worden, R. H., Bottrell, S. H., Wang, L. & Yang, C. Thermochemical sulphate reduction and the generation of hydrogen sulphide and thio- (mercaptans) in Triassic carbonate reservoirs from the Sichuan Basin, China. Chem. Geol. 202, 39–57 (2003).
15. Cai, W. et al. Methane-dominated thermochemical sulphate reduction in the Triassic Feixianguan Formation East Sichuan Basin, China: towards
prediction of fatal H₂S concentrations. Mar. Petrol. Geol. 21, 1265–1279 (2004).

16. Mullis, J., Dubessy, J., Poty, B. & O’Neil, J. Fluid regimes during late stages of a continental collision: physical, chemical, and stable isotope measurements of fluid inclusions in fission quartz from a geotransverse through the Central Alps, Switzerland. Geochim. Cosmochim. Acta 58, 2239–2267 (1994).

17. Allen, P. A. & Allen, J. R. Basin Analysis: Principles and Application to Petroleum Play Assessment (John Wiley & Sons, New York, 2013).

18. Kallmeyer, J. & Boetius, A. Effects of temperature and pressure on sulfite reduction and anaerobic oxidation of methane in hydrothermal sediments of Guaymas Basin. Appl. Environ. Microb. 70, 1231–1233 (2004).

19. Peters, K. E., Walters, C. C. & Moldowan, J. M. The Biomarker Guide Ch. 16 (Cambridge University Press, Cambridge, 2005).

20. Jia, H. et al. A retreating fan-delta system in the northwestern Junggar Basin, NW China: Carboniferous marine and Baikouquan Formation in the Mahu Sag, Junggar Basin.

21. Liu, Q. Y. et al. TSR versus non-TSR processes and their impact on gas geochemistry and carbon stable isotopes in Carboniferous, Permian and Lower Triassic marine carbonate gas reservoirs in the Eastern Sichuan Basin, China. Geochim. Cosmochim. Acta 100, 96–115 (2013).

22. Tanartola, A., Mullis, J., Vennemann, T., Dubessy, J. & de Capitani, C. Oxidation of methane at the CH₄/CH₃OH–CO₂ transition zone in the external part of the Central Alps, Switzerland: Evidence from stable isotope investigations. Chem. Geol. 237, 329–357 (2007).

23. Tanartola, A. et al. Oxidation of CH₃ to CO₂, and H₂O by chloritization of detrital biotite at 270 ± 5 °C in the external part of the Central Alps, Switzerland. Lithos 112, 497–510 (2009).

24. Kiyosu, Y. & Imaizuami, S. Carbon and hydrogen isotope fractionation during oxidation of methane by metal oxides at temperatures from 400 to 530 °C. Chem. Geol. 133, 279–287 (1996).

25. Sobbe, E. R., De Boer, B. A. & Geus, J. W. The reduction and anaerobic oxidation of methane and manganese oxides and fault-related hydrologies in Brent Group diagenesis: North Sea. Geol. Soc. Lond. Spec. Publ. 61, 401–419 (1992).

26. Sun, Y. et al. Lethally hot temperatures during the Early Triassic greenhouse. Science 338, 366–370 (2012).

27. Roberts, J., Turchyn, A. V., Wignall, P. B., Newton, R. J. & Vane, C. H. Disentangling diagenesis from the rock record: an example from the Permo-Triassic Wordie Creek Formation, East Greenland. Geochim. Geophys. Geosyst. 19, 99–113 (2014).

28. James, A. T. & Burns, R. J. Microbial alteration of subsurface natural gas accumulations. AAPG Bull. 68, 957–960 (1984).

29. Machel, H. G. Bacterial and thermochemical sulfate reduction in diagenetic carbonate formation. Chem. Geol. 140, 143–153 (1997).

30. Orphan, V. J., House, C. D., Rittenour, T. R., Neve, M. D., Schoell, K. D. & Delong, E. F. Methane-consuming archaea revealed by directly coupled isotope and phylogenetic analysis. Science 293, 484–487 (2001).

31. Coleman, D. D., Risatti, J. B. & Worden, R. H. Enrichment of nitrogen and ¹³C of methane in natural gases from the Khuff Formation, Saudi Arabia, caused by thermocatalytic sulfate reduction. Org. Geochem. 82, 54–68 (2015).

32. Orphan, V. J. et al. Lethally hot temperatures during the Early Triassic greenhouse. Science 338, 366–370 (2012).

33. Coleman, D. D., Risatti, J. B. & Worden, R. H. Enrichment of nitrogen and ¹³C of methane in natural gases from the Khuff Formation, Saudi Arabia, caused by thermocatalytic sulfate reduction. Org. Geochem. 82, 54–68 (2015).

34. Wronkiewicz, D. J. & Condie, K. C. Geochemistry of Archean shales from the Witwatersrand Supergroup, South Africa: source-area weathering and provenance. Geochim. Cosmochim. Acta 45, 1033–1037 (1981).

35. Krouse, H. R., Viau, C. A., Eliuk, L. S., Ueda, A. & Halas, S. Chemical and isotopic evidence of thermochemical sulphate reduction by light hydrocarbon gases in deep carbonate reservoirs. Nature 333, 415–419 (1988).

36. Machel, H. G. Bacterial and thermochemical sulfate reduction in diagenetic settings—old and new insights. Sediment. Geol. 30, 143–153 (2013).

37. Orphan, V. J. et al. Methane-consuming archaea revealed by directly coupled isotope and phylogenetic analysis. Science 293, 484–487 (2001).

38. Machel, H. G. Bacterial and thermochemical sulfate reduction in diagenetic carbonate formation. Chem. Geol. 140, 143–153 (1997).

39. Orphan, V. J. et al. Methane-consuming archaea revealed by directly coupled isotope and phylogenetic analysis. Science 293, 484–487 (2001).

40. Machel, H. G. Bacterial and thermochemical sulfate reduction in diagenetic carbonate formation. Chem. Geol. 140, 143–153 (1997).
W.-X.H. developed the evaluation model for CH4 sink; J.C. provided the oil and gas samples and participated in the organic geochemical experiments; X.-L.W. participated in the interpretation of the data; B.F. contributed a lot in the in situ stable isotope analyses; H.-G.W. participated in the core sampling and EPMA analyses.

Additional information
Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-018-07267-x.

Competing interests: The authors declare no competing interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2018