Supplemental Material

SAMPLES

Fifteen sandy conglomerate samples were newly collected from Lower Triassic Baikouquan Fm. from ten wells. These samples were examined for calcites using diluted HCl and observed under thin sections strained with alizarin red, some of which were analyzed for SEM, EMPA, bulk C and O isotopes, SIMS C and O isotopes; and clumped isotopes.

Well	Depth	Lithology	Analysis items				
	(11)						
Ma15	3069.99		SEM; EMPA; Bulk C and O isotopes; SIMS; Clumped				
			isotopes				
Ma154	3028.63		SEM; Bulk C and O isotopes				
Ma154	3031.05		SEM; EMPA; Bulk C and O isotopes; Clumped isotopes				
Ma154	3031.34		SEM; EMPA; Bulk C and O isotopes; SIMS; Clumped isotopes				
MH1	4105.4	Grey sandy	SEM; Bulk C and O isotopes; Clumped isotopes				
AH1	3863.4	conglomerates, all examined for calcites	SEM; EMMPA; Bulk C and O isotopes				
AH2	2286.48		SEM; EMPA; Bulk C and O isotopes; failed clumped				
	5200.40		isotopes				
Ma6	3883.57	using diluted	SEM; EMPA; Bulk C and O isotopes				
Ma6	3875.40	thin sections	SEM; EMPA; Bulk C and O isotopes; SIMS				
л Ц 1 2	3814.3	- thin sections	SEM; EMPA; Bulk C and O isotopes; SIMS; failed				
АПІЗ			clumped isotopes				
Ma18	3852.3		Trace calcites (<0.5%)				
Ma18	3858.52		Trace calcites (<0.5%)				
AH11			SEM; EMPA; Bulk C and O isotopes; SIMS; failed				
	3803.40		clumped isotopes				
Ma9	3679.40		Trace calcites (<0.5%)				
Ma9	3678.80		Trace calcites (<0.5%)				

METHODS

EPMA: quantitative measurements of points from manganese-bearing carbonates were made using wavelength-dispersive spectrometry (WDS) using a JEOL JXA-8100 advanced Electron Probe Microanalyzer (**EPMA**) at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). The samples were analyzed for their major element compositions, operated at 15 kV, with a 10.5 nA beam current, using a 5 μ m beam diameter and 10–30 s counting time. The precision for the analyzed oxides was better than \pm 5%.

Carbon and oxygen and clumped isotope analyses:

Bulk calcite cements were obtained using a dental driller from sandy conglomerates. Because the samples contained only about 50% calcite, an aliquot of 8-12 mg was used for the analyses. In IGGCAS, CO₂ was released from calcites using 105% orthophosphoric acid in 72°C and measured $\delta^{13}C$ and $\delta^{18}O$ values using MAT253 on samples from three wells M6, AH1 and AH2 with standard deviation of 0.15‰ and 0.20‰, respectively. In the Stable Isotope Laboratory of the Carbonate Research Group at Imperial College London (ICL), δ^{13} C and δ^{18} O values and clumped isotope data from three other wells Ma154, Ma15 and Ma1 were measured. We used an in-house, automated clumped isotope system (The IBEX) to prepare the samples online. Preparation included acidification at 90°C in a common acid bath of 105% orthophosphoric acid, followed by cryogenic separation of the CO₂ gas from water. Contaminants were removed from the CO_2 gas by passing the CO_2 through a poropak-Q trap held at -35°C using helium as a carrier gas following similar procedure previously described (Huntington et al., 2009). The resulting clean gas CO₂ was captured in a cold finger and transferred to a ThermoFisher (Bremen, Germany) MAT 253 mass spectrometer equipped with a dual inlet. The detailed measurement integration time and mass spectrometry procedures were previously described in Dale et al. (2014). All clumped isotope data were processed using the free software 'Easotope' (John et al., 2016). Non-linearity correction was performed using the PBL method (Bernasconi et al., 2013) and acid fractionation was corrected using the appropriate factor (Defliese et al., 2015). Two internal standards (carrara marble - ICM, and the Oamaru Limestone - IOL) as well as four

interlaboratory standards (ETH1, 2, 3, and 4) (Meckler et al., 2016) were used to correct the data and project it into the absolute reference frame (Dennis et al., 2011). Temperatures were calculated using the internal calibration of Davies and John (2019), and should be viewed as maximum estimate of temperatures, since recrystallization in either closed or semi-closed system during subsequent burial cannot be ruled out.

Mn incorporation in carbonate does not skew the oxygen isotope measurements through variations in the phosphoric acid fractionation factor in our experiments. Logvina et al. (2018) showed the difference in δ^{18} O between calcite and rhodochrosite is -0.5‰ at 72°C using phosphoric acid solution and pure calcite NBS-19 as the standard. Our calcite samples have MnO from 0.5 to 9.1 wt%, thus, this part of Mn incorporated into calcites are expected to have the differences between pure calcite and Mn-bearing calcite in δ^{18} O <0.05‰ compared with pure calcite. The values are within the measurement error, and thus we conclude that <10 wt.% Mn incorporation in carbonate does not changes our measurement result using pure calcite GBW04405 or IOL as the standard.

SIMS calcite carbon isotope analyses

Small pieces of polished thin sections of carbonate samples from wells Ma6, Ma15, AH13, AH11 and Ma154 were mounted in Buehler EpoFix epoxy resin, together with carbonate reference materials such as NBS-19 calcite. Secondary ion mass spectroscopy (SIMS) analyses of carbon and oxygen isotopes were performed *in situ* using the Sensitive High Resolution Ion Microprobe for Stable Isotopes (SHRIMP SI) located in Research School of Earth Sciences (RSES), the Australian National University (ANU), Canberra. The analytical procedure was similar to Ickert et al. (2008) for oxygen isotopes. Note that carbon isotopes (¹²C and ¹³C) were measured on the

spots by two Faraday cups in a single analytical session with peak switching, using an ~15 kV Cs + primary ion beam focused over an area of ~30 μ m in diameter. ¹²CH was completely resolved with collector slits of 150 μ m for ¹³C and 300 μ m for ¹²C, the former measured with an electrometer in charge mode (Ireland et al. 2014).

Sequences of sample analyses (typically three to five measurements) were bracketed by 1–2 analyses of standards. All the data for unknowns were calibrated initially against NBS19 calcite and further corrected for matrix effects, similar to that of Śliwiński et al. (2016a, 2016b). Corrected ¹³C/¹²C ratios are reported in standard δ notation, relative to Vienna Pee Dee Belemnite (VPDB). Duplicate δ^{13} C analyses of the calcite standard NBS-19 yield an external (spot to spot) precision (1 σ) of better than ±0.50‰, respectively. MnO content in the calcite samples is from 0.9–9.2 mol. %. Such small amount of Mn has less measurable matrix effects on SIMS δ^{13} C bias than Fe²⁺ (Śliwiński, M. G. et al., 2016). Contamination of measurements by organic carbon was avoided by carefully choosing spots free of micro fractures or inclusions. Thus the potential error associated with matrix effect and organic inclusions is considered to be insignificant relative to isotopic variation.

Visible diffuse reflectance spectrum (DRS)

DRS measurements were used to determine what kinds of iron oxides and made at wavelengths from 300 to 800 nm in 0.5 nm steps at a scan speed rate of 300 nm/min using a Varian Cary 5000 spectrophotometer equipped with a $BaSO_4$ -coated integrating sphere. The DRS data were smoothed using the Varian instrument software (Savitzky-Golay method) with a filtering factor of 5 and were then transformed into Kubelka-Munk (K-M) functions [(1-R)²/2R], where R is the reflectance. The second derivatives of the K-M functions were calculated using the

Varian software with a filtering factor of 29. The characteristic band positions of hematite and goethite are ~535nm (P535 nm) and ~425nm (P425 nm), respectively (Hu et al., 2016; Torrent et al., 2007).

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Supplemental Material DR2

Supplementary Figures



Figure S1 Diagenetic sequence and charge of biogenic gas and thermogenic petroleum overprinted on burial and thermal history



Figure S2 The results of the thermodynamic calculation for direct vs indirect methane oxidation using Mn oxides. The range of values used in the calculation is presented in Table S3. Our results indicate a higher favorability of direct methane oxidation using Mn oxides.



Figure S3 The natural gas plot with calcite δ^{13} C values plot for comparison, showing that all Mahu gas mixed with biogenic methane.

Supplemental Material DR3

Supplementary Tables

	Calcite Name	δ ¹³ C	CaO	MgO	FeO	MnO	FeO/MnO
		(‰, VPDB)	(w%)	(wt%)	(w%)	(wt%)	
	NBS19 (average, n=36)	1.95					
	OKA (average, n=7)	-4.95					
	UWC3 (average, n=7)	-0.91					
Biogenic	Ma15	-32.43	48.772	0.196	0.393	5.860	0.067
calcites		-30.10	46.503	0.151	0.470	9.015	0.052
		-30.35	46.243	0.182	0.627	8.633	0.073
		-29.51	44.749	0.112	1.181	9.164	0.129
		-29.43	45.446	0.142	0.800	8.574	0.093
		-30.20	47.151	0.135	0.487	8.297	0.059
		-30.24	46.243	0.182	0.627	8.633	0.073
		-30.14	44.749	0.112	1.181	9.164	0.129
	AH13	-40.04	47.898	0.034	0.145	4.675	0.031
		-41.91	47.222	0.043	0.388	4.277	0.091
		-43.36	51.119	0.011	0.162	2.001	0.081
		-40.97	51.605	0.035	0.059	1.032	0.057
		-40.02	51.12	0.016	0.169	1.443	0.117
		-40.26	51.12	0.016	0.169	1.443	0.117
		-40.17	52.341	0	0.053	1.070	0.050
		-40.47	50.848	0	0.125	1.796	0.070
		-40.91	51.217	0.029	0.125	2.239	0.056
		-42.50	51.041	0	0.100	2.297	0.044
	AH11	-44.65	53.212	0	0.055	2.520	0.022
		-45.21	53.564	0.044	0.017	2.127	0.008
		-50.10	53.564	0.044	0.017	2.127	0.008
		-44.24	53.780	0	0.064	1.792	0.036
		-56.77	53.212	0	0.055	2.520	0.022
		-56.57	52.172	0.012	0.002	2.798	0.001
		-54.45	53.467	0	0.075	2.394	0.031
		-47.93	53.684	0	0.087	2.232	0.039
		-48.09	53.564	0.044	0.017	2.127	0.008
		-57.04	53.387	0.066	0.075	2.141	0.035
		-57.74	53.780	0	0.064	1.792	0.036
		-58.07	53.780	0	0.064	1.792	0.036
		-47.64	53.212	0	0.055	2.520	0.022
		-48.08	52.172	0.012	0.002	2.798	0.001
		-50.64	53.467	0	0.075	2.394	0.031
		-51.10	53.812	0.026	0	2.310	0

Table S1 SIMS $\delta^{13}C$ and $\delta^{18}O$ values and EMPA Ca, Mg, Fe and Mn contents of T1b calcites

	Ma6	-46.93	54.244	0	0.010	0.752	0.013
		-48.10	54.244	0	0.010	0.752	0.013
		-48.87	55.160	0	0.027	1.154	0.023
		-48.19	54.254	0	0.052	0.952	0.055
		-44.71	54.254	0	0.052	0.952	0.055
		-50.70	54.254	0	0.052	0.952	0.055
	Average					3.29	0.048
	Standard deviation					2.72	0.035
Thermogenic	Ma154	-4.69	53.778	0.062	0.565	1.775	0.318
calcites		-15.31	53.241	0.060	0.511	1.631	0.313
		-5.62	51.913	0.103	1.081	1.683	0.642
		-5.84	52.038	0.203	1.176	1.592	0.739
		-5.47	52.151	0.070	0.786	1.698	0.463
			52.096	0.843	0.170	2.812	0.060
			52.096	0.843	0.170	2.812	0.060
			52.323	0.825	0.199	2.570	0.077
			52.323	0.825	0.199	2.570	0.077
			52.665	0.607	0.201	2.341	0.086
			52.665	0.607	0.201	2.341	0.086
			52.316	0.622	0.224	2.370	0.095
			52.316	0.622	0.224	2.370	0.095
			52.098	0.894	0.105	2.396	0.044
	Average					2.21	0.23
	Standard deviation					0.43	0.23

Table S2 Elemental compositions of hematites from T₁b sandy conglomerates by EMPA (wt%)

Well	MgO	CaO	MnO	FeO	BaO	SrO	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	TiO ₂	MnO/FeO
	0.668	0.328	2.111	62.283	0.274	0.117	4.277	2.247	0.219	0.205	0.308	0.034
	0.752	1.46	1.964	47.547	0	0.107	9.126	4.501	0.247	0.606	0.125	0.041
	0.614	0.346	2.101	63.364	0.135	0.06	3.599	1.614	0.142	0.181	0.316	0.033
AH2	0.614	0.249	1.407	71.359	0.103	0.036	2.815	1.622	0.193	0.161	0.224	0.020
	1.498	0.086	2.523	69.176	0	0.112	2.729	3.687	0.101	0.081	0.03	0.036
	0.979	0.046	2.022	74.189	0	0.06	1.685	3.397	0.078	0.071	0.198	0.027
	1.169	0.023	2.335	72.296	0.031	0.039	2.368	3.176	0	0	0.174	0.032
Ma15	0.245	0.342	3.029	63.454	0.051	0.063	1.672	2.811	0.165	0.289	7.429	0.047
	0.573	0.093	5.719	51.214	0	0.075	1.284	4.486	0.071	0.232	2.929	0.112

Table S3 The range of parameters used in the thermodynamic calculation of direct and indirect methane oxidation

Parameter	Range
[HS ⁻], sulfide concentration	1-100 μM
[CH ₄], methane concentration	10-100 μM
[HCO ₃ ⁻], bicarbonate concentration	1000-5000 μM
[Mn ⁺], manganese concentration	10-100 μM
[HCO ₃ ⁻], bicarbonate concentration	1000-5000 μM
pH	6.5-7.5