
Reply to comments by Mastalerz, V. on “Shallow gas off the Rhône prodelta, Gulf of Lions” *Marine Geology* 234 (215–231)

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Abstract:

We really appreciate the interest and comments regarding our manuscript. We hope we address all the lingering issues in this reply. This also gives us the opportunity of publishing an update on our dataset that will complete the original manuscript (see Table 1). We have followed the author pattern in our answers: 1-Gas sampling procedure, 2-Reported gas concentrations results, 3-General remarks, 4-Conclusions.

Keywords: shallow gas, biogenic methane, flood deposits, Rhone prodelta, Gulf of Lions

1-Gas sampling procedure

The gas data are reported in ppm by volume (raw data) and in microliters gas/liter wet sediment. The later units normalize the gas concentration to sediment sample volume. The gas data is reported with 3 significant figures for both units (ppm and $\mu\text{l/l}$)-see updated table. Phase partitioning of methane was not corrected for in the gas concentration. If it were done, the concentration of the methane would be about 1.25 times higher than reported. It should be emphasized that gas collected from cored sediment is especially prone to error when the saturation of any compound is exceeded during recovery. Thus the concentration reported reflects residual sediment gas and is not the *in situ* gas concentration. The data does allow for semi-quantitative interpretations of relative gas concentration from one sample to another and the presence or absence of any particular compound. Our statement about the concentration of methane typically observed in coastal sediments is strictly empirical and is based on the authors experience measuring methane in surficial sediments. The statement relies on the principal that for our samples, each is handled and packaged in our standard 0.5 L cans and calibrated to a 100mL headspace and contains about the same sample mass.

Adding salt as a bactericide is meant to inhibit microbial action, not stop it. We feel that freezing the sample until analysis is an effective way to prevent microbial alteration of the gases.

2-Reported gas concentrations results

As the author points out, table 1 is in the units of microLiters/Liter $\mu\text{L/L}$ wet sediment NOT mL/L milliLiters/Liter. Unfortunately this typo was published in the original version. We have attached a new corrected Table 1. We have taken this

opportunity to add the results for isotopes we obtained recently and requested by the reply to our paper.

The following are the particulars about the GC analysis:

Hydrocarbon gas composition determination

A Shimadzu GC-14A gas chromatograph equipped with a Chemipack C-18, 6 ft. x 1/8 in. 80/100 mesh stainless steel column was used to measure C₁-C₈ hydrocarbon gases. The GC-14A is configured with a 1 mL, valve-actuated, sample loop for injection, and a flame ionization detector (FID) for gas detection. Samples were introduced by syringe at atmospheric pressure, and a minimum of 10 mL of gas was used to flush the injection loop. Run conditions were 35°C for 1.5 minutes ramping up at 20°/minute to 150°C, and held. Helium was used as the carrier gas at a constant mass flow rate of 3 kg/cm². FID temperature was held at 150°C.

Results are reported relative to the volume of cuttings or weight of core material from which the gases were extracted, i.e., microliters of gas per liter of wet sediment (µL/L). Gas concentration data are reported for a series of hydrocarbons given in order of elution (Table 1); methane (C₁), ethane (C₂), and propane (C₃). Approximate detection limits for all hydrocarbon compounds are 0.05 parts per million by volume (ppmv).

CO₂, determination

Carbon dioxide (CO₂) with a Hewlett-Packard P-200 micro gas chromatograph equipped with a 4 m long by 50 µm diameter carboplot column and a micro-machined thermal conductivity detector. Run conditions were isothermal at 60°C with a run time of 2 minutes. Helium carrier gas column head pressure was maintained at 18.5 psi. Approximate detection limits for CO₂ are about 50 ppm.

Hydrocarbon gas isotopic composition determination

Subsamples of sediment gas were transferred by syringe to dry, evacuated 30-ml, serum vials sealed with a isobutyl rubber stopper. Each vial was overpressured with sample gas and the septum sealed with silicon glue to prevent sample leakage and inadvertent isotopic fractionation.

Stable carbon isotope ratio determinations of C₁, C₂, and CO₂ were made on a Continuous Flow–Isotope Ratio Mass Spectrometer (Finnigan MAT 252 GC-C-IRMS) at the School of Earth and Ocean Sciences (SOES), University of Victoria, Canada.

Samples are introduced by syringe into a SRI gas chromatograph (GC) via a gas sample valve (loop volumes: 10, 100 or 200 µL). Analytes are separated at 40°C on a 30 m GS-Q column (0.32 mm ID) with a carrier gas flow of 1.8 mL/min ultra-high purity helium. After gas partitioning on the GC, the gas then passes through

a CuO/Pt microcombustion oven at 850°C. This oven quantitatively converts the hydrocarbon gases to carbon dioxide and water. The combusted sample products are then passed through a Nafion™ tube to remove water from the combustion and any that may be in the carrier gas. The purified CO₂/He pulse is scaled by an open-split interface, and then transferred into the GC-C-IRMS. Isotope ratios are referenced to the conventional PDB standard through a known CO₂ isotope standard that is added at the open split to the sample runs several times during the analysis.

For stable carbon isotope ratio measurements on the sample CO₂, the gas was partitioned on the GC as above. The microcombustion oven was bypassed for the CO₂ measurements, but the gas stream was dried, split and measured by CF-IRMS in a manner similar to the light hydrocarbons.

3-General remarks

We have included all the final isotopic information in the table. The results show that the methane collected from the Rhone delta sediments is from microbial sources. Methane oxidation is likely in several samples (g31, h30, e56, j63, e48b, BF05, BF06, BF09). It is unknown if this reflects methane oxidation in the environment or the aerobic oxidation of methane to carbon dioxide in the sample container.

4-Conclusions

We hope the manuscript is now more complete and all the issues are addressed with the updated table and the explanations regarding the methodology and sampling. From our point of view the paper presents a complete new dataset for shallow gas off the prodelta and we hope it is useful to further studies in the area.

OCTOBER 04 DATASET													
SITE	CORE TYPE	WATER DEPTH (m)	SAMPLE DEPTH b.s.f. (cm)	C1 (uL/L wet sed)	C2 (uL/L wet sed)	C3 (uL/L wet sed)	C1 (ppm)	C2 (ppm)	C3 (ppm)	CO2	δ13C (CH4)	δ13C (CO2)	CH4 oxidized
ke28 150	KC	28	150	128700	0.00	3.31	82200	0.00	2.11	21900	-73.4	-24.2	
ke28 205	KC	28	205	127500	0.00	2.76	87400	0.00	1.89	46200	-75.8	-17.1	
ke33 216	KC	33	216	12700	0.00	3.39	81300	0.00	2.16	36300	-75.7	-13.2	
ke28 100	KC	28	100	77600	0.00	1.17	66900	0.00	1.01	24600	-71.6	-21.3	
e33	BC	33	30	51900	0.20	2.26	23200	0.09	1.01	88700	-60.7	-28.6	
f58b	BC	58	30	48800	0.36	1.53	31800	0.24	1.00	43300	-74.9	-37.4	
g31	BC	31	40	44600	0.02	1.00	36900	0.02	0.83	44500	-56.8	-28.4	oxidized
ke33 160	KC	33	160	41400	0.38	4.88	32400	0.30	3.81	22000	-69.5	-17.4	
ke33 105	KC	33	105	31000	0.20	1.61	25700	0.16	1.34	34600	-57.0	-26.6	
f32	BC	31	28	18000	0.03	0.35	8900	0.02	0.17	10000	-60.4	-23.5	
h30	BC	30	17	17900	0.26	2.21	9600	0.14	1.19	53000	-44.2	-39.3	oxidized
e56	BC	56	28	14200	1.26	2.41	5400	0.48	0.92	32300	-27.1	-20.7	oxidized
j63	BC	63	28	12200	0.42	0.66	10200	0.35	0.55	29000	-46.3	-22.7	oxidized
f47	BC	47	30	10500	0.29	1.24	6200	0.17	0.73	14700			
e48b	BC	48	34	5900	0.27	0.78	4500	0.20	0.59	10000	-48.4	-28.5	oxidized
e65	BC	65	32	4700	1.93	1.60	3000	1.23	1.02	18100	-61.2	-23.8	
i50	BC	51	30	4500	1.10	1.15	3100	0.75	0.78	13300	-64.2	-24.2	
g47	BC	47	33	4000	1.05	1.62	2500	0.67	1.03	22300	-61.7	-25.7	
j52	BC	52	30	4000	3.29	0.56	2800	2.29	0.39	16400		-19.2	
i42	BC	42	32	3700	0.73	0.54	3500	0.69	0.51	8100	-63.3	-24.7	
i68	BC	68	35	3700	2.04	0.53	2800	1.58	0.41	8800	-70.3	-22.9	
f58s	BC	58	0	3000	3.47	14.48	1100	1.21	5.04	11000	-65.2	-26.4	
g57	BC	57	41	2500	1.26	1.04	2000	0.98	0.81	28700	-67.9	-27.6	
i32	BC	32	25	2400	1.95	0.73	1800	1.49	0.56	19800	-67.4	-26.3	
i58	BC	58	35	2200	1.50	1.12	1600	1.07	0.80	18900	-65.2	-24.3	
g65	BC	65	38	1400	2.07	0.87	900	1.29	0.54	12000	-70.5	-24.2	
h62	BC	62	33	1100	2.75	0.93	700	1.69	0.57	35100	-65.3	-24.4	
k72	BC	72	42	1100	0.48	0.39	800	0.37	0.30	4400	-69.1	-19.7	
j36	BC	36	33	900	2.01	0.43	600	1.38	0.30	14300	-77.7	-22.4	
h45	BC	45	29	800	1.05	1.11	700	0.88	0.94	11100	-68.1	-25.1	
j46	BC	46	38	600	1.21	0.30	500	1.06	0.26	9600	-72.9	-24.7	
h56	BC	56	33	300	0.70	0.72	200	0.59	0.61	13700	-73.4	-28.8	
j70	BC	72	32	300	2.88	0.30	200	2.45	0.26	12700	-72.0	-20.0	
k65	BC	65	34	200	1.28	0.35	200	0.86	0.24	16500			
k28	BC	28	30	200	0.69	0.20	200	0.62	0.18	3000			
j28	BC	28	32	200	0.63	0.28	200	0.64	0.29	3100	-65.4	-20.7	
k43	BC	43	31	200	1.16	0.20	100	0.85	0.15	7000			
k57	BC	57	35	100	0.69	0.21	100	0.43	0.13	2200			
MARCH04 DATASET													
SITE	CORE TYPE	WATER DEPTH (m)	SAMPLE DEPTH b.s.f. (cm)	C1 (uL/L wet sed)	C2 (uL/L wet sed)	C3 (uL/L wet sed)	C1 (ppm)	C2 (ppm)	C3 (ppm)	CO2	δ13C (CH4)	δ13C (CO2)	CH4 oxidized
BF05	FC	27	25	9900	0.00	0.64	16100	0.00	1.05	35300	-59.9	-29.5	oxidized
BF06	FC	28	25	2500	0.16	0.39	4000	0.24	0.61	24600	-53.1	-30.5	oxidized
BF07	FC	43	25	800	1.01	1.44	1300	1.58	2.25	19200	-81.9	-25.8	
BF09	FC	30	25	4800	0.20	0.43	7100	0.29	0.63	35600	-53.2	-31.3	oxidized
BF18	FC	60	25	400	0.44	0.26	600	0.63	0.36	5400	-69.9	-22.7	
BF20	FC	20?	25	300	0.93	0.45	400	1.24	0.61	3100	-67.5	-22.6	
BF14	FC	57	25	400	1.19	1.05	500	1.54	1.35	2900	-68.5	-17.8	
BF90	FC	94	25	200	0.41	0.60	300	0.61	0.90	5200			
BF50	FC	95	25	100	0.57	0.96	100	0.75	1.27	4400			
Chenal 30	FC	30?	45	27900	0.00	0.70	33700	0.00	0.85	37900	-67.5	-30.0	
BF16KB	FC	14	40	400	1.25	0.62	500	1.42	0.70	22200			
BF19	FC	76	25	100	0.80	0.27	0	0.78	0.27	2800			
BF22	FC	74	25	0	0.29	0.09	0	0.30	0.09	2800			
BF101	FC	76	25	300	1.29	0.50	200	1.19	0.46	9300			
BF102	FC	80	25	200	3.49	0.40	200	3.57	0.41	5400			
BF04	FC	86	25	0	0.42	0.15	0	0.49	0.17	2600			
R4	FC	47	25	0	1.88	0.20	0	1.76	0.19	2700			
BF01bis	FC	26	25	200	0.21	0.22	200	0.22	0.23	1100			

Table 1. Headspace gas analyses and isotopic results for cores acquired on the Grand Rhône prodelta during 2004 EuroSTRATAFORM cruises. KC for kasten core, BC for box core, FC for flunchat core. Abbreviations: b.s.f., below seafloor.