

**SUPPLEMENTARY INFORMATION AND DATA****ADDITIONAL DATA REPOSITORY FILES:**

Table DR1

Table DR2

Table DR3

Table DR4

**ORGANIC CARBON – A SEEMINGLY OBVIOUS, YET INEFFECTIVE ATTEMPT TO DISTINGUISH OIL- FROM METHANE-SEEP DEPOSITS IN THE FOSSIL RECORD**

One of the envisioned methods to distinguish ancient methane- from oil-dominated seep deposits in the scope of this study was to compare bulk rock total carbon (TC) and total organic carbon (TOC) contents, as well as their respective isotope values. Specifically, the  $\delta^{13}\text{C}$  values in oil- and methane-seep deposits are likely to be different. Higher hydrocarbons are present as crude oil in modern seep deposits, which is preserved as metamorphosed crude oil (referred to as impsonite or pyrobitumen) in ancient seep limestones (cf. Peckmann et al., 2001, 2007). Methane on the other hand, is not preserved within the TOC fraction of seep carbonates. The TOC fraction of methane-seep deposits could therefore exhibit rather different stable carbon isotope compositions than the TOC fraction of oil-seep deposits. Furthermore, the observation that modern oil-seep carbonates exhibit much higher TOC contents than their methane-derived counterparts (Table DR1) suggests that this comparison should serve as a potent tool in identifying oil-seep deposits in the rock record. The potential of these rather simple and obvious methods to discriminate oil- from methane-seep deposits has not been tested to date and was systematically assessed as part of this study.

For total carbon (TC) measurements, 10 samples from each site were ground to fine powder, after which a fraction of each powder was decalcified by slow addition of 0.1%

hydrochloric acid (HCl). When all carbonate was dissolved, the remaining material was rinsed with dichloromethane-cleaned water, centrifuged, and dried at 70°C to obtain the non-carbonate residue. This residual powder, as well as untreated powders of each sample were heated to 1000°C at a steady rate of 20°C/min. using a LECO RC-612 Carbon Analyzer (St. Joseph, MI, USA), equipped with a solid-state infrared detector at the Department of Environmental Geosciences at the University of Vienna. We employed this two-step measurement procedure, because determining TOC contents of the Late Devonian *Dzieduszyckia* oil-seep limestones was not possible using untreated powders where TC contents well over 12% were determined (Table DR1). Pyrobitumen most likely blended with TIC measured above 550°C in these samples, as inert pyrobitumen completely converts to carbon dioxide only if heated to at least 650°C (cf. Grinko and Golovko, 2011). This precluded a straightforward determination of both TOC and total inorganic carbon (TIC) in one measurement. TC content of untreated and corresponding residue powders was determined by measuring the released carbon dioxide up to a temperature of 1000°C. Prior to sample measurements a pure calcium carbonate standard (Co. Merck) was measured three times. A standard deviation of 0.18% as well as a relative standard deviation of 1.48% were calculated. A Synthetic Carbon Leco standard (LECO-Nr. 502-029) was measured nine times prior to sample analyses and a standard deviation of 0.02% as well as a relative standard deviation of 2.5% was calculated. The TOC content of bulk samples was obtained by relating TC content of residue powder to the mass ratio of powder prior to and after decalcification.

TC and TOC, as well as respective  $\delta^{13}\text{C}$  values are shown in Table DR1. Interestingly, the total non-carbonate fraction varies widely among the different seep deposits. For the Oligocene methane-seep deposit (SR4), the non-carbonate fraction greatly exceeds that of the Late Devonian *Dzieduszyckia* deposit. The non-carbonate fraction of the methane-seep deposit

amounts to 20% of the total rock mass, whereas it constitutes only 1% in the putative oil-seep deposit (Table DR1). TC mean values of the non-carbonate fraction are significantly higher in the *Dzieduszyckia* deposit than in SR4 limestones. These results have a profound impact on calculated bulk rock TOC values. Due to the relatively large non-carbonate fraction of SR4 limestones, bulk rock TOC values are an order of magnitude greater than for the *Dzieduszyckia* deposit. Our analyses do not arrive at the intuitive conclusion that ancient oil-seep carbonates should yield higher bulk rock TOC values than pure methane-derived carbonates. The large non-carbonate fraction in SR4 limestones, in combination with an extraordinarily low non-carbonate fraction of the Late Devonian oil-seep carbonates, leads to contrary results than expected. It is likely that the large portion of heterogeneous microcrystalline calcite (i.e. micrite) within Oligocene samples may be responsible for this outcome. Micrite is the volumetrically most prominent mineral phase in most studied seep limestones from Cenozoic successions from Washington State (e.g. Goedert et al., 2000; Peckmann et al., 2002, 2003; Kuechler et al., 2012; Zwicker et al., 2015). This phase exhibits substantial amounts of detrital material derived from the clay-rich marine host sediments. It is likely that detrital organic matter was also incorporated and cemented as part of the bulk limestone, which would account for the relatively high bulk rock TOC contents. In contrast, microcrystalline calcite is negligible in the Late Devonian *Dzieduszyckia* deposit. Here, the only non-carbonate constituent of the bulk limestone is very fine grained particulate material, most probably pyrobitumen (own observation after decalcification with HCl), which, however, only amounts to very little of the total rock volume. Consequently, discrimination between oil- and methane-seep deposits cannot be accomplished by mere comparison of bulk rock TC and TOC data in this case.

The second unexpected observation is that bulk rock  $\delta^{13}\text{C}$  values of TOC ( $\delta^{13}\text{C}_{\text{TOC}}$ ) do not differ significantly in any of the fossil or modern samples (Table DR1). As mentioned above,

methane is not part of the TOC fraction of seep limestones – a distinction that should be apparent in  $\delta^{13}\text{C}_{\text{TOC}}$  of methane- and oil-seep carbonates. However,  $\delta^{13}\text{C}_{\text{TOC}}$  values from all four sites are too similar as to allow for a distinction between carbon sources (Table DR1).  $\delta^{13}\text{C}_{\text{TOC}}$  values of Gulf of Mexico samples are slightly higher than those of Makran, but for the ancient samples this trend is reversed. This suggests that the heterogeneity of organic carbon – especially in the ancient samples – does not allow for a distinction between oil- and methane-seep limestones.  $\delta^{13}\text{C}$  values of bulk rock powders ( $\delta^{13}\text{C}_{\text{TC}}$ ) do show a distinct trend in that oil-seep deposits are more enriched in  $^{13}\text{C}$  than their methane-dominated counterparts (Table DR1). However, as with phase-specific stable carbon isotope determination, the varying sources of carbon cannot be distinguished for ancient samples as the degree of mixing is unknown (cf. Peckmann and Thiel, 2004).

Besides analyzing TC and TOC contents, an elegant approach to distinguish oil- from methane-seep limestones could be the analysis of fluid inclusions. Fluid inclusion studies have been successfully applied in constraining formation temperatures of carbonate cements, as well as hydrocarbon characterization (e.g. Bodnar, 1990; Orange et al., 1996; Parnell et al., 2002; Haeri-Ardakani et al., 2013; Mathieu et al., 2013). In the scope of this study, the emphasis would have to lie on the determination of the composition of hydrocarbon compounds within fluid inclusions of clear aragonite cement, since later diagenetic cements do not reflect the composition of seepage fluids. However, in the case of clear, fibrous aragonite cement this method is hampered by the small size of fluid inclusions. Natalicchio (2010) attempted to analyze fluid inclusions from fibrous aragonite and to determine their composition, but obtained conflicting results. Using conventional methods, the identification of hydrocarbon compounds in small fluid inclusions of fibrous aragonite cement remains challenging.

In summary, TC and TOC contents,  $\delta^{13}\text{C}_{\text{TOC}}$  values, as well as conventional fluid inclusion analyses do not allow for the discrimination between oil- and methane-derived seep cement in the fossil record.

## MATERIAL AND METHODS

Rock samples from seeps in the southern Gulf of Mexico and Makran were collected with R/V Sonne and R/V Meteor during research cruises SO174 and M74 in 2003 and 2007, respectively (Bohrmann et al., 2004, 2008). Carbonate samples from the Campeche Knolls were collected from the Chapopote asphalt volcano and are described in Naehr et al. (2009). Makran limestones were retrieved at Flare 15 (cf. Himmeler et al., 2015) and are described therein. Samples from the *Dzieduszyckia* and SR4 deposits are detailed in Peckmann et al. (2007) and Peckmann et al. (2002), respectively.

In situ analyses of trace element concentrations were carried out by laser-ablation ICP-MS at the Department of Geosciences, University of Bremen, using a NewWave UP193 solid-state laser coupled to a Thermo-Finnigan Element 2 HR-ICP-MS. The full data set is presented in Table DR2. Samples and standards were ablated with an irradiance of approximately  $1 \text{ GW cm}^{-2}$ , spot sizes of 35 to 100  $\mu\text{m}$ , and a laser pulse rate of 5 Hz. Plasma power was 1200 W, helium (approximately  $0.8 \text{ L min}^{-1}$ ) was used as sample gas, and argon (approximately  $0.8 \text{ L min}^{-1}$ ) was subsequently added as make-up gas. All isotopes were analyzed at low resolution with 5 samples in a 20% mass window and a total dwell time of 25 ms for each isotope. Blanks were measured for 25 s prior to ablation. NIST610 glass was analyzed for external calibration after every 8 to 12 samples using the values of Jochum et al. (2011).

For data quantification the Cetac GeoProTM software was used with  $^{43}\text{Ca}$  as internal standard. Because of high Sr concentrations in many samples of this study, the interference of

$^{86}\text{Sr}^{++}$  on  $^{43}\text{Ca}^+$  was corrected for all carbonate analyses using a factor derived from regular analyses of a Sr-rich carbonate standard (MACS-3). Data quality was assessed by regular analyses of USGS reference materials BCR2G and BHVO2G (basaltic glasses) along with the samples; the data are summarized in Table DR3. External precision and accuracy for these standards are better than 5% for most elements. For consecutive analyses of NIST614 and NIST616 glasses the precision for most REE is better than 5% at the 1 ppm level, and 14 to 55% at the 0.02 ppm level. In Table DR2 all quantified data are shown (except for negative values, which are marked as zero), but we note that values below approximately 0.02 ppm are close to the detection limits.

The low concentrations of Si, Al, Fe, Mn, and Mg in all analyses indicate that the amount of clay minerals, particulate matter, and Fe- and Mn-oxides analyzed together with the carbonates is negligible. For example, Si concentrations below 200 ppm as in most analyses limit the maximum amount of clay minerals (35 to 55 wt.%  $\text{SiO}_2$ ) in the analyzed volume to 0.08 to 0.12 wt.%. Likewise, Mn and Fe contents below 200 ppm imply the presence of less than approximately 0.03 wt.% of Fe- or Mn-oxides.

## CORRELATION COEFFICIENTS

Correlation coefficients between phase-specific  $\sum\text{REE+Y}$ , Mo, and U values and other elements were calculated to determine potential contamination from foreign sources including particulate matter, clay minerals, and Fe- and Mn-oxides (cf. Nothdurft et al., 2004).  $\sum\text{REE+Y}$ , Mo, and U do not correlate with each other, nor do they correlate with any other measured element. Correlation coefficients are shown in Table DR4.

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**TABLE DR1: Sample weights before and after decalcification and resulting non-carbonate fraction of bulk rock samples. Bulk rock total carbon (TC) and total organic carbon (TOC) results and respective stable carbon isotope values. Isotope ratios given in ‰ relative to VPDB.**

Locality	Hand sample designation	Sample prior to decalcification [mg]	Sample after decalcification [mg]	Non-carbonate fraction [%]	TC prior to decalcification [%]	TC after decalcification [%]	Bulk rock TOC [%]	$\delta^{13}\text{C}_{\text{TC}} [\text{\textperthousand}]$	$\delta^{13}\text{C}_{\text{TOC}} [\text{\textperthousand}]$
Chapopote (modern)	TVG-6	21689	1867	8.6	18.9	23.0	2.0	-26.7	-27.8
		20424	1046	5.1	24.4	43.7	2.2	-26.7	-27.6
		17981	1355	7.5	19.7	35.0	2.6	-26.9	-27.4
		17057	1451	8.5	20.8	32.5	2.8	-25.7	-27.7
		15707	1450	9.2	19.8	32.2	3.0	-26.8	-27.9
		16679	1166	7.0	18.3	30.6	2.1	-26.1	-27.1
		16760	1681	10.0	20.8	44.5	4.5	-27.3	-27.6
		18054	20.8	0.1	18.1	23.8	0.03	-26.5	-28.4
		12558	2495	19.9	20.0	17.1	3.4	-27.2	-28.1
		22272	1544	6.9	18.4	20.6	1.4	-27.3	-28.2
Average		17918	1407	8.3	19.9	30.3	2.4	-29.0	-34.4
<i>Dzieduszyckia</i> (Late Devonian)	2.11.5a	17000	45	0.3	13.0	13.9	0.04	-0.7	-31.4
		19500	55	0.3	12.4	15.2	0.04	-1.6	-30.7
		17000	150	0.9	12.4	4.2	0.04	-0.2	-28.2
	2.11.5b	18500	380	2.1	12.8	1.6	0.03	0.3	-29.6
		22000	245	1.1	12.5	2.6	0.03	-1.9	-31.3
		14000	218	1.6	12.9	2.4	0.04	-1.0	-31.9
	2.11.5d	18200	145	0.8	13.0	3.2	0.03	-0.7	-33.3
		13100	148	1.1	13.0	6.5	0.07	-1.7	-32.6
		15700	180	1.1	13.3	5.7	0.07	-1.4	-32.0
		17222	174	1.0	12.8	6.1	0.04	-1.0	-32.2
Makran (modern)	GeoB 12324-2	11200	2115	18.9	0.9	2.7	0.5	-43.3	-32.6
		12500	2373	19.0	0.8	2.4	0.5	-42.3	-30.6
		14800	4394	29.7	0.7	1.5	0.4	-34.4	-32.3
		11200	1923	17.2	0.9	2.1	0.4	-40.1	-30.8
		10000	1792	17.9	1.0	2.4	0.4	-39.4	-30.4
		15000	2846	19.0	0.7	2.2	0.4	-41.2	-29.9
	GeoB 12338-13	13900	2852	20.5	0.7	2.0	0.4	-40.7	-30.1
		10000	2255	22.6	1.0	2.0	0.5	-41.8	-30.2
		10300	1273	12.4	1.0	3.4	0.4	-41.6	-30.0
		12000	1359	11.3	0.8	3.0	0.3	-38.3	-31.3
		12090	2318	18.8	0.8	2.4	0.4	-40.5	-30.3
SR4 (Oligocene)	581a	10100	1935	19.2	10.9	1.5	0.3	-31.2	-31.8
		10500	2410	23.0	9.9	1.7	0.4	-35.4	-28.9
		9000	2101	23.3	9.9	1.5	0.3	-40.0	-52.9
		8200	1540	18.8	10.9	1.6	0.3	-2.7	-46.0
		9600	1859	19.4	10.1	1.5	0.3	-28.9	-28.2
		9200	1714	18.6	10.5	1.8	0.3	-32.0	-28.6
		9300	2860	30.8	9.6	1.8	0.6	-30.2	-34.2
		9300	1895	20.4	9.8	1.6	0.3	-32.4	-27.7
		9400	1705	18.1	10.5	1.9	0.3	-28.3	-31.4
		9400	2002	21.3	10.2	1.7	0.4	-26.9	-27.9

TABLE DR2: Trace and rare earth element contents of clear aragonite cement, all values in ppm. Chapopote samples numbers referred to as “7\_1” and “7\_2” represent two separate thin sections from the sample no. 7; all others referred to as “10” represent one thin section from sample no. 10. Samples “7” and “10” were both collected from TVG-6. Makran sample numbers denoted “1\_1” and “2\_2” represent two thin sections from one hand sample (GeoB 12353-11). For the ancient sites Dzieduszycka and SR4 one thin section was analyzed, respectively. All quantified data are shown, but we note that values below ca. 0.02 ppm are close to the detection limits.

Hand sample designation	Chapopote																												
Sample No.	Mg	Al	Si	Mn	Fe	Ni	Zn	As	Sr	Y	Mo	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	U	$\Sigma REE+Y$	Mo/U
237_7_1	125	0.251	103	0.625	49.1	0.029	0.129	0.355	7691	0.026	0.147	7.76	0.001	0.002	0.002	0.000	0.000	0.003	0.007	0.002	0.000	0.002	0.000	0.000	0.000	5.03	0.044	0.029	
238_7_1	137	0.181	65.8	0.134	57.3	0.184	0.064	0.231	7274	0.032	0.169	8.19	0.002	0.001	0.001	0.009	0.000	0.006	0.000	0.003	0.000	0.000	0.002	0.000	4.81	0.058	0.035		
239_7_1	148	6.33	113	0.572	53.8	0.030	0.044	0.220	8463	0.074	1.16	8.68	0.001	0.014	0.005	0.011	0.006	0.003	0.006	0.001	0.008	0.002	0.000	0.001	0.002	6.14	0.136	0.188	
241_7_1	137	0.277	117	0.836	37.7	0.255	0.239	0.094	7708	0.038	0.237	8.12	0.001	0.001	0.000	0.012	0.000	0.002	0.003	0.000	0.002	0.001	0.000	0.001	0.010	0.001	5.30	0.073	0.045
243_7_1	176	3.272	107	0.746	63.2	0.611	0.221	0.157	8866	0.131	0.554	9.73	0.088	0.073	0.013	0.044	0.026	0.004	0.062	0.003	0.006	0.005	0.010	0.000	0.008	0.002	5.91	0.475	0.094
244_7_1	140	0.417	51.1	0.575	47.2	0.273	0.019	0.231	7236	0.059	0.181	7.41	0.002	0.004	0.001	0.004	0.005	0.004	0.002	0.001	0.000	0.006	0.001	0.006	0.000	6.10	0.096	0.030	
245_7_1	128	0.321	88.2	0.593	43.4	0.332	0.046	0.209	7136	0.026	0.085	8.44	0.008	0.005	0.000	0.003	0.000	0.004	0.004	0.000	0.002	0.000	0.001	0.000	0.002	4.30	0.055	0.020	
246_7_1	110	0.175	98.4	0.473	47.5	0.232	0.064	0.270	7224	0.047	0.256	8.50	0.004	0.005	0.001	0.003	0.004	0.000	0.003	0.000	0.000	0.002	0.001	0.002	3.27	0.074	0.078		
249_7_1	127	1.224	88.8	0.922	58.3	0.031	0.138	0.149	9510	0.117	0.378	9.59	0.014	0.045	0.003	0.033	0.011	0.004	0.004	0.000	0.018	0.005	0.015	0.002	0.005	0.000	4.27	0.277	0.089
250_7_1	119	0.729	36.0	1.11	46.6	0.377	0.016	0.147	9311	0.107	0.380	9.14	0.006	0.010	0.001	0.006	0.005	0.009	0.002	0.001	0.002	0.008	0.001	0.001	0.008	0.002	4.29	0.169	0.089
251_7_1	123	0.885	51.8	0.003	68.5	0.311	0.121	0.048	8944	0.126	0.546	9.19	0.029	0.050	0.005	0.025	0.015	0.004	0.043	0.005	0.040	0.004	0.010	0.001	0.005	0.001	3.69	0.362	0.148
252_7_1	110	0.380	60.7	0.508	65.6	0.379	0.098	0.234	9342	0.086	0.405	8.01	0.003	0.007	0.000	0.000	0.004	0.003	0.006	0.002	0.011	0.000	0.005	0.000	0.001	4.76	0.129	0.085	
253_7_1	107	0.586	64.0	0.303	55.0	0.049	0.051	0.054	9218	0.054	0.289	7.78	0.002	0.004	0.001	0.000	0.000	0.003	0.002	0.001	0.000	0.000	0.000	0.000	0.002	5.06	0.070	0.057	
254_7_1	105	2.41	84.5	0.479	41.9	0.572	0.008	0.101	9523	0.160	0.466	10.2	0.009	0.011	0.002	0.000	0.014	0.004	0.000	0.001	0.003	0.001	0.006	0.003	0.033	0.001	2.41	0.247	0.193
255_7_1	129	3.71	80.1	0.637	50.2	0.146	0.124	0.222	9213	0.095	0.664	7.57	0.017	0.020	0.004	0.003	0.016	0.002	0.004	0.001	0.005	0.002	0.012	0.002	0.003	0.001	5.07	0.189	0.131
256_7_1	115	4.49	81.1	0.046	41.1	0.652	0.168	0.046	8467	0.093	0.499	8.74	0.031	0.048	0.007	0.044	0.000	0.000	0.026	0.005	0.022	0.002	0.006	0.000	0.003	0.002	4.11	0.289	0.121
257_7_1	113	1.22	80.4	0.338	50.2	0.248	0.115	0.142	9615	0.121	0.519	7.38	0.004	0.018	0.003	0.006	0.020	0.000	0.007	0.002	0.024	0.003	0.007	0.001	0.003	0.001	5.06	0.220	0.103
258_7_1	106	0.713	75.2	0.255	54.1	0.044	0.102	0.097	9512	0.113	0.535	7.66	0.015	0.036	0.005	0.012	0.001	0.005	0.010	0.001	0.010	0.000	0.006	0.001	0.001	0.001	5.51	0.218	0.097
776_7_1	110	0.361	93.9	0.948	98.9	0.161	0.539	0.175	7094	0.074	0.120	7.20	0.000	0.010	0.001	0.000	0.010	0.000	0.001	0.001	0.009	0.002	0.012	0.001	0.003	0.001	3.85	0.129	0.031
777_7_1	108	0.693	125	0.458	66.0	0.098	0.114	0.059	7710	0.195	0.255	9.13	0.075	0.161	0.026	0.098	0.031	0.013	0.044	0.007	0.017	0.007	0.013	0.001	0.002	0.000	3.55	0.690	0.072
778_7_1	147	1.90	101	0.027	69.2	0.383	0.256	0.189	8299	0.413	0.694	9.35	0.164	0.320	0.062	0.241	0.030	0.017	0.067	0.015	0.061	0.011	0.041	0.003	0.025	0.004	5.66	1.475	0.123
779_7_1	145	4.01	135	0.948	73.3	0.537	0.592	0.103	8985	0.369	1.176	9.06	0.117	0.292	0.043	0.219	0.061	0.017	0.056	0.012	0.062	0.009	0.041	0.006	0.013	0.003	5.71	1.320	0.206
780_7_1	123	0.320	98.4	0.927	59.7	0.364	0.060	0.070	8893	0.356	0.423	8.52	0.080	0.152	0.021	0.088	0.034	0.003	0.045	0.008	0.074	0.014	0.021						

	898_10	158	5.03	155	0.481	98.8	1.12	0.597	0.205	9316	0.226	0.438	12.9	0.170	0.365	0.052	0.187	0.039	0.013	0.034	0.003	0.126	0.028	0.073	0.032	0.201	0.004	5.84	1.55	0.075
	900_10	161	12.6	153	0.078	101	3.26	0.771	0.060	8632	0.258	0.543	11.7	0.255	0.523	0.071	0.361	0.069	0.004	0.048	0.010	0.067	0.008	0.023	0.001	0.019	0.007	4.96	1.72	0.109

### Dzieduszycka

Sample No.	Mg	Al	Si	Mn	Fe	Ni	Zn	As	Sr	Y	Mo	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	U	ΣREE+Y	Mo/U	
2.11.5e	010_bbc_002	3229	6.28	63.1	294	270	0.11	0.51	0.11	316	1.25	0.045	6.86	0.453	0.209	0.087	0.401	0.113	0.026	0.148	0.026	0.157	0.044	0.105	0.009	0.105	0.017	1.45	3.15	0.031
	011_bbc_003	3084	9.05	71.8	283	543	0.42	1.81	0.20	329	1.33	0.462	7.12	0.480	0.288	0.087	0.401	0.087	0.026	0.131	0.017	0.148	0.035	0.113	0.017	0.096	0.017	1.29	3.28	0.359
	012_bbc_004	3187	6.52	58.0	322	263	0.39	0.44	0.06	321	0.861	0.054	7.34	0.270	0.139	0.052	0.218	0.061	0.009	0.070	0.017	0.061	0.026	0.052	0.009	0.070	0.009	0.779	1.92	0.070
	013_bbc_005	2318	6.22	74.5	312	200	0.46	0.61	0.03	336	0.689	0.018	7.50	0.192	0.113	0.044	0.201	0.017	0.009	0.070	0.009	0.087	0.017	0.052	0.009	0.035	0.009	0.789	1.55	0.023
	014_bbc_006	2716	10.1	97.3	285	782	0.23	1.24	0.14	307	0.715	0.281	9.40	0.218	0.113	0.044	0.244	0.044	0.009	0.078	0.009	0.070	0.017	0.061	0.009	0.061	0.009	0.516	1.70	0.544
	015_bbc_007	2765	5.63	90.8	266	171	0.11	0.70	0.05	350	0.535	0.027	8.00	0.157	0.079	0.026	0.148	0.044	0.009	0.044	0.009	0.070	0.017	0.052	0.000	0.035	0.009	0.481	1.23	0.057
	016_bbc_008	2738	8.21	96.8	268	697	0.70	1.00	0.07	319	0.861	0.091	7.84	0.244	0.122	0.044	0.209	0.052	0.026	0.087	0.017	0.087	0.017	0.061	0.009	0.044	0.009	0.870	1.89	0.104
	017_bbc_009	2485	7.26	78.2	277	273	0.49	0.48	0.04	344	0.95	0.200	7.98	0.323	0.131	0.070	0.340	0.079	0.026	0.113	0.017	0.113	0.026	0.070	0.009	0.061	0.009	0.880	2.34	0.227
	021_bbc_011	4682	8.17	61.1	246	275	0.27	0.36	0.00	336	0.861	0.118	8.86	0.340	0.131	0.061	0.270	0.061	0.026	0.087	0.009	0.105	0.017	0.052	0.009	0.061	0.009	1.10	2.10	0.107
	022_bbc_012	1577	1.50	45.5	74.8	84.9	0.14	0.63	0.07	614	2.23	0.046	4.09	0.973	0.221	0.150	0.708	0.195	0.053	0.248	0.035	0.265	0.053	0.159	0.018	0.142	0.018	1.31	5.47	0.035
	024_bbc_014	2176	4.63	64.0	258	187	0.45	0.68	0.08	318	0.897	0.036	7.62	0.340	0.157	0.070	0.279	0.078	0.026	0.105	0.017	0.096	0.026	0.070	0.009	0.078	0.009	1.23	2.26	0.029
	025_bbc_015	1988	6.76	86.0	349	146	0.18	0.61	0.09	289	0.859	0.018	8.12	0.305	0.157	0.052	0.209	0.052	0.017	0.096	0.009	0.104	0.026	0.070	0.009	0.061	0.017	0.841	2.04	0.022
	026_bbc_016	1743	6.64	82.4	364	112	0.40	0.48	0.04	283	1.08	0.054	6.07	0.409	0.217	0.078	0.339	0.070	0.026	0.104	0.017	0.122	0.035	0.087	0.017	0.078	0.017	1.08	2.70	0.050
	027_bbc_017	2167	5.90	89.2	304	209	0.37	2.03	0.03	353	0.726	0.073	8.47	0.253	0.122	0.052	0.210	0.044	0.017	0.070	0.017	0.052	0.009	0.044	0.009	0.653	1.71	0.111		
	028_bbc_018	3149	6.85	76.8	278	351	0.44	1.59	0.08	292	1.21	0.045	7.12	0.444	0.226	0.096	0.435	0.104	0.017	0.131	0.026	0.139	0.035	0.113	0.017	0.096	0.017	0.787	3.11	0.057
	029_bbc_019	2560	6.94	88.9	277	374	0.37	2.42	0.10	313	1.04	0.091	6.63	0.383	0.183	0.087	0.331	0.096	0.026	0.148	0.017	0.148	0.035	0.096	0.009	0.087	0.017	0.471	2.71	0.192
	030_bbc_020	2533	6.59	68.4	308	222	0.45	1.22	0.12	293	1.27	0.054	6.36	0.435	0.200	0.096	0.444	0.087	0.026	0.165	0.026	0.157	0.035	0.096	0.017	0.113	0.017	0.724	3.18	0.075

### Makran

Sample No.	Mg	Al	Si	Mn	Fe	Ni	Zn	As	Sr	Y	Mo	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	U	ΣREE+Y	Mo/U
GeoB 12353-11	343_1_1	262	0.058	73.8	2.36	81.6	0.240	0.156	0.047	7100	0.031	0.281	11.4	0.002	0.000	0.001	0.000	0.015	0.003	0.000	0.000	0.002	0.000	0.000	0.000	0.005	2.45	0.063	0.115
	344_1_1	340																											

**Table DR3: LA-ICP-MS data of reference standards analyzed along with the samples**

Element	Unit	BHVO-2			BCR-2		
		Mean (N=22)	RSD%	Ref. value	Mean (N=22)	RSD%	Ref. value
Mg	wt.%	4.04	3.1	4.30	1.92	2.4	2.15
Al	wt.%	7.85	2.5	7.20	7.51	3.0	7.09
Si	wt.%	23.8	2.5	23.01	24.8	2.0	25.39
Mn	wt.%	0.134	2.9	0.132	0.149	2.9	0.155
Fe	wt.%	9.69	12.2	8.78	10.3	12.2	9.64
Ni	µg/g	125	2.2	119	12.1	6.0	18
Zn	µg/g	115	7.1	103	143	6.4	127
As	µg/g	3.71	11.0	-	4.13	9.2	-
Sr	µg/g	411	11.0	396	333	1.9	340
Y	µg/g	24.3	4.2	26	33.2	1.6	37
Mo	µg/g	4.28	5.8	3.8	250	2.4	270
Ba	µg/g	137	3.7	131	684	3.2	677
La	µg/g	15.7	2.6	15.2	25.0	3.1	24.9
Ce	µg/g	38.4	1.5	37.5	51.9	2.2	52.9
Pr	µg/g	5.36	2.3	5.35	6.61	2.6	6.7
Nd	µg/g	24.9	4.1	24.5	28.3	3.1	28.7
Sm	µg/g	6.55	5.9	6.07	6.81	5.8	6.58
Eu	µg/g	2.26	7.8	2.07	2.03	8.3	1.96
Gd	µg/g	6.40	5.0	6.24	6.78	4.5	6.75
Tb	µg/g	0.940	5.4	0.92	1.03	4.0	1.07
Dy	µg/g	5.45	6.2	5.31	6.48	4.2	6.41
Ho	µg/g	1.000	6.5	0.98	1.29	4.3	1.28
Er	µg/g	2.59	6.0	2.54	3.72	4.2	3.66
Tm	µg/g	0.349	5.8	0.33	0.508	6.9	0.54
Yb	µg/g	2.13	5.6	2.00	3.46	4.5	3.38
Lu	µg/g	0.297	8.5	0.274	0.506	6.8	0.503
U	µg/g	0.470	3.7	0.403	1.73	4.3	1.69

Reference data are preferred values from the GeoReM data base as of February 2016.

N: number of analyses; RSD%: relative standard deviation.

Table DR4: Correlation coefficients between relevant trace elements in clear aragonite cement.

Seepage system	Oil seep		Methane seep	
Age	Modern	Late Devonian	Modern	Oligocene
Locality	Chapopote	<i>Dzieduszyckia</i>	Makran	SR4
Fe:REE	0.26	-0.22	0.18	0.22
Mn:REE	0.02	-0.64	0.21	0.21
Al:REE	0.36	-0.51	0.54	-0.14
Mo:REE	0.29	0.07	0.58	-0.20
U:REE	-0.13	0.57	0.4	-0.27
Fe:Mo	0.23	0.64	0.26	-0.11
Mn:Mo	0.12	-0.02	0.05	-0.15
Al:Mo	0.06	0.61	0.54	-0.31
Fe:U	-0.09	-0.22	-0.15	0.21
Mn:U	-0.36	-0.30	-0.12	0.19
Al:U	-0.03	-0.29	-0.02	0.03
Mo:U	0.04	0.12	0.17	-0.03