

SUPPLEMENTARY INFORMATION

Geological Background

- *Demerara Rise Basin*

Demerara Rise is a prominent submarine plateau located at 5°N off the coasts of Suriname and French Guyana, South America. The rise stretches 380 km along the coast of Suriname and most of the plateau lies in shallow water (700 m). Demerara Rise consists of rifted continental crust of Precambrian and early Mesozoic age, overlain by 2-3 km thick shallow-marine to pelagic sediments of Cretaceous to Holocene age. The South American margin in the vicinity of Demerara Rise was one of the last areas in contact with West Africa during the opening of the equatorial Atlantic (Erbacher et al., 2004).

The oldest marine sediments of Demerara Rise are Lower Cretaceous (Berriasian-Barremian) in age. Organic-rich sediments occur as laminated black shales from the late Albian to the early Campanian. They are occasionally characterized by very high TOC contents (up to 29% in the Cenomanian to Turonian). Rock-Eval pyrolysis analyses indicate a predominantly marine origin for the organic matter of the shales even at the shallowest sites (Erbacher et al., 2005). Different from black shales deposited in semi-sheltered sub-basins off tropical Africa (e.g. ODP Site 959), Demerara Rise was fully exposed to open marine currents. Seismic data do not support a silled-basin model for the

deposition of the black shales. Instead, an intensified oxygen-minimum layer impinging on the Demerara Rise is believed to have caused long-term oxygen deficiency (Erbacher et al., 2004).

Materials and methods

All samples were powdered, ashed and digested according to the procedures described in previous studies (Weyer et al., 2008). U concentrations were determined with a Thermo Finnigan Element 2 ICP-MS. Separation of U from the sample matrix was achieved with a chromatographic extraction method, based on Eichrom® UTEVA resin (Weyer et al., 2008). U samples were spiked with a $^{236}\text{U}/^{233}\text{U}$ mixed isotopic tracer before the chemical separation to correct for instrumental mass bias (Stirling et al., 2005). U isotopes were measured with a Thermo Finnigan Neptune MC-ICP-MS (Weyer and Schwieters, 2003) at J. W. Goethe University in Frankfurt.

In order to measure the Total Organic Carbon (TOC) in the samples, they were prepared according to the following procedure: 200 mg of powdered sample were taken and pre-dried at 100° C. After drying, ~100 mg of sample were taken into an oven where they were heated up to 550° C to burn the organic carbon, then the heating continued up to 1000° C to burn the inorganic carbon. From the CO_2 that was formed during the two burning phases, the fraction of organic/inorganic carbon was calculated. All measurements were done using a carbon analyzer LECO EC-412 at J. W. Goethe University in Frankfurt.

Supplementary Equations

The U mass balance was modeled assuming that an enhancement of anoxic versus oxic sinks for U results in a shift of the U isotope composition of seawater and sediments, respectively (similarly as earlier modeled for Mo (Arnold et al., 2004)). The isotopic budget of oceanic U can be expressed in terms of a steady state mass balance equation:

$$\delta^{238}U_{\text{input}} = (f_{\text{other}} \times \delta^{238}U_{\text{other}}) + (f_{\text{anox}} \times \delta^{238}U_{\text{anox}}), \quad (1)$$

where the subscripts “input” denotes the riverine input, “other” is the sum of oxic, suboxic and hydrothermal sinks, “anox” indicates anoxic and euxinic sinks, and “ f_{other} ” and “ f_{anox} ” represent the fraction of U that is removed into each sink.

According to the data from previous (Weyer et al., 2008) and this study, the modern conditions of the U isotopic ocean budget are:

$$\delta^{238}U_{\text{input}} = -0.3\text{‰}$$

$$\delta^{238}U_{\text{anox}} = 0.1\text{‰}$$

$$f_{\text{other}} = 90\%$$

$$f_{\text{anox}} = 10\%$$

When applying the previous values to Eq. 1, we obtained that the U isotope composition of the modern “other” sinks (the sum of oxic, suboxic and hydrothermal sinks) is equal to $-0.34\text{‰} \approx -0.3\text{‰}$, reflecting the weak isotope fractionation between seawater and all other sinks (Weyer et al., 2008).

Equation 1 can be used to find the fraction of U removed to each sink during the OAE2, assuming that the input of U to the oceans has a constant U isotope composition

through time and that the fractionation between seawater and the different U sinks is constant. For our model we assume a $\sim 0.15\text{‰}$ offset towards lighter isotopic compositions for all U sinks during the OAE2 compared to modern conditions to model the fractions “ f_{other} ” and “ f_{anox} ”. Such an offset is indicated by the $\delta^{238}\text{U}$ shift of black shales within the OAE2 interval relative to modern black shales and those from above and below OAE2 ($\approx 0.15\text{‰}$). Applying this offset the values for “ $\delta^{238}\text{U}_{\text{other}}$ ” and “ $\delta^{238}\text{U}_{\text{anox}}$ ” during the OAE2 become -0.45‰ and -0.05‰ , respectively. If replacing “ f_{anox} ” by $1 - f_{\text{other}}$ Eq. 1 takes the form:

$$\delta^{238}\text{U}_{\text{input}} = \left(f_{\text{other}} \times \delta^{238}\text{U}_{\text{other}} \right) + \left[(1 - f_{\text{other}}) \times \delta^{238}\text{U}_{\text{anox}} \right], \quad (1.1)$$

Solving Eq. 1.1 for “ f_{anox} ” or “ f_{other} ” gives a value of $\approx 40\%$ for the fraction of U that is removed to anoxic and/or euxinic sinks and a value of $\approx 60\%$ for U removal to the sum of all other sinks during the OAE2. For an estimation of the error, we applied an analytical uncertainty of $\pm 0.1\text{‰}$ to the observed shift (comparable with the 2SE for the black shales within the OAE2 – 0.09‰). Applying these values, we obtained a fraction of U removed to anoxic and/or euxinic sinks of 20% at minimum and 60% at maximum (which defines a range of $40 \pm 20\%$) for the OAE2.

In order to calculate the change of U concentration in the water column during the OAE2, a non-steady state equation was used.

$$\frac{\Delta C}{C} = \frac{\Delta A}{A} = \frac{F_{\text{out}} - F_{\text{in}}}{\tau \times F_{\text{in}}}, \quad (2)$$

where the subscripts “in” and “out” refer to U input and output to the ocean per year, “ C ” refers to the total U concentration in the water column, “ ΔC ” denotes the change in U concentration in the water column (per year), “ A ” is the total amount of U in the oceans, “ ΔA ” is the change of U in the oceans per year “ F_{out} ” and “ F_{in} ” represents the fraction of U going in and out of the water column (per year) and “ τ ” represents the present day U residence time in the oceans (in years).

We assume that during the OAE2, the fraction of U removed to the sum of all other sinks stayed constant but the fraction of U removed to the anoxic and/or euxinic sinks increased to 0.7 times the fraction of U removed to the sum of all other sinks (this follows by the isotope mass balance above, which suggests an increase of the anoxic and/or euxinic sinks to $\approx 40\%$ and a decrease of the other sinks to $\approx 60\%$). From that, it follows that:

$$F_{\text{out}} = 90F_{\text{other}} + 60F_{\text{anox}} = 1.5F_{\text{in}} , \quad (2.1)$$

and

$$F_{\text{out}} - F_{\text{in}} = 0.5F_{\text{in}} , \quad (2.2)$$

where “ F_{other} ” and “ F_{anox} ” are the U output per year into the sum of all other sinks and into anoxic and euxinic sinks during the OAE2. Applying this to Eq. 2 gives:

$$\frac{\Delta C}{C} = \frac{0.5F_{\text{in}}}{\tau * F_{\text{in}}} = \frac{0.5}{500.000} , \quad (2.3)$$

(which is the relative change of the U concentration per year).

The change of the U concentration with time can be expressed as:

$$\frac{C_t}{C} = \left(1 - \frac{\Delta C}{C}\right)^t, \quad (2.4)$$

where “ t ” represents time, e.g. the duration of OAE2 (in years).

From this latter equation, it follows that during an OAE period of ≈ 500 k.y. (the present U oceanic residence time (Colodner et al., 1995)) the U concentration in the seawater was reduced to about 0.6 times its present day concentration.

The decreasing U concentration in the water column during the OAE2 also diminishes the U oceanic residence time compared to modern values. The new U residence time was obtained using the following non-steady state equation:

$$\Delta C = \frac{F_{\text{in}}}{V} - \frac{C}{\tau_{\text{non}}}, \quad (3)$$

where “ V ” denotes the volume of the ocean and “ τ_{non} ” refers to the U oceanic residence under non-steady state conditions, with

$$\Delta C = \frac{F_{\text{out}} - F_{\text{in}}}{V}, \quad (3.1)$$

It follows that:

$$\frac{F_{\text{out}} - F_{\text{in}}}{V} = \frac{F_{\text{in}}}{V} - \frac{C}{\tau_{\text{non}}}$$

Assuming that $\approx 40\%$ of U was removed to anoxic and/or euxinic sinks during the OAE2,

and with that $F_{\text{out}} - F_{\text{in}} = 0.5F_{\text{in}}$, it follows that:

$$\frac{C}{\tau_{\text{non}}} = \frac{F_{\text{in}}}{V} - \frac{F_{\text{out}} - F_{\text{in}}}{V} = \frac{F_{\text{in}} - (-0.5F_{\text{in}})}{V} = \frac{1.5F_{\text{in}}}{V}$$

and

$$\tau_{\text{non}} = \frac{C * V}{1.5 F_{\text{in}}} = \frac{A}{1.5 F_{\text{in}}} = \frac{1}{1.5} \tau_{\text{pres}}$$

where “ τ_{pres} ” is the present day steady state ocean residence time. Accordingly, the ocean residence time of U during the OAE2 was ≈ 300 k.y. This number represents a real ocean residence time for OAE2, assuming a global event.

TABLE DR1. SUMMARY OF U ISOTOPE COMPOSITIONS, U CONCENTRATIONS, TOC VALUES AND Fe_T/Al IN MODERN AND MID-CRETACEOUS BLACK SHALES

Sample		[U] (ppm)	TOC (%)	n	$\delta^{238}\text{U}$ (‰)	2SD	2SE	Fe (%)	Al (%)	Fe/Al
<u>Black Sea Unit I</u>										
BS5	5 cm	11.14	2.55	3	0.17			3.10	1.65	1.88
BS7 [†]	7 cm	13.99	2.59	3	0.03			2.82	1.19	2.37
BS10-1*	N.D.	N.D.*	N.D.	4	-0.04			N.D.	N.D.	N.D.
BS15	15 cm	11.75	2.65	3	0.14			3.43	1.72	2.00
BS17 [†]	17 cm	11.51	2.93	3	0.16			3.14	1.24	2.54
BS20	20 cm	7.14	3.90	3	0.20			4.15	3.36	1.23
BS21-1*	N.D.	N.D.	N.D.	3	-0.03			N.D.	N.D.	N.D.
BS21-2*	N.D.	N.D.	N.D.	2	-0.02			N.D.	N.D.	N.D.
BS25-1*	N.D.	N.D.	N.D.	2	0.04			N.D.	N.D.	N.D.
BS27 [†]	27 cm	15.28	2.52	3	-0.10			2.46	1.04	2.36
BS37 [†]	37 cm	10.52	2.51	3	-0.12			2.76	1.12	2.47
BS43-1*	N.D.	N.D.	N.D.	3	0.05			N.D.	N.D.	N.D.
BS43-2*	N.D.	N.D.	N.D.	2	-0.06			N.D.	N.D.	N.D.
BS55-4*	N.D.	N.D.	N.D.	2	0.04			N.D.	N.D.	N.D.
average		11.62	2.70		0.03	0.20	0.05	3.12	1.62	2.12
<u>Black Sea Unit II</u>										
BS25	25 cm	9.38	4.26	2	0.15			3.71	2.41	1.54
BS25-2*	N.D.	N.D.	N.D.	4	0.21			N.D.	N.D.	N.D.
BS30	30 cm	12.08	6.29	3	0.30			3.82	3.02	1.27
BS40	40 cm	9.98	8.87	3	0.40			3.61	3.33	1.09
BS45	45 cm	16.26	5.11	3	0.00			3.16	1.73	1.82
BS50	50 cm	10.94	4.20	3	0.13			3.56	2.03	1.75
BS55-3*	N.D.	N.D.	N.D.	4	0.43			N.D.	N.D.	N.D.
average		11.73	5.22		0.23	0.31	0.12	3.57	2.50	1.49

average Black Sea black shales				0.10	0.30	0.07	3.31	1.99	1.86
<u>OAE2</u>									
1261A 48 2w 67-68 630.23 mcd	10.97	19.20	3	-0.05			1.96	2.85	0.69
1261A 48 2w 139-140 630.95 mcd	7.18	12.10	2	-0.15			1.47	1.56	0.94
1261A 48 3w 79-80 631.85 mcd	7.97	14.80	3	0.03			1.91	2.93	0.65
1261A 48 3w 141-142 632.47 mcd	9.68	15.50	4	-0.23			1.75	1.35	1.29
1261A 48 4w 142-143 633.97 mcd	8.51	19.60	3	0.12			2.25	3.21	0.70
1261A 48 5w 78-79 634.79 mcd	8.70	18.30	2	-0.07			1.08	1.61	0.67
1261A 48 6w 3-4 635.54 mcd	68.24	34.00	3	-0.14			2.23	2.08	1.07
average	17.32	21.34		-0.07	0.24	0.09	1.81	2.23	0.86
<u>OAE2 after</u>									
1261A 46 1w 30-31 610 mcd	6.16	6.03	2	0.07			0.49	0.63	0.78
1261A 46 1w 90-91 610.60 mcd	13.92	9.25	3	-0.07			0.75	1.61	0.46
1261A 46 5w 130-131 616.84 mcd	12.86	4.99	3	0.16			0.56	0.53	1.04
1261A 47 1w 11-12 619.41 mcd	7.51	12.90	3	0.12			1.33	2.48	0.54
1261A 47 2w 141-142 622.10 mcd	5.66	13.50	3	-0.02			1.61	3.84	0.42
1261A 47 4w 91-92 624.53 mcd	12.87	14.20	3	0.19			1.08	1.97	0.55
1261A 47 5w 91-92 625.98 mcd	7.32	15.80	3	0.07			1.18	2.23	0.53
1261A 47 6w 81-82 627.38 mcd	6.60	3.66	3	0.26			0.81	0.94	0.86
1261A 48 1w 69-70 628.75 mcd	8.45	15.10	3	-0.03			1.32	2.61	0.50
1261A 48 2w 19-20 629.75 mcd	24.46	14.40	2	-0.12			2.88	2.21	1.30
average	10.58	15.69		0.06	0.24	0.08	1.20	1.91	0.70
<u>OAE2 before</u>									
1261A 48 6w 32-33 635.83 mcd	4.26	7.22	4	0.18			0.64	1.18	0.54
1261A 49 1w 125-126.5 638.52 mcd	5.91	6.35	3	0.13			0.91	1.21	0.75

1261A 49 2w 60-61.5 639.35 mcd	37.36	12.80	3	-0.02			1.01	1.75	0.58
1261A 49 4w 1-2 641.76 mcd	24.01	10.10	2	0.05			1.32	1.86	0.71
1261A 49 5w 55-56 643.80 mcd	3.70	3.23	3	-0.06			0.60	0.64	0.93
average	15.05	14.64		0.06	0.20	0.09	0.90	1.33	0.70
average OAE2 before/after				0.06	0.22	0.06	1.10	1.71	0.70

All samples were measured at J. W. Goethe Frankfurt University except for * which were taken from previous studies (Weyer et al., 2008). Black Sea samples were taken during the expedition M72-5 core 25-GC1 and core 25-MUC (*), at a water depth of 418 m (Lat/Lon 42° 6.21' N / 36° 37.43'). Cenomanian-Turonian OAE2 samples and the samples from the before/after intervals come from the ODP Leg 207, site 1261A Demerara Rise, off Suriname, western tropical Atlantic. $\delta^{238}\text{U}$ (‰) refers to the average sample standard bracketing (SSB) obtained from the *n* measurements of each sample. All samples were measured against the SRM-950a U standard. mcd = meters composite depth, *N.D. = not determined.

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