

# Concomitant enrichments of uranium, molybdenum and arsenic in suboxic continental margin sediments

Uranium  
Molybdenum  
Arsenic  
Suboxic continental  
margin sediments  
Removal

Uranium  
Molybdène  
Arsenic  
Sédiments suboxiques  
des marges continentales  
Piégeage

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## ABSTRACT

Elemental analyses were carried out by Neutron Activation Analysis on eleven sediment cores from the North-East Tropical Atlantic, collected at two sites of the French EUMELI programme. Total uranium, molybdenum and arsenic concentrations increase from the surface to about 20 cm depth in cores from the eutrophic site, but remain constant in cores from the mesotrophic site. These profiles clearly highlight an enrichment of the three elements in the sediments from the eutrophic site, linked to the suboxic conditions encountered in these sediments. This entrapping of uranium in suboxic sediments, observed in previous studies (Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991), is thus confirmed at the EUMELI eutrophic site. Furthermore, other elements, such as molybdenum and arsenic, known to be trapped in anoxic sediments, are found to exhibit a similar behaviour in the suboxic sediments. Simple calculations allow the evaluation of the flux of these three elements into suboxic continental margin sediments and the assessment of the importance of this removal in their oceanic budgets. The results confirm the important removal of uranium into suboxic sediments, and suggest, on the other hand, moderate and low removals for molybdenum and arsenic, respectively. Furthermore, the concomitant increase of uranium, molybdenum and arsenic concentrations may be used as a tool to highlight changes in the paleoproductivity of ocean margins.

## RÉSUMÉ

Enrichissements concomitants en uranium, molybdène et arsenic dans les sédiments suboxiques des marges continentales

Onze carottes de sédiment, prélevées sur deux sites du programme français EUMELI situé dans l'Atlantique tropical nord-est, ont été analysées par activation neutronique. Les concentrations d'uranium, de molybdène et d'arsenic dans le sédiment augmentent depuis la surface jusqu'à 20 cm de profondeur dans l'ensemble des carottes du site eutrophe, mais restent constantes dans celles du site mésotrophe. Ces distributions mettent en évidence un enrichissement de ces trois éléments, lié aux conditions suboxiques trouvées dans les sédiments du site eutrophe. Le piégeage de l'uranium dans les sédiments suboxiques, observé lors de précédents travaux (Barnes et Cochran, 1990; Klinkhammer et Palmer, 1991), est ainsi confirmé au site eutrophe du programme EUMELI. En outre, d'autres éléments, comme le molybdène et l'arsenic, connus pour être piégés dans les sédiments anoxiques, présentent un comportement similaire dans les sédiments suboxiques. Les distributions obtenues dans le sédiment ont permis, à l'aide de

calculs simples, d'évaluer les flux de ces trois éléments dans les sédiments suboxiques des marges continentales et d'estimer ainsi l'importance de ce puits dans leur budget océanique. Les résultats confirment le piégeage important de l'uranium dans les sédiments suboxiques, et suggèrent, d'autre part, un piégeage moyen pour le molybdène et faible pour l'arsenic. Cependant, l'augmentation concomitante des concentrations d'uranium, de molybdène et d'arsenic dans les sédiments pourrait constituer un outil approprié pour étudier les variations de paléoproduktivité dans les marges continentales.

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## INTRODUCTION

The hemipelagic sediments of ocean margins, which cover only 7-9% of the world ocean area (Barnes and Cochran, 1990), play an important role in the biogeochemical budgets of some elements. Several studies have shown that they are a major sink for particle-reactive chemical species that are removed from sea water to ocean margin sediments at greater rates than they are deposited in open ocean sediments (Anderson *et al.*, 1983; Lao *et al.*, 1993). This process is termed, "boundary scavenging" (Anderson *et al.*, 1990).

Ocean margin sediments also play an important role in the biogeochemical budget of redox-sensitive elements. Indeed, these sediments tend to be organic-rich and often become suboxic at depth. For example, they may be a source of manganese to the overlying waters, due to the recycling of manganese oxides under the reducing conditions found in these sediments (Heggie *et al.*, 1987). On the other hand, they may be an important sink for elements which are soluble under oxygenated conditions, but which become insoluble under reducing conditions. The best-documented element in this second category is uranium. Many studies have emphasized the occurrence of uranium entrapment in anoxic sediments and highlighted high U fluxes in these sediments (Mo *et al.*, 1973; Anderson, 1987; Barnes and Cochran, 1991). However, in earlier calculations of the oceanic U balance, hemipelagic sediments of the continental shelf and slope were not taken into account (Cochran, 1982). Recently, studies have demonstrated the occurrence of uranium enrichments in the hemipelagic continental margin sediments. Evaluations of U fluxes have shown that the U removal into suboxic sediments could account for 25 to 75% of its riverine input (Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991). Therefore hemipelagic sediments appear to be an important sink for uranium. Unfortunately, up to now, only few estimates of the importance of this sink in the oceanic U budget are available.

Furthermore, other redox-sensitive elements, such as chromium, vanadium, molybdenum and arsenic, have been shown to become enriched in anoxic sediments. Indeed, particulate Cr, V and Mo distributions have clearly highlighted the presence of enrichments of these three elements in anoxic sediments (Malcolm, 1985; Francois, 1988; Pedersen *et al.*, 1989; Shaw *et al.*, 1990) and the occurrence of arsenic removal in these sediments have been emphasized from dissolved As depletion in pore waters (Edenborn *et al.*, 1986; Peterson and Carpenter, 1986). On the

other hand, less attention has been paid to the distribution and possible enrichment of these four elements in suboxic continental margin sediments.

In the present study, total element concentrations have been measured in the suboxic continental margin sediments from the EUMELI eutrophic site. The aim of this study is (1) to check the occurrence of uranium enrichments in these continental margin sediments, (2) to compare the new evaluation of U fluxes into suboxic sediments to the previous works and (3) to identify in these suboxic sediments the possible entrapment of chromium, vanadium, molybdenum and arsenic, known to become enriched in anoxic sediments.

## SAMPLING SITES AND EXPERIMENTAL METHODS

### *Sampling and sediment description*

The sediment cores were collected at two sites, mesotrophic and eutrophic, in the North-East Tropical Atlantic during four cruises of the EUMELI programme (France-JGOFS) (Fig. 1). The integrated primary production has

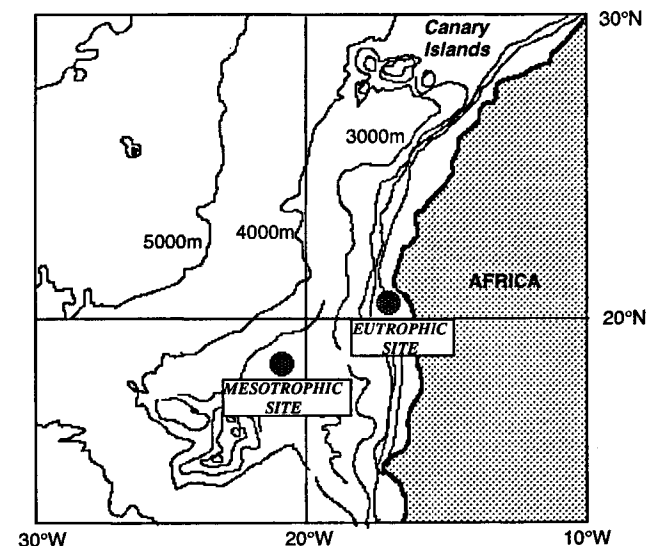


Figure 1

*Location of the mesotrophic and eutrophic EUMELI sites in the North-East Tropical Atlantic.*

Situation des sites mésotrophe et eutrophe du programme EUMELI dans l'Atlantique tropical nord-est.

Table 1

Location of the studied cores. Core KS 04 is indicated in italics, because uranium contents have been measured by  $\alpha$  spectrometry after radiochemical separation. For all other cores, determinations of trace element concentrations have been performed by Neutron Activation Analysis.

Position des carottes étudiées. La carotte KS 04 est indiquée en italique, car les teneurs en uranium ont été mesurées par spectrométrie  $\alpha$  après séparation chimique. Pour toutes les autres carottes, les concentrations des éléments en trace ont été déterminées par activation neutronique.

Core	Site	Coring date	Corer	Depth	Location
KG 06	Eutrophic	July 1989 (cruise EUMELI 1)	Box Corer	1019 m	N 20° 34 W 18° 09
KG 08	Eutrophic	July 1989 (cruise EUMELI 1)	Box Corer	1415 m	N 20° 33 W 18° 27
KB 04	Eutrophic	July 1989 (cruise EUMELI 1)	Tripod Corer	1010 m	N 20° 35 W 18° 09
KTB 09	Eutrophic	February 1991 (cruise EUMELI 2)	Multicorer	2030 m	N 20° 32 W 18° 35
KTB 16	Eutrophic	May-June 1992 (cruise EUMELI 4)	Multicorer	2042 m	N 20° 32 W 18° 36
KTB 17	Eutrophic	May-June 1992 (cruise EUMELI 4)	Multicorer	1259 m	N 20° 32 W 18° 20
KGS 38	Eutrophic	February 1991 (cruise EUMELI 2)	Box Corer	1556 m	N 20° 36 W 18° 29
KGS 71	Eutrophic	May-June 1992 (cruise EUMELI 4)	Box Corer	2046 m	N 20° 32 W 18° 36
<i>KS 04</i>	<i>Eutrophic</i>	<i>July 1989</i> <i>(cruise EUMELI 1)</i>	<i>Piston corer</i>	<i>1010 m</i>	<i>N 20° 35</i> <i>W 18° 09</i>
KTB 11	Mesotrophic	September 1991 (cruise EUMELI 3)	Multicorer	3099 m	N 18° 30 W 21° 05
KTB 14	Mesotrophic	May-June 1992 (cruise EUMELI 4)	Multicorer	3104 m	N 18° 28 W 21° 03
KG 03	Mesotrophic	July 1989 (cruise EUMELI 1)	Box Corer	3112 m	N 18° 33 W 20° 58

been evaluated to about 125 gC/m<sup>2</sup>/y for the mesotrophic site and more than 180 gC/m<sup>2</sup>/y for the eutrophic site. The sedimentation rates have been determined at the two sites from long-lived radionuclide <sup>230</sup>Th<sub>xs</sub> (the excess activity

beyond that in secular equilibrium with <sup>234</sup>U) and <sup>231</sup>Pa<sub>xs</sub> (the excess relative to <sup>235</sup>U) distributions in the sedimentary column. They are respectively 15 mm/ky at the mesotrophic site and 44 mm/ky at the eutrophic site (Auffret *et al.*, 1992).

The redox conditions found in the sediments from these two sites have been studied and described in Rabouille *et al.* (1993) and Gaillard *et al.* (1994). At the mesotrophic site, oxygen is consumed by about 4-5 cm; nitrate is depleted to near zero at about 8-10 cm; the reduction of manganese and iron oxyhydroxides occurs from about 7 and 10 cm depth, respectively. At the eutrophic site, the diagenetic sequence is compressed towards the sediment-water interface: oxygen is completely consumed within the top two centimetres, and nitrate within the top four centimetres. Mn and Fe are used as oxidants to decompose the organic matter, and reduction followed by release of dissolved Mn and Fe occurs from 2 and 5 cm depth, respectively. Although SO<sub>4</sub><sup>2-</sup> concentrations do not display any significant depletion, the increase with depth of the concentration of NH<sub>4</sub><sup>+</sup>, known to indicate the occurrence of sulphate reduction, and the detection of H<sub>2</sub>S by smell suggest that some H<sub>2</sub>S probably occurs at depth in the sediments from this site. Therefore, suboxic conditions prevail at depth in the sediments from the eutrophic site, whereas these conditions are not found in the sediments from the mesotrophic site.

Nine sediment cores were studied from the eutrophic site, an area submitted to the Mauritanian upwelling regime, and three from the mesotrophic site (Tab. 1). The sediments taken from box cores have been studied in order to determine the nature and the mineral composition of the sediments. At the eutrophic site, the CaCO<sub>3</sub> content is 35-45 % and the clay fraction is essentially kaolinite with some smectite. The mineral composition of these sediments does not vary with depth in the top 30 cm. At the mesotrophic site, the CaCO<sub>3</sub> content is 50-60 % in the top 15 cm, and increases to about 80 % below 15 cm depth. The clay fraction mainly contains kaolinite and smectite. Subsampling of all cores was accomplished on board ship and samples were preserved in polyethylene bags. Back in the laboratory, wet sediment samples were dried at 110° C and ground in an agate mortar.

Table 2

Description of the Instrumental Neutron Activation Analysis (INAA) and Epithermal Neutron Activation Analysis (ENAA) experiments.

Caractéristiques de l'analyse par activation neutronique instrumentale (INAA) et épithermique (ENAA).

Neutron Activation Analysis	Elements	Cores	Reactor	Irradiation duration
Instrumental (INAA)	V	KTB 09	ORPHEE (flux: $2 \times 10^{13}$ n/cm <sup>2</sup> /s)	30 seconds
	Mn	all cores		30 seconds
	U, As, Cr, Sc, Th, Fe	KG 03 (*)		2 hours
Epithermal (ENAA)	U, Mo, As, Cr, Sc, Th, Fe	Eutrophic site: KG 06, KG 08, KB 04, KTB 09, KTB 16, KTB 17, KGS 38, KGS 71 Mesotrophic site: KTB 11, KTB 14	OSIRIS (flux: $1.24 \times 10^{14}$ n/cm <sup>2</sup> /s, 10% epithermal neutrons)	2 hours

(\*) Elemental analyses were carried out by INAA for core KG 03, because the OSIRIS reactor was not available.

Table 3

Chemical composition of core KG 06 from the eutrophic site. Concentration errors ( $1\sigma$ ) are based on  $\gamma$  counting statistics.

Composition chimique de la carotte KG 06 du site eutrophe. Les incertitudes ( $1\sigma$ ) sont basées sur les erreurs de comptage.

Depth (cm)	U ( $\mu\text{g/g}$ )	Mo ( $\mu\text{g/g}$ )	A ( $\mu\text{g/g}$ )	Cr ( $\mu\text{g/g}$ )	Sc ( $\mu\text{g/g}$ )	Th ( $\mu\text{g/g}$ )	Mn ( $\mu\text{g/g}$ )	Fe (%)	CaCO <sub>3</sub> (%)
0 - 0.5	2.01 $\pm$ 0.03	n. m.	3.10 $\pm$ 0.44	60.5 $\pm$ 1.0	8.10 $\pm$ 0.02	4.70 $\pm$ 0.02	190 $\pm$ 19	1.69 $\pm$ 0.01	42
1 - 1.5	1.98 $\pm$ 0.03	0.60 $\pm$ 0.06	2.90 $\pm$ 0.44	52.5 $\pm$ 0.7	6.85 $\pm$ 0.02	5.63 $\pm$ 0.01	172 $\pm$ 17	1.68 $\pm$ 0.01	44
4 - 4.5	3.48 $\pm$ 0.03	0.78 $\pm$ 0.06	3.83 $\pm$ 0.41	56.2 $\pm$ 0.4	7.48 $\pm$ 0.01	5.36 $\pm$ 0.01	161 $\pm$ 16	1.75 $\pm$ 0.01	43.6
7 - 8	3.71 $\pm$ 0.02	0.89 $\pm$ 0.05	4.65 $\pm$ 0.42	58.9 $\pm$ 0.8	7.29 $\pm$ 0.02	5.18 $\pm$ 0.01	145 $\pm$ 15	1.77 $\pm$ 0.01	41
9 - 10	4.07 $\pm$ 0.03	n. m.	5.30 $\pm$ 0.47	62.4 $\pm$ 1.1	8.01 $\pm$ 0.03	5.70 $\pm$ 0.02	186 $\pm$ 19	1.80 $\pm$ 0.01	42
11 - 12	3.27 $\pm$ 0.03	0.95 $\pm$ 0.07	4.63 $\pm$ 0.47	53.2 $\pm$ 0.7	7.36 $\pm$ 0.02	5.05 $\pm$ 0.01	153 $\pm$ 16	1.74 $\pm$ 0.01	43
17 - 18	4.38 $\pm$ 0.02	1.29 $\pm$ 0.05	6.16 $\pm$ 0.45	58.1 $\pm$ 1.3	7.93 $\pm$ 0.03	6.09 $\pm$ 0.02	187 $\pm$ 18	2.02 $\pm$ 0.01	41
24 - 25	5.35 $\pm$ 0.03	1.63 $\pm$ 0.07	6.34 $\pm$ 0.38	55.1 $\pm$ 1.0	7.16 $\pm$ 0.03	5.33 $\pm$ 0.02	163 $\pm$ 16	1.82 $\pm$ 0.01	44.2
28 - 29	5.34 $\pm$ 0.04	1.52 $\pm$ 0.08	6.15 $\pm$ 0.37	52.5 $\pm$ 1.0	6.37 $\pm$ 0.03	4.37 $\pm$ 0.01	144 $\pm$ 14	1.61 $\pm$ 0.01	43.8

n. m.: not measured

### Analytical methods

Elemental analyses were carried out by Instrumental Neutron Activation Analysis (INAA) and by Epithermal Neutron Activation Analysis (ENAA) at the Pierre Süe Laboratory (Saclay, France) (Tab. 2). Two USGS standards, Mag1 and P1, were used. Most elemental analyses were carried out by ENAA, because this analytical method allows a better detection of some elements, such as molybdenum and uranium (Chayla *et al.*, 1973). However, since sediment samples and standards were enclosed in aluminium bags for ENAA, corrections were made for each element by subtracting the contribution of the bags (this correction is <10%, except for molybdenum in the top sediment levels, where it may sometimes reach 40%, because the surface sediments contain less Mo).

After irradiation, sediment samples and standards were twice measured for V with a GeLi detector (FWHM 2.1 keV at 1332 keV; relative efficiency: 20%) at the Pierre Süe Laboratory to observe the radioactive decay of <sup>52</sup>V with time. For the other elements, samples and standards were measured with an HP Ge detector (FWHM 1.7 keV at 1332 keV; relative efficiency: 20%) at the Centre des Faibles Radioactivités.

The carbonate content (% CaCO<sub>3</sub>) has been determined with a calcimeter by the CO<sub>2</sub> volumetric method. Precision was estimated to about 2 %.

Many recent papers have demonstrated that, to obtain reliable trace element distributions in pore waters, special sampling procedures are required, specially for measurements of uranium concentrations in reducing marine sediments. Indeed, a brief exposure of these sediments to air can alter *in situ* pore-water U values and lead to anoma-

Table 4

Chemical composition of core KTB 09 from the eutrophic site (errors as in Table 3).

Composition chimique de la carotte KTB 09 du site eutrophe (incertitudes, cf tableau 3).

Depth (cm)	U ( $\mu\text{g/g}$ )	Mo ( $\mu\text{g/g}$ )	As ( $\mu\text{g/g}$ )	Cr ( $\mu\text{g/g}$ )	V ( $\mu\text{g/g}$ )	Sc ( $\mu\text{g/g}$ )	Th ( $\mu\text{g/g}$ )	Mn ( $\mu\text{g/g}$ )	Fe (%)	CaCO <sub>3</sub> (%)
0 - 1	2.38 $\pm$ 0.03	1.01 $\pm$ 0.25	5.30 $\pm$ 0.22	79 $\pm$ 2	67 $\pm$ 15	10.22 $\pm$ 0.06	7.37 $\pm$ 0.03	351 $\pm$ 11	2.65 $\pm$ 0.02	31
1 - 2	2.37 $\pm$ 0.02	0.92 $\pm$ 0.18	5.29 $\pm$ 0.28	81 $\pm$ 2	78 $\pm$ 16	10.68 $\pm$ 0.06	7.54 $\pm$ 0.03	375 $\pm$ 23	2.70 $\pm$ 0.02	31.4
2 - 3	2.79 $\pm$ 0.02	1.15 $\pm$ 0.17	3.92 $\pm$ 0.20	68 $\pm$ 2	59 $\pm$ 12	9.66 $\pm$ 0.06	6.51 $\pm$ 0.03	239 $\pm$ 10	2.20 $\pm$ 0.02	35.8
3 - 4	2.92 $\pm$ 0.03	1.10 $\pm$ 0.21	4.34 $\pm$ 0.24	70 $\pm$ 1	66 $\pm$ 14	9.87 $\pm$ 0.04	7.16 $\pm$ 0.02	282 $\pm$ 17	2.36 $\pm$ 0.01	35
4 - 5	2.89 $\pm$ 0.02	1.18 $\pm$ 0.17	4.60 $\pm$ 0.19	74 $\pm$ 1	65 $\pm$ 13	10.49 $\pm$ 0.04	7.12 $\pm$ 0.02	253 $\pm$ 10	2.53 $\pm$ 0.01	34
6 - 7	2.97 $\pm$ 0.01	1.39 $\pm$ 0.13	4.03 $\pm$ 0.19	68 $\pm$ 1	60 $\pm$ 11	9.63 $\pm$ 0.04	7.06 $\pm$ 0.02	255 $\pm$ 10	2.27 $\pm$ 0.01	35
8 - 9	3.89 $\pm$ 0.02	1.20 $\pm$ 0.10	5.91 $\pm$ 0.25	74 $\pm$ 2	72 $\pm$ 11	9.94 $\pm$ 0.04	7.08 $\pm$ 0.02	240 $\pm$ 29	2.35 $\pm$ 0.02	34
10 - 11	3.90 $\pm$ 0.01	1.28 $\pm$ 0.07	6.33 $\pm$ 0.27	69 $\pm$ 1	76 $\pm$ 18	9.93 $\pm$ 0.04	6.74 $\pm$ 0.02	240 $\pm$ 10	2.36 $\pm$ 0.02	33.8
12 - 13	4.69 $\pm$ 0.02	1.46 $\pm$ 0.08	6.83 $\pm$ 0.33	72 $\pm$ 1	58 $\pm$ 13	9.99 $\pm$ 0.04	7.38 $\pm$ 0.02	233 $\pm$ 10	2.36 $\pm$ 0.02	33
14 - 15	5.10 $\pm$ 0.04	1.56 $\pm$ 0.20	6.72 $\pm$ 0.16	69 $\pm$ 1	62 $\pm$ 11	9.63 $\pm$ 0.04	6.80 $\pm$ 0.02	203 $\pm$ 10	2.25 $\pm$ 0.01	34.3
16 - 17	4.94 $\pm$ 0.02	1.48 $\pm$ 0.12	6.73 $\pm$ 0.12	75 $\pm$ 1	62 $\pm$ 11	10.08 $\pm$ 0.03	6.93 $\pm$ 0.01	238 $\pm$ 25	2.49 $\pm$ 0.01	33
23 - 24	5.29 $\pm$ 0.02	1.71 $\pm$ 0.08	8.23 $\pm$ 0.15	70 $\pm$ 1	61 $\pm$ 16	9.60 $\pm$ 0.04	6.55 $\pm$ 0.02	212 $\pm$ 15	2.32 $\pm$ 0.01	36.3

Table 5

Chemical composition of six other cores from the eutrophic site (errors as in Table 3).

Composition chimique de six autres carottes du site eutrophe (incertitudes, cf tableau 3).

Core	Depth (cm)	U ( $\mu\text{g/g}$ )	Mo ( $\mu\text{g/g}$ )	As ( $\mu\text{g/g}$ )	Cr ( $\mu\text{g/g}$ )	Sc ( $\mu\text{g/g}$ )	Th ( $\mu\text{g/g}$ )	Mn ( $\mu\text{g/g}$ )	Fe (%)	CaCO <sub>3</sub> (%)
KG 08	0 - 0.5	1.96 ± 0.02	0.74 ± 0.13	2.38 ± 0.11	42.1 ± 1.3	6.74 ± 0.05	4.76 ± 0.02	222 ± 6	1.52 ± 0.01	41.1
	14 - 15	4.10 ± 0.03	1.68 ± 0.13	4.68 ± 0.15	46.6 ± 1.2	7.45 ± 0.04	5.86 ± 0.02	196 ± 7	1.65 ± 0.01	40.2
KB 04	0 - 1	2.70 ± 0.02	0.81 ± 0.13	3.13 ± 0.18	48.1 ± 1.6	7.05 ± 0.05	5.27 ± 0.03	206 ± 6	1.48 ± 0.01	41
	19 - 20	3.76 ± 0.02	1.13 ± 0.15	4.64 ± 0.17	45.2 ± 0.8	6.95 ± 0.03	5.07 ± 0.02	192 ± 6	1.53 ± 0.01	40.8
	29 - 30	5.22 ± 0.03	2.62 ± 0.14	5.73 ± 0.19	51.3 ± 0.8	7.46 ± 0.02	5.28 ± 0.02	201 ± 7	1.68 ± 0.01	39.6
KTB 16	0 - 0.5	1.58 ± 0.01	0.82 ± 0.13	3.68 ± 0.12	57.3 ± 2.0	8.75 ± 0.06	5.87 ± 0.03	407 ± 11	2.08 ± 0.02	37.8
	15 - 16	4.37 ± 0.03	1.66 ± 0.15	5.30 ± 0.10	64.5 ± 1.4	9.55 ± 0.05	6.47 ± 0.04	193 ± 9	2.09 ± 0.02	35.8
	19 - 20	4.40 ± 0.03	1.66 ± 0.11	5.01 ± 0.08	57.6 ± 1.0	8.86 ± 0.03	6.17 ± 0.02	189 ± 8	2.04 ± 0.01	36
KTB 17	0 - 0.5	1.52 ± 0.01	0.81 ± 0.13	3.88 ± 0.21	43.3 ± 1.3	6.55 ± 0.04	4.97 ± 0.02	326 ± 9	1.59 ± 0.02	38.8
	15 - 16	3.92 ± 0.03	1.29 ± 0.21	6.83 ± 0.21	51.6 ± 1.2	7.85 ± 0.04	5.47 ± 0.04	193 ± 6	1.90 ± 0.01	37
	20 - 21	3.82 ± 0.02	1.92 ± 0.14	4.84 ± 0.17	52.3 ± 1.2	7.56 ± 0.04	5.27 ± 0.02	191 ± 5	1.73 ± 0.01	37.5
KGS 38	0 - 1	1.54 ± 0.01	1.03 ± 0.11	3.98 ± 0.23	51.2 ± 1.8	7.75 ± 0.06	5.37 ± 0.03	407 ± 11	1.88 ± 0.02	37.6
	15 - 16	3.38 ± 0.02	1.56 ± 0.13	5.15 ± 0.21	57.4 ± 1.1	8.55 ± 0.04	6.37 ± 0.02	223 ± 6	1.98 ± 0.01	40.4
KGS 71	0 - 1	1.60 ± 0.01	0.91 ± 0.09	3.28 ± 0.14	56.5 ± 1.0	8.26 ± 0.03	6.07 ± 0.02	341 ± 9	1.94 ± 0.01	39
	14 - 15	4.31 ± 0.03	1.50 ± 0.17	5.70 ± 0.15	61.8 ± 1.4	8.95 ± 0.04	6.07 ± 0.04	212 ± 8	2.01 ± 0.02	38.8
	19 - 20	4.51 ± 0.02	2.09 ± 0.14	5.34 ± 0.10	66.2 ± 1.0	9.36 ± 0.03	6.78 ± 0.02	224 ± 6	2.18 ± 0.01	38.7

lously high pore-water concentrations (Barnes and Cochran, 1988, 1990; Anderson *et al.*, 1989). Moreover, air exposure experiments of sediment have shown that this increase of pore-water uranium content occurs rapidly (Anderson *et al.*, 1989; Nagao *et al.*, 1992), further supporting the contention that sampling in an inert atmosphere is required to obtain reliable results of U concentrations. As pore-water extraction, performed in other cores from these two sites during the EUMELI cruises, was not carried out in suitable conditions, *i.e.* in an inert atmosphere, measurements of pore-water concentrations of trace elements are not reported in the present study.

## RESULTS

Detailed trace element distributions have been obtained for two cores from the eutrophic site, KG 06 and KTB 09 (Tab. 3 and 4). In the other cores from this site, two or three samples have been analysed, one at the top and the others at about 20 cm depth (Tab. 5). Elemental analyses show that uranium, molybdenum and arsenic concentrations increase with depth in both cores KG 06 and KTB 09, reaching, in these two cores, mean maximal values of about 5.3  $\mu\text{g/g}$ , 1.65  $\mu\text{g/g}$  and 6.5  $\mu\text{g/g}$  for uranium, molybdenum and arsenic, respectively, at about 20 cm depth (Fig. 2). The concentrations of these three elements exhibit similar increases between the top and about 20 cm depth in the other cores from the eutrophic site (Tab. 5). These distributions are typical of entrapments of uranium, molybdenum and arsenic in the sediments from the eutrophic site. On the other hand, chromium and vanadium, two other redox-sensitive elements, do not exhibit any increase of their concentrations with depth (Tab. 3, 4 and 5), sugges-

ting no significant enrichment of these elements in the sediments from the eutrophic site.

Table 6 reports total uranium, molybdenum, arsenic and chromium concentrations in cores from the mesotrophic site (note that for core KG 03, analysed only by INAA, molybdenum concentrations could not be measured). The concentrations of these four elements do not exhibit any increase with depth in the sediments from the mesotrophic site. Furthermore, below about 15 cm depth, the concentrations of all elements, including U, Mo, As, Cr, Sc, Th and Fe, decrease, indicating a change in the bulk sediment composition (Tab. 6). This change was obvious during the sampling of the cores: the sediment colour becomes lighter below 15 cm depth, suggesting a higher carbonate content (% CaCO<sub>3</sub> data in Table 6 are in agreement with these observations).

## DISCUSSION

### *Entrapping of uranium, molybdenum and arsenic in the sediments from the eutrophic site*

Trace element distributions clearly reveal entrapments of uranium, molybdenum and arsenic in the sediments from the eutrophic site, whereas chromium and vanadium, known to become enriched in anoxic sediments (Francois, 1988; Shaw *et al.*, 1990), do not display any significant enrichment in these suboxic sediments. The increases of uranium, molybdenum and arsenic concentrations might be due to changes in the bulk sediment composition. Therefore, it is of importance to check whether this composition does not vary with depth in these sediments. Variations of the concentrations of scandium and thorium, mainly associated with clays (Chester and Aston, 1976), and of the carbonate content would reflect modifications in the sedi-

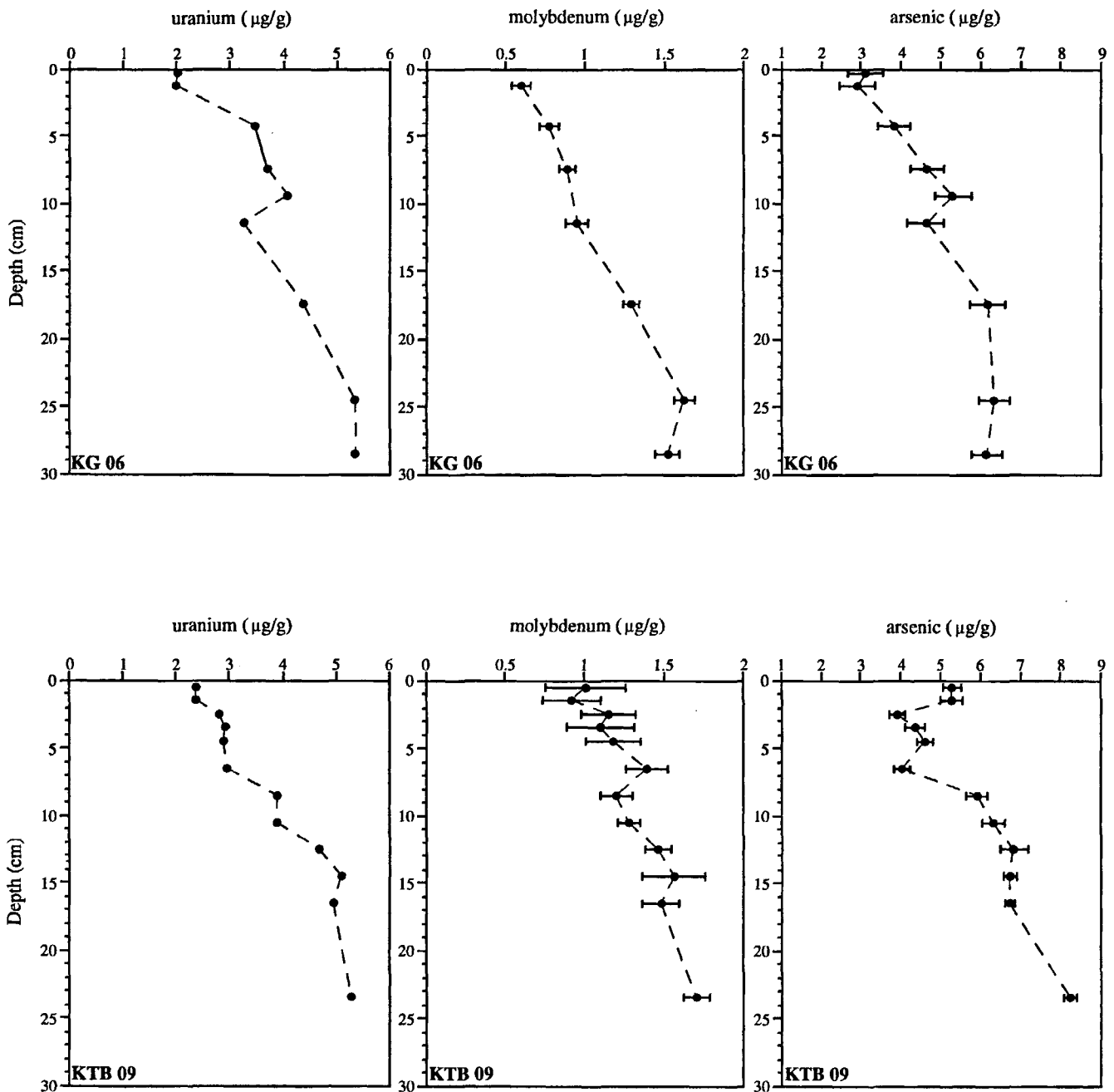


Figure 2

Uranium, molybdenum and arsenic distributions in cores KG 06 and KTB 09 from the eutrophic site. Counting uncertainties for U are approximately size of symbols.

Distributions de l'uranium, du molybdène et de l'arsenic dans les carottes KG 06 et KTB 09 du site eutrophe. Les incertitudes de comptage pour l'U sont approximativement de la taille des symboles.

ment composition. But, since Sc (Fig. 3) and Th contents and % CaCO<sub>3</sub> remain nearly constant (with variations less than 25%) (Tab. 3, 4 and 5), increases of U, Mo and As concentrations with depth can not be explained by changes in the bulk sediment composition. Furthermore, from the observation of lower pore-water uranium values in box cores from the Northeast Atlantic relative to samples collected *in situ* by harpoon, Toole *et al.*, (1984) suggested that pressure changes associated with retrieval of cores might lead to U removal from pore water by carbonate precipitation. But, since pore-water uranium concentrations are about 3 orders of magnitude lower than that in the bulk

sediment, the enrichments found in the sediments from the eutrophic site can not be explained by this process. They are most probably linked to the suboxic conditions encountered in the sediments from this site.

To distinguish between the fraction of the elements incorporated in the detrital phase and the authigenic fraction linked to the redox conditions found in the sedimentary column, we have normalized, for all studied cores from the eutrophic and mesotrophic sites, U, Mo and As concentrations to the Sc content, which is known to be representative of the detrital fraction of the sediment (Fig. 4). The concentration ratios U/Sc, Mo/Sc and As/Sc smoothly

Table 6

Chemical composition of the three cores from the mesotrophic site (errors as in Table 3).

Composition chimique des trois carottes du site mésotrophe (incertitudes, cf tableau 3).

Core	Depth (cm)	U ( $\mu\text{g/g}$ )	Mo ( $\mu\text{g/g}$ )	As ( $\mu\text{g/g}$ )	Cr ( $\mu\text{g/g}$ )	Sc ( $\mu\text{g/g}$ )	Th ( $\mu\text{g/g}$ )	Mn ( $\mu\text{g/g}$ )	Fe (%)	CaCO <sub>3</sub> (%)
KTB 11	0 - 0.5	0.93 ± 0.01	0.87 ± 0.13	3.96 ± 0.15	32.0 ± 0.8	5.45 ± 0.03	4.27 ± 0.02	486 ± 14	1.37 ± 0.01	55.5
	1.5 - 2	0.82 ± 0.01	0.54 ± 0.14	3.60 ± 0.20	33.4 ± 1.2	5.32 ± 0.02	4.33 ± 0.02	740 ± 20	1.43 ± 0.01	54
	6 - 6.5	0.76 ± 0.01	0.72 ± 0.12	3.70 ± 0.20	33.5 ± 0.6	5.25 ± 0.01	4.02 ± 0.01	757 ± 18	1.39 ± 0.01	52
	9 - 10	0.87 ± 0.01	0.61 ± 0.10	3.41 ± 0.11	34.0 ± 1.4	5.54 ± 0.06	4.06 ± 0.03	765 ± 19	1.42 ± 0.02	61.6
	26 - 27	0.62 ± 0.01	0.32 ± 0.13	1.32 ± 0.12	11.8 ± 0.9	2.50 ± 0.02	1.26 ± 0.01	440 ± 12	0.51 ± 0.01	84.7
KTB 14	0 - 0.5	0.94 ± 0.01	1.08 ± 0.12	4.31 ± 0.13	32.3 ± 0.9	5.56 ± 0.03	4.27 ± 0.02	517 ± 14	1.43 ± 0.01	49.8
	10 - 11	0.93 ± 0.01	0.62 ± 0.14	3.56 ± 0.14	34.7 ± 0.9	5.76 ± 0.03	4.27 ± 0.02	502 ± 12	1.54 ± 0.01	48.2
	22 - 23	0.57 ± 0.02	0.38 ± 0.16	1.39 ± 0.17	15.3 ± 0.6	2.30 ± 0.02	1.46 ± 0.01	322 ± 9	0.53 ± 0.01	79.6
KG 03	0	0.86 ± 0.15	n. m.	3.70 ± 0.34	35.3 ± 0.7	6.40 ± 0.03	3.90 ± 0.06	n. m.	1.56 ± 0.01	47.3
	2 - 3	0.86 ± 0.11	n. m.	3.30 ± 0.26	37.0 ± 0.5	6.42 ± 0.02	3.90 ± 0.04	n. m.	1.53 ± 0.01	49.9
	14 - 15	0.80 ± 0.11	n. m.	2.50 ± 0.25	32.8 ± 0.6	5.00 ± 0.03	3.10 ± 0.07	780 ± 20	1.19 ± 0.01	57.4

n. m.: not measured

increase with depth in all cores from the eutrophic site. The results highlight enrichments of these three elements relative to shales, at depth in the suboxic sediments from this site. On the other hand, the concentration ratios remain nearly constant in cores from the mesotrophic site, with values close to the U/Sc, Mo/Sc and As/Sc ratios in shales (Wedepohl, 1969; Gromet *et al.*, 1984; Taylor and McLen-

nan, 1985). However, Mo/Sc and As/Sc ratios exhibit distinctly higher values near the sediment-water interface, at depths corresponding to the oxygen penetration zone of the sediments from the mesotrophic site (Rabouille *et al.*, 1993). This oxic environment favours the precipitation of manganese and iron oxyhydroxides. The Mo and As enrichments at the top of the cores from the mesotrophic site probably reflect the association of these elements with manganese and/or iron oxyhydroxides, as mentioned in earlier studies (Berrang and Grill, 1974; Crecelius, 1975; Edenborn *et al.*, 1986; Shimmield and Price, 1986; Shaw *et al.*, 1990).

The removal of uranium into the sediments from the eutrophic site can be explained by the diffusion of dissolved U (VI) as  $\text{UO}_2(\text{CO}_3)_3^{4-}$  (Langmuir, 1978) from the overlying waters into pore waters of the sediments, followed by the chemical reduction of U (VI) to insoluble U (IV), which precipitates (Anderson, 1987; Anderson *et al.*, 1989; Barnes and Cochran, 1988). Core KS 04 from the eutrophic site, taken with a piston corer, has been analysed by radiochemistry for its uranium content. For the analytical method, we followed the procedure described by Ku (1965), except that we used a  $^{236}\text{U}$ - $^{229}\text{Th}$  spike. Core KS 04 displays a constant U content between 30 and 600 cm depth with a mean concentration value of 4.6  $\mu\text{g/g}$  (Fig. 5), close to those obtained by ENAA at about 20 cm depth in the other cores from this site (Tab. 3, 4 and 5), when U is trapped in the sediment. With a sedimentation rate of 44 mm/ky at the eutrophic site (Auffret *et al.*, 1992), this profile highlights the presence of an uranium enrichment in the sediments of this area over the last 140,000 years at least.

Increasing molybdenum and arsenic concentrations found in the sediments from the eutrophic site demonstrate that Mo and As enrichments are not only observed in very reducing sediments, such as nearshore sediments from the Namibian shelf, estuarine sediments and anoxic sediments of Saanich Inlet, Ucluelet Inlet and Puget Sound (Calvert and Price, 1983; Malcolm, 1985; Peterson and Carpenter, 1986; Edenborn *et al.*, 1986; Francois, 1988; Pedersen *et al.*, 1989), but also occur in suboxic sediments of continen-

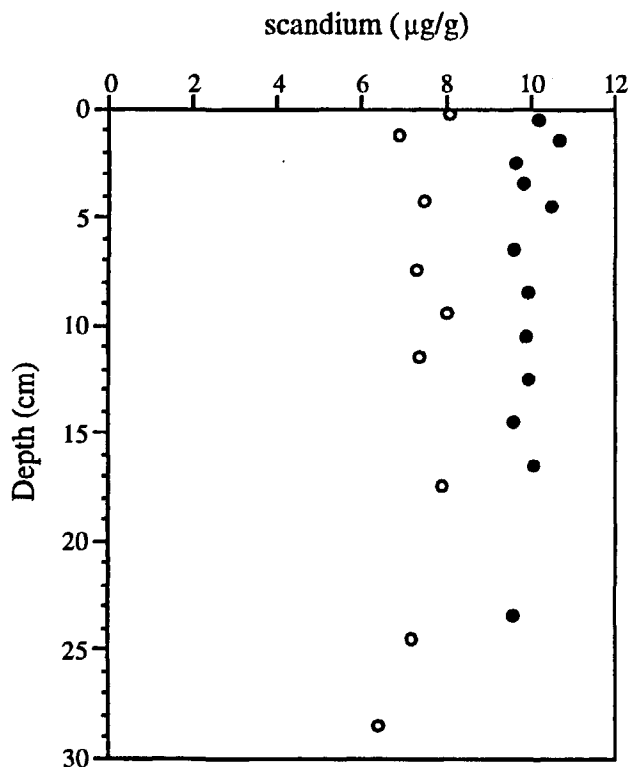


Figure 3

Scandium distributions in cores KG 06 (open circles) and KTB 09 (closed circles) from the eutrophic site. Counting uncertainties for Sc are approximately size of symbols.

Distributions du scandium dans les carottes KG 06 (cercles vides) et KTB 09 (cercles pleins) du site eutrophe. Les incertitudes de comptage pour le Sc sont approximativement de la taille des symboles.

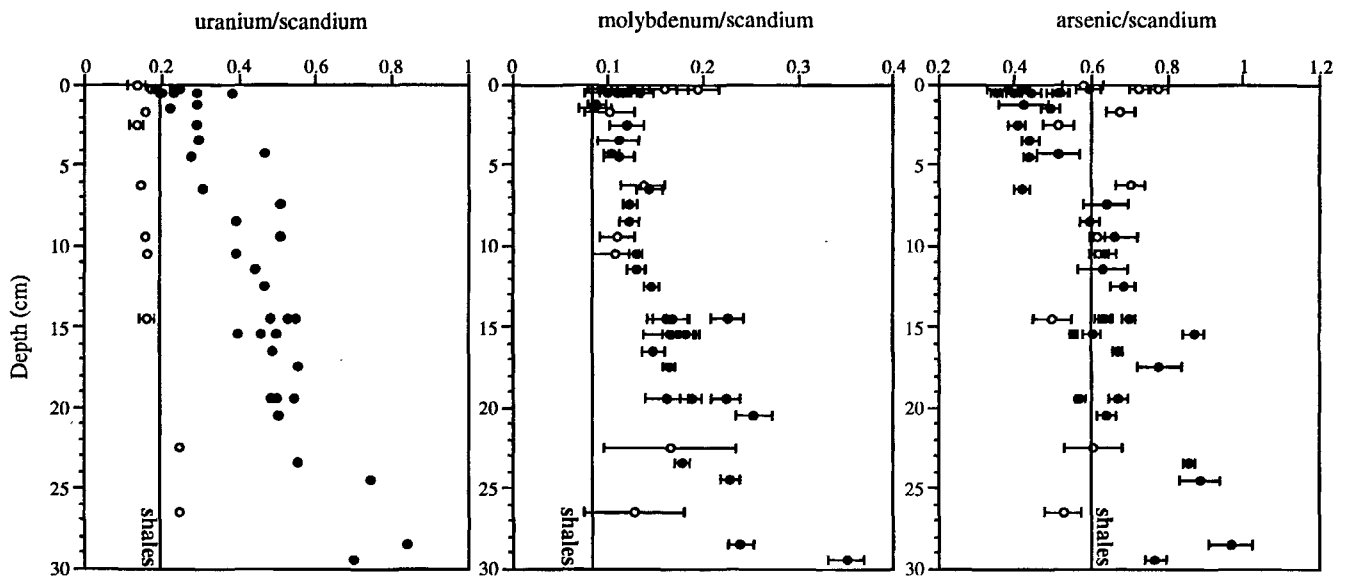


Figure 4

Concentration ratios U/Sc, Mo/Sc and As/Sc versus depth in all cores from the eutrophic (closed circles) and mesotrophic (open circles) sites. The average values of the ratios in shales (Wedepohl, 1969; Gromet *et al.*, 1984; Taylor and McLennan, 1985) are indicated for comparison. Counting uncertainties for U/Sc are approximately size of symbols. The high errors, associated with the Mo/Sc concentration ratios at depth in cores from the mesotrophic site, are due to the dilution of these two elements by carbonates deeper than 15 cm.

Rapports U/Sc, Mo/Sc et As/Sc en fonction de la profondeur dans l'ensemble des carottes des sites eutrophe (cercles pleins) et mésotrophe (cercles vides). Les valeurs moyennes de ces rapports dans les schistes argileux (Wedepohl, 1969; Gromet *et al.*, 1984; Taylor and McLennan, 1985) sont indiquées pour comparaison. Les incertitudes de comptage pour U/Sc sont approximativement de la taille des symboles. Les incertitudes élevées, associées aux rapports Mo/Sc en profondeur dans les carottes du site mésotrophe, sont liées à la dilution de ces deux éléments par les carbonates au-delà de 15 cm de profondeur.

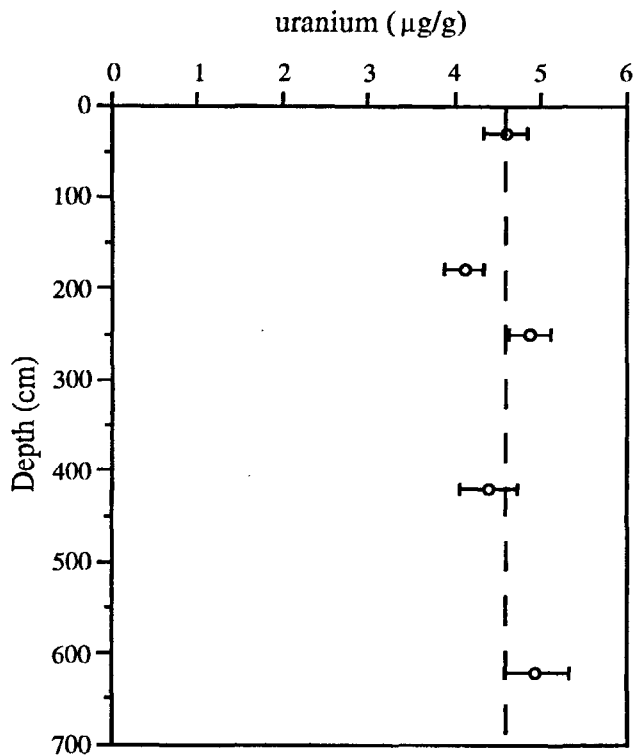


Figure 5

Uranium distribution in core KS 04 from the eutrophic site. The dashed line indicates the mean uranium concentration of 4.6 µg/g.

Distribution de l'uranium dans la carotte KS 04 du site eutrophe. La ligne en pointillés indique la concentration moyenne d'uranium de 4,6 µg/g.

tal shelf and slope. Moreover, the As entrapping in the sediments from the eutrophic site is directly observed from As distributions in the bulk sediment, whereas previous studies have suggested the incorporation of As in anoxic sediments only from the observation of a dissolved As depletion in pore waters (Peterson and Carpenter, 1986; Edenborn *et al.*, 1986).

The occurrence of H<sub>2</sub>S at depth in the sediments from the eutrophic site is probably the main difference with the sediments from the mesotrophic site. Entrapping of Mo in these suboxic sediments may result from coprecipitation of Mo, supplied from pore waters, with FeS in the sediment column, as it has been suggested for anoxic sediments (Bertine, 1972; Pedersen *et al.*, 1989). Arsenic entrapping may be explained by As coprecipitation with iron sulphides or precipitation of distinct As sulphides (Edenborn *et al.*, 1986). As the sediment-water interface is oxic at the eutrophic site, the coprecipitation of Mo and As with FeS or the precipitation of As sulphides probably occur at depth, where the sediments become more reducing.

Special mention must be made of arsenic distribution in core KTB 09, because it exhibits high As concentrations within the top two centimetres (Fig. 2), *i.e.* in correlation to the high Mn contents found in these top levels (Fig. 6). Indeed, the manganese content in core KTB 09 is about 350 µg/g in the top two centimetres, and then decreases to about 250 µg/g deeper in the core. This distribution of manganese, which is one of the electron acceptors available in the sedimentary column (Froelich *et al.*, 1979), well agrees with pore-water oxygen profiles (Rabouille *et*



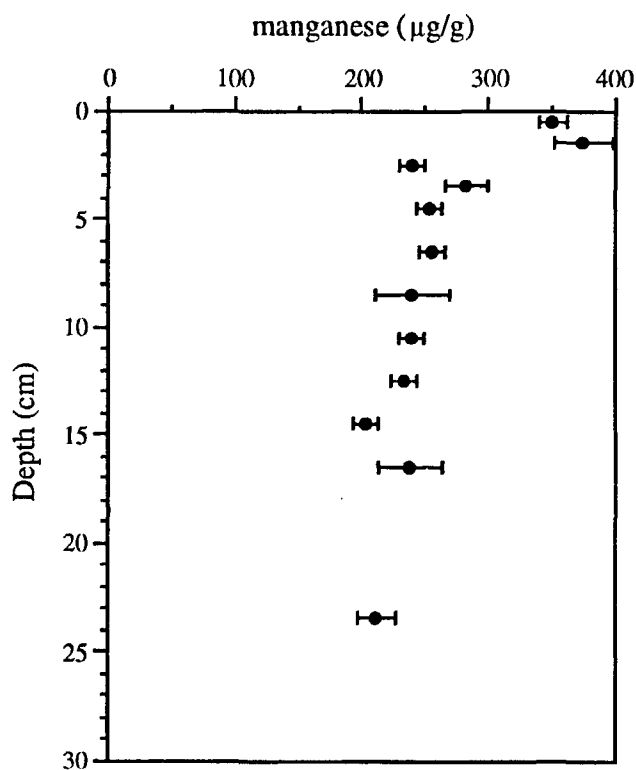


Figure 6

Manganese distribution in core KTB 09 from the eutrophic site.

Distribution du manganèse dans la carotte KTB 09 du site eutrophe.

*al.*, 1993) and illustrates the behaviour of Mn as electron acceptor during the organic matter degradation: the occurrence of oxygen in the top two centimetres favours the precipitation of Mn as oxides; whereas Mn concentrations decrease below this oxic top layer, because of the reduction of  $MnO_2$  to dissolved  $Mn^{2+}$ , which occurs when oxygen is depleted. The correlation between high arsenic and manganese contents within the top two centimetres of core KTB 09 clearly indicates an association of As with the Mn oxides. But, since most of the Fe in the solid phase is associated with the detrital component of the sediment, the coprecipitation of As with Fe oxyhydroxides, emphasized by previous studies (Creclius, 1975; Peterson and Carpenter, 1986; Edenborn *et al.*, 1986), can not be highlighted. However, even if a small fraction (10%) of the Fe content in the surface sediments represents authigenic Fe oxyhydroxides, this phase will be at least an order of magnitude more abundant than the authigenic Mn phase (about 1500 to 2000  $\mu\text{g/g}$  versus 100  $\mu\text{g/g}$ ), and may also contribute significantly to the high As concentrations found at the top of the core.

#### Fluxes of uranium, molybdenum and arsenic into suboxic continental margin sediments

The profiles obtained are characteristic of uranium, molybdenum and arsenic enrichments in continental margin sediments. Since the redox conditions found in the sedimentary column from the eutrophic site are similar to those encountered in other marine borderland sediments (Barnes and

Cochran, 1988; Bender *et al.*, 1989; Reimers *et al.*, 1992), these sediments are representative of those produced in most continental margins. Therefore, the distributions of uranium, molybdenum and arsenic are suitable to the evaluation of their burial rate into the sediments from the eutrophic site and to the assessment of the importance of this sink in their oceanic budgets.

#### 1) Uranium flux into the sediments

Previous estimates of the importance of the suboxic continental margin sediments in the oceanic U balance have shown that this sink accounts for about 25% (Barnes and Cochran, 1990) or 75% (Klinkhammer and Palmer, 1991) of the river inflow. Results found in the present study allow the determination of the uranium flux into hemipelagic sediments and the comparison with the previous evaluations.

The rate of U accumulation in the sediments  $R_U$  can be determined from the solid phase data, using the relationship:

$$R_U = U_A \rho S \quad (1)$$

where  $U_A$  is the authigenic uranium activity at depth in the sediment,  $\rho$  the dry bulk sediment density ( $\text{g dry sediment} / \text{cm}^3$  wet sediment) and  $S$  the sediment accumulation rate. The authigenic uranium contents of the sediments have been calculated as:

$$U_A = U_T - (U/Sc)_{sh} \times Sc_T \quad (2)$$

where A refers to the authigenic fraction and T to the total measured concentration.  $(U/Sc)_{sh}$  represents the U/Sc concentration ratio in shales (0.195, Taylor and McLennan, 1985).

Authigenic uranium contents display a smooth increase with depth in all cores from the eutrophic site, reaching an  $U_A$  content of about 4  $\mu\text{g/g}$  at depth, whereas no or very little authigenic uranium is found in cores from the mesotrophic site (Fig. 7a). With a sedimentation rate of 44 mm/ky (Auffret *et al.*, 1992), a measured dry-bulk sediment density of 0.55  $\text{g/cm}^3$  and an authigenic uranium concentration  $U_A$  of about 4  $\mu\text{g/g}$ , we have estimated an uranium flux into the sediments from the eutrophic site of about 9.7  $\mu\text{g/cm}^2/\text{ky}$ . This value is in the range of uranium fluxes calculated by Barnes and Cochran (1990) in the NW Atlantic hemipelagic sediments from pore-water uranium profiles (0 – 16  $\mu\text{g/cm}^2/\text{ky}$ ).

We can try to estimate from our particulate U profiles, the amount of uranium trapped in the hemipelagic sediments. With an ocean area of  $2.9 \times 10^{17} \text{ cm}^2$  for hemipelagic sediments (Klinkhammer and Palmer, 1991), we obtain a rate of U accumulation in these continental margin sediments of  $2.8 \times 10^9 \text{ g U/y}$ . This uranium accumulation rate falls in the range of U removal in suboxic sediments estimated by Barnes and Cochran (1990) ( $2.5 - 3.2 \times 10^9 \text{ g U/y}$ ) (Tab. 7). However, our removal value is lower than the rate found by Klinkhammer and Palmer (1991) from their uranium profiles in sediment pore-waters ( $6.7 - 28.6 \times 10^9 \text{ g U/y}$ ) (Tab. 7). The discrepancy between various estimates of U accumulation rates in hemipelagic sediments may be explained by local variations of the importance of U removal in suboxic sediments; therefore, a better oceanic uranium balance requires more particulate

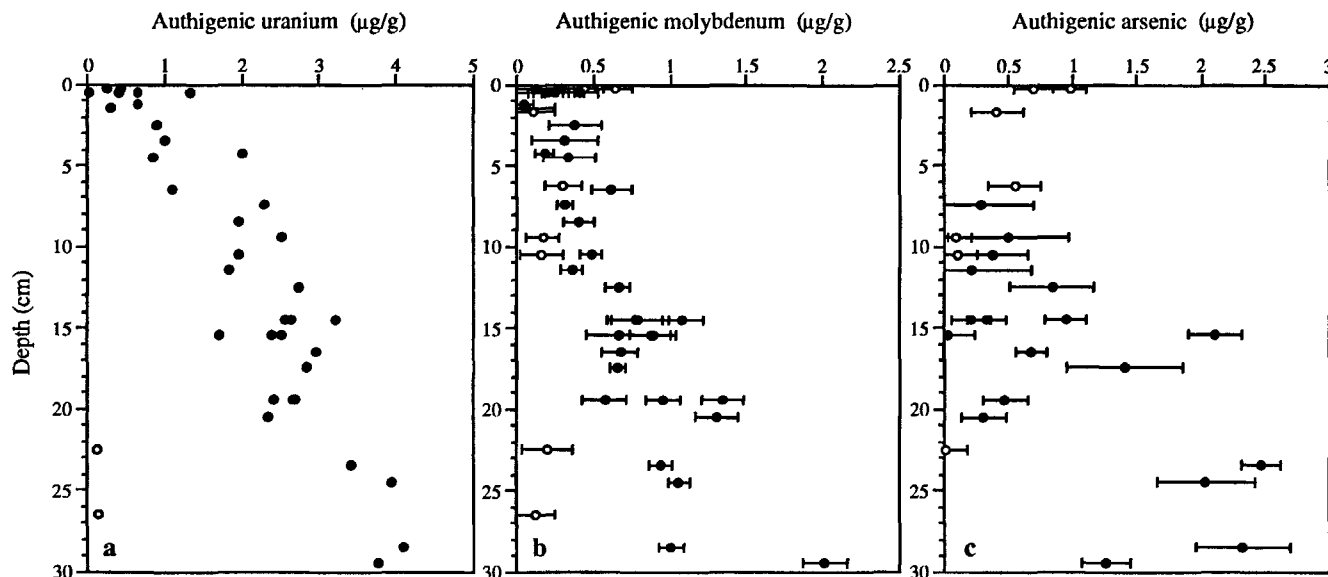


Figure 7

Authigenic uranium (a), molybdenum (b) and arsenic (c) concentrations versus depth in all cores from the eutrophic (closed circles) and mesotrophic (open circles) sites. Counting uncertainties for authigenic U are approximately size of symbols.

Concentrations d'uranium (a), de molybdène (b) et d'arsenic (c) authigènes en fonction de la profondeur dans l'ensemble des carottes des sites eutrophe (cercles pleins) et mésotrophe (cercles vides). Les incertitudes de comptage pour l'U authigène sont approximativement de la taille des symboles

and pore-water uranium data in hemipelagic sediments from several different locations. Using an uranium supply from the world's rivers (which is the only significant source of dissolved uranium to the oceans) of about  $9.84 \times 10^9$  g U/y ( $8.48 \times 10^9$  g U/y from the river inflow (Sarin *et al.*, 1990) and  $1.36 \times 10^9$  g U/y from the Amazon shelf sediments (McKee *et al.*, 1987)), the removal of uranium in hemipelagic sediments accounts for about 29% of the riverine input by our estimate.

2) Molybdenum and arsenic fluxes into the sediments

Using the same relationship (1) for molybdenum and arsenic distributions, we determine Mo and As fluxes into the sediments from the eutrophic site. Authigenic molybdenum and arsenic have been obtained in the same way as for ura-

anium (relationship (2)), with  $(Mo/Sc)_{sh}$  and  $(As/Sc)_{sh}$  values of 0.08 and 0.6, respectively (Wedepohl, 1969; Gromet *et al.*, 1984; Taylor and McLennan, 1985).

Both the authigenic Mo and As contents exhibit smooth increases with depth in the sediments from the eutrophic site (Fig. 7b and 7c). However, As only displays authigenic contents deeper than 7 to 10 cm. At the mesotrophic site, authigenic Mo and As contents do not exhibit any increase with depth and remain very low, except at the sediment-water interface, where the higher contents reflect the probable association of these two elements with Mn and/or Fe oxyhydroxides, as it has already been discussed.

With an authigenic concentration at depth in cores from the eutrophic site of about 1.3 to 2 µg/g for molybdenum and

Table 7

Authigenic concentrations, accumulation rates in the sediments from the eutrophic site, and evaluation of the importance of the removal into suboxic continental margin sediments in the oceanic budgets of uranium, molybdenum and arsenic.

Concentrations authigènes, taux d'accumulation dans les sédiments du site eutrophe, et évaluation de l'importance du piégeage dans les sédiments suboxiques des marges continentales dans les budgets océaniques de l'uranium, du molybdène et de l'arsenic.

Elements	Authigenic concentration (µg/g)	Flux into the sediments from the eutrophic site (µg/cm <sup>2</sup> /ky)	Accumulation rates in hemipelagic sediments (g/y)	Dissolved input to the oceans (g/y)	Importance of the removal in hemipelagic sediments (%)	References
uranium	4	9.7	$2.8 \times 10^9$	$9.84 \times 10^9$	29	this study
			$2.5-3.2 \times 10^9$	$11.4 \times 10^9$	21.9 - 28.1	Barnes and Cochran (1990)
			$6.7 \times 10^9$	$8.6 \times 10^9$	78	Klinkhammer and Palmer (1991)
molybdenum	1.3-2	3.1-4.8	$0.9-1.4 \times 10^9$	$16.5 \times 10^9$	5.5-8.5	this study
arsenic	2.4	5.8	$1.7 \times 10^9$	$56.1 \times 10^9$	3	this study

2.4  $\mu\text{g/g}$  for arsenic (Fig. 7b and 7c), we obtain fluxes in the hemipelagic sediments from this site of about 3.1 to 4.8  $\mu\text{g/cm}^2/\text{ky}$  and 5.8  $\mu\text{g/cm}^2/\text{ky}$  for molybdenum and arsenic, respectively. As the selected authigenic contents at depth correspond to the highest authigenic concentrations of molybdenum and arsenic encountered in the whole cores from the eutrophic site, these estimates should be regarded as upper limits for the fluxes of Mo and As into the sediments from this site. Just as for uranium, we try to evaluate Mo and As amount trapped in hemipelagic sediments as well as the importance of this sink in their biogeochemical cycle in the ocean. We obtain accumulation rates of  $0.9$  to  $1.4 \times 10^9$  g Mo/y and  $1.7 \times 10^9$  g As/y in hemipelagic sediments. Using a riverine dissolved Mo average concentration of 0.5  $\mu\text{g/l}$  (Martin and Meybeck, 1979) and a total river discharge of  $3.3 \times 10^{16}$  l/y (Milliman, 1991), we obtain a dissolved molybdenum riverine input of  $16.5 \times 10^9$  g Mo/y. The same calculation, made for As with a mean dissolved As concentration in the rivers of 1.7  $\mu\text{g/l}$  (Martin and Windom, 1991), leads to a dissolved arsenic input to the oceans of  $56.1 \times 10^9$  g As/y. The removal of molybdenum and arsenic in hemipelagic sediments accounts for respectively about 5.5 to 8.5 % and 3% of their respective input in the oceans.

These results clearly demonstrate that suboxic sediments from continental margins are an important, moderate and weak sink for uranium, molybdenum and arsenic, respectively (Tab. 7). From this study, it appears that the removal of uranium in the sediments probably requires less reducing conditions than for molybdenum and arsenic. Indeed, authigenic contents rapidly increase from the first top centimetres for uranium (Fig. 7a), suggesting that the U removal probably begins near the sediment-water interface; whereas, in the top 10 cm, they exhibit only a small increase for molybdenum and are not visible for arsenic (Fig. 7b and 7c). Thermodynamics predict that reduction of uranium could occur before the dissolution of ferric hydroxide (Cochran *et al.*, 1986). Uranium reduction also could take place through the oxidation of  $\text{HS}^-$  (Langmuir, 1978; Cochran *et al.*, 1986; Klinkhammer and Palmer, 1991). The removal of molybdenum and arsenic into the sediments probably occurs deeper in the sediment column, suggesting that more reducing conditions, *i. e.* reduction of  $\text{SO}_4^{2-}$  and presence of  $\text{H}_2\text{S}$ , are required to allow an effective entrapping of these elements in the sediments. The sediment cores from the eutrophic site do not probably exhibit enough reducing conditions to allow higher enrichments for these two elements.

Although continental margin sediments only are a moderate and weak sink for molybdenum and arsenic, respectively, the concomitant enrichments of U, Mo and As in the sediments lead to a peculiar chemical composition with increasing concentrations of these three elements. Since in this region of the world ocean, the composition of the sediment and pore-water reflects the trophic conditions of the upper water column (Rabouille *et al.*, 1993), this specific chemical behaviour of U, Mo and As, linked to the redox conditions encountered in the sedimentary column, might be used as a tool for qualitatively reconstructing changes in the paleo-productivity of ocean margins. On the other hand, the absence of such concomitant enrichment in the

sediment strongly suggests that suboxic conditions are not present in the sedimentary column and allows the confirmation that sedimentation has occurred under oxygenated bottom water conditions.

Chromium and vanadium, trapped in anoxic sediments (Francois, 1988; Shaw *et al.*, 1990), do not display any significant enrichment in the suboxic sediments from the eutrophic site. However, simple calculations prove that our vanadium data in core KTB 09 (Tab. 4) do not allow us to conclude whether or not vanadium is removed into the suboxic sediments. With a dissolved vanadium riverine input of  $33.7 \times 10^9$  g V/y (estimated from a mean concentration of vanadium in the rivers of 1  $\mu\text{g/l}$  (Broecker and Peng, 1982)), calculation shows that a 30% removal (similar to the uranium removal found in this study) in hemipelagic sediments would correspond to an enrichment of about 15  $\mu\text{g/g}$  of vanadium in the core, which represents only an increase of about 25% of the vanadium concentration in the sediment (*versus* an increase of about 210%, 240% and 75% for uranium, molybdenum and arsenic, respectively). This enrichment is too low and the analytical errors on vanadium data too important to allow the observation of a vanadium concentration increase with depth in the core, even if hemipelagic sediments represent a sink of 30% in the oceanic vanadium budget. In the same way, if chromium is removed in suboxic sediments, with the Cr authigenic fraction remaining very low compared to the fraction incorporated in the detrital phase, a marked increase of Cr concentrations will not be found in the sediments from the eutrophic site. Studies of pore-waters appear to be required to ascertain whether or not vanadium and other elements are actively trapped by hemipelagic sediments.

## CONCLUSION

The present study highlights uranium entrapping in the suboxic continental margin sediments of the North-East Tropical Atlantic. Simple calculations prove the importance of the hemipelagic sediments in the oceanic balance of this element: the removal of uranium accounts for 29% of its riverine input by our estimate. This removal value confirms Barnes and Cochran's (1990) evaluation. However, the discrepancy between Klinkhammer and Palmer's value (1991) and our estimate shows that more uranium data in hemipelagic sediments are required to draw up a better oceanic uranium balance.

Two other elements, *i. e.* molybdenum and arsenic, known to be trapped in anoxic sediments, also display enrichments in the continental margin sediments from the eutrophic site. However, these suboxic sediments probably represent a less important sink for these two elements (5.5 to 8.5% and 3% of the molybdenum and arsenic riverine input, respectively). Molybdenum and arsenic require more reducing conditions than uranium in the sedimentary column to become enriched in the suboxic continental margin sediments. However, the concomitant increases of uranium, molybdenum and arsenic concentrations in the sediments, linked to the primary production found in the overlying

surface waters, may be used as proxy indicators of the changes in the paleo-productivity of the ocean margins.

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