



Mobility of Mo, U, As, and Sb within modern turbidites

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ARTICLE INFO

Article history:

Received 23 May 2007

Received in revised form 8 May 2008

Accepted 9 June 2008

Keywords:

modern turbidites

uranium

molybdenum

arsenic

antimony

ABSTRACT

We present and discuss porewaters and sediment data of Mn, Fe, Mo, U, As, and Sb within four recent turbidites from the Capbreton Canyon (SW-France). The deposition of turbidites on continental margins exerts strong influence on the fate of trace-metals, causing trace-metal migration and/or immobilization. The down-core distribution of the elements here depends entirely of ongoing diagenetic processes. Rather than the diffusion of O_2 , the persistence of Fe/Mn-oxides under anoxic conditions led to anoxic reoxidation of numerous species as NH_4^+ , reduced S compounds, and trace-metals. Metal-oxides thus control the immobilization of Mo and As in the solid phase, and the remobilization of U and Sb to the porewaters. Although the low sulphide production prevents anoxic authigenesis of Mo and As, reducing conditions below each horizon rich in Mn/Fe-oxides resulted in U and Sb accumulation. The exact mechanisms of Sb immobilization are not known, but it is most certainly different from that of As.

The profile shapes of Mn and U were used to estimate the age of the turbidite deposits, which cannot be determined by conventional radionuclide methods. Our interpretations, however, depend on calculations of diffusion coefficient, particularly for U. A simple diffusive model applied to Mn suggested that the age of the latest deposit (noted T1) was ~22 months. This date is close to the time elapsed between the core sampling and the last known turbiditic event in the Capbreton Canyon (i.e., Martin Storm, ~18 months). Using the U data set and depending on diffusion coefficients used, the estimated ages of the deeper layers were 4–7 yr for T2 and 7.5–14 yr for T3. The reliability and precision of this new approach to date sediments at short timescales is limited by the ignorance of a precise value for U diffusion coefficient. Reducing uncertainty on U diffusion coefficient will greatly support application of the proposed approach.

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1. Introduction

Steady-state conditions are often assumed to describe early diagenetic processes in modern sediment. In reality, disruption of steady-state situations by changing organic carbon input, oxygen content of bottom water, sedimentation rate or biological activity, results in transient state diagenesis (Sundby, 2006). Seabed reworking caused by sediment-resuspension, -transport, and -deposition as well as low-frequency disturbances such as large storms and mass flows has also had an impact on diagenetic reactions and benthic communities (Aller, 1989; Saulnier and Mucci, 2000; Anschutz et al., 2002; Deflandre et al., 2002; Mucci et al., 2003; Chaillou et al., 2007).

Distal deep-sea turbidites, which cover geological periods (i.e. a few thousands of years to several hundreds of thousands of years), are considered as an ideal “natural laboratory” to study the postdepositional mobility of elements sensitive to redox conditions (Colley and Thomson, 1985; De Lange et al., 1987; Jarvis et al., 1988; Middelburg, 1993; Rosenthal et al., 1995; Crusius and Thomson, 1999, 2003;

Thomson et al., 1998a,b). One of their diagenetic features is their potential to extend the oxic/anoxic front on several decimetres or meters depth, creating well-separated diagenetic reaction zones (e.g. oxygen consumption, nitrate reduction, Mn- and Fe-oxide reduction, then sulphate reduction; Froelich et al., 1979), and well-developed redox-controlled separation of trace-metals. On continental margin environments, where the organic carbon rain rates are high, specific redox zones are contracted below the sediment/water interface favouring their vertical overlap. In addition, the time elapsed between successive sedimentary events are often too short to allow complete ecosystem recovery (Aller, 1989; Anschutz et al., 2002; McKee et al., 2004) provoking a complex behaviour of trace-metals.

Sensitivity of trace-metals to sediment redox conditions is one prerequisite for using as redox or bio-productivity indicators (Calvert and Pedersen, 1993; Morford and Emerson, 1999; Böning et al., 2004; McManus et al., 2005, 2006; Morford et al., 2005; Tribouillard et al., 2006). Despite correlations between concentration of trace-metals and sediment redox conditions, it is not clear whether the relationship is predictable particularly under non-steady state conditions. In this paper, we report the behaviours of manganese (Mn), iron (Fe), molybdenum (Mo), arsenic (As), antimony (Sb), and uranium (U) in recent multi-layers of sediment formed by four successive turbidites, using both porewater and sediment metal profiles. Because the frequency of turbidity currents

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is high within this system (Mulder et al., 2001; Gaudin et al., 2006), the Capbreton Canyon, a submarine canyon which incises the Aquitain Margin (SW-France), is an ideal environment to investigate the coupled transport-reaction processes under non-steady state conditions. Our objective was to understand how physical reworking of the seabed which is common on continental margin influences the authigenic behaviour of trace-metals.

2. Methods

2.1. Sampling

In June 2001, a 50-cm sedimentary core (10 cm diameter) was recovered from 748 m water depth in the axis of Capbreton Canyon (43°36.238'N–1°45.544'W, station R, Fig. 1) with a SMBA-type multicorer which collects overlying bottom water and an undisturbed sediment/water interface (SWI). The overlying water was sampled immediately after core recovery for both dissolved O₂ measurements by Winkler titration and dissolved trace-metals. Profiles of O₂ in sediment porewaters were measured on board using a voltammetric microelectrode technique (Brendel and Luther, 1995; Luther et al., 1998) and completed within 15 min after core recovery. The core was then sub-sampled at 0.5 cm intervals near the SWI and up to 2 cm intervals at depth (see Electronic data). One sub-sample was immediately stored in a pre-weighed plastic vial and frozen under inert atmosphere (N₂) for water content (porosity), radionuclide activities determination, and sediment composition. Another sub-sample was centrifuged under N₂ at 5000 rpm for 20 min to extract porewaters. Porewater samples were immediately filtered (0.2 μm, cellulose acetate syringe filter purged with N₂) and acidified (1/100

ultrapur HNO₃ 65%) for metal analysis. A second tube from the same multi-core deployment was opened on board for sedimentological observations. On return to the laboratory, this core was analyzed by X-ray imagery and sampled for grain size measurements, determined by laser diffractometry (Malvern Mastersizer).

2.2. Analytical methods

Sediment sub-samples were freeze-dried and homogenized by grinding using an agate mortar and pestle. Total C, total S, and organic C concentrations were measured on 50 mg freeze-dried sediments by infrared spectroscopy using a LECO C-S 125 (Cauwet et al., 1990). Organic carbon was measured after acidification with 2 M HCl to remove carbonates. Inorganic carbon concentration was estimated from the difference between total and organic C. The precision of these analyses was ±3 μmol/g.

Sediment aliquots (30 mg) were digested in closed Teflon reactors (Savillex®) with 2000 μl of HF (suprapure), 250 μl of HNO₃ (65% ultrapur), and 750 μl of 30% ultrapur HCl as described elsewhere (Chaillou et al., 2002, 2003; Schäfer and Blanc, 2002; Audry et al., 2006). The reliability of the analytical methods was continuously monitored by parallel analyses of international certified reference materials (MESS-2, SL-1, NIST 1646; Table 1) in each batch of samples. Freeze-dried sediments were leached with an ascorbate solution to remove elements associated to the reactive pool of reducible Fe(III)-oxides and Mn(III/IV)-oxides (Kostka and Luther, 1994; Anschutz et al., 2005; Hyacinthe et al., 2006). A separate extraction was also performed on freeze-dried sediment with 1 N suprapur HCl to dissolve reactive elements associated with ferrous Fe minerals (AVS, Fe-carbonates, Fe-monosulphides, and clay minerals) and reactive Fe

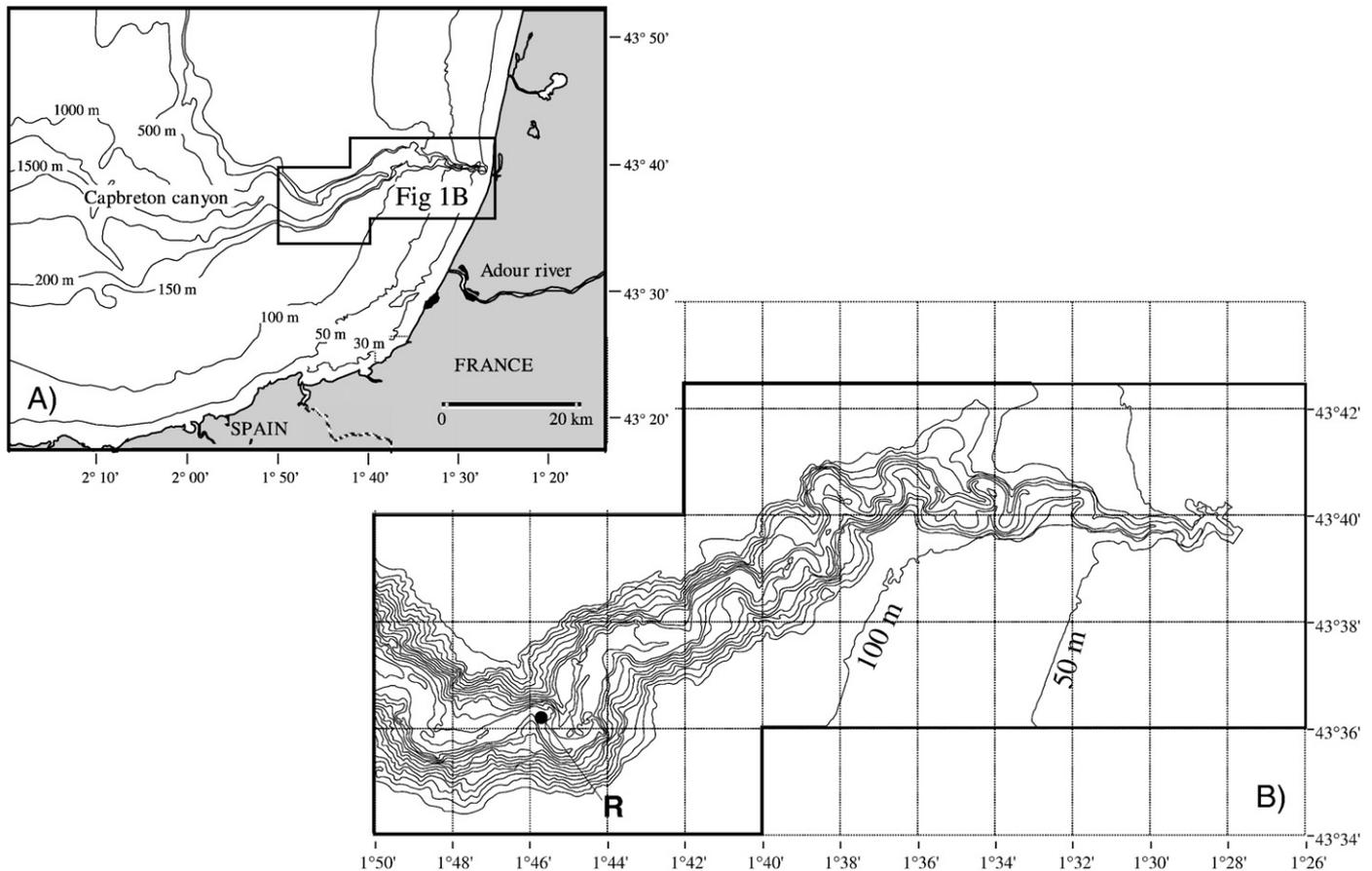


Fig. 1. (A) Location map of the Capbreton Canyon in the south-eastern part of the Bay of Biscay; (B) Location map of the site R in the Capbreton Canyon.

Table 1
Replicate analyses of certified reference materials (SL-1, NIST 1646, and MESS-2) are reported for target elements

Reference	SL-1				NIST 1646a				MESS2			
	(n=6)				(n=10)				(n=10)			
Metals	Certified	2σ	Measured	2σ	Certified	2σ	Measured	2σ	Certified	2σ	Measured	2σ
Mo(μg/g)	1.3 ^a		1.5	0.3	1.8 ^a		1.6	0.4	2.9	0.1	2.8	0.1
U(μg/g)	14.0	1.0	13.8	1.5	5.8 ^a		5.0	0.6	^b		3.1	0.3
As(μg/g)	27.5	2.9	22.5	0.9	6.2	0.2	5.9	0.9	20.7	0.1	19.5	1.7
Sb(μg/g)	1.3	0.1	1.7	0.4	0.3		0.29	0.1	1.1	0.1	1.3	0.2

The certified value (Certified) and measured concentrations (Measured) are reported with their standard deviation at the 95% confidence limit. Note: n is the number of replicate digestions.

^a Recommended value, not certified.

^b Concentration not reported.

(III)-oxides (Kostka and Luther, 1994; Keon et al., 2001; Hyacinthe et al., 2006). To analyze reactive trace-metals, the supernatants of the both extractions were diluted in 1% ultrapur HNO₃.

Molybdenum and U concentrations were measured by ICP-MS (Perkin Elmer, Elan 5000). Furthermore, standard additions were carried out for Mo and U leached by selective ascorbate extraction to minimize matrix effects. Precision for total (Mo_{TOT} and U_{TOT}) and ascorbate extraction analyses (Mo_{ASC} and U_{ASC}) were better than 6% and 9% for U and Mo, respectively. The results obtained for the total digestions were generally within the ranges of the certified values (e.g. Table 1).

Arsenic and Sb extracted by total and HCl digestions (As_{TOT}, Sb_{TOT}, As_{ASC}, and Sb_{ASC}) were analyzed after a pre-reduction by KI/ascorbic acid (0.1/0.06 mol/l) in 2.4 mol/l HCl, using hydride-generation flow injection atomic absorption spectrometry (HG-FIAS; Perkin Elmer AA300) as described elsewhere (Yamamoto et al., 1985; Chaillou et al., 2003). The precision of this method was better than 10% for both total As and Sb (Table 1).

Ascorbate and 1 N HCl extractable Fe and Mn were analyzed using flame atomic absorption (Perkin Elmer AA300) in an air/acetylene flame. Precision of the analyses was about 3% for Mn and 7% for Fe.

Dissolved Mn was measured by flame atomic absorption spectrometry (Perkin Elmer AA300) in an air/acetylene flame with a precision

around 3%. Dissolved Fe was analyzed by the ferrozine procedure described by Stookey (1970) and the precision was better than 5%. Dissolved Mo and U were analyzed by ICP-MS after a 1/20 dilution in 1% ultrapur HNO₃. The precision of the analyses based on 10 replicate measurements of the overlying bottom water sample was 4% and 2% for Mo and U, respectively. Total dissolved As and Sb concentrations were measured by HG-FIAS after treatments as described above. Precisions were better than 9%.

3. Results and discussion

3.1. Elemental composition of the sediment

X-ray imagery system (e.g. SCOPIX system; Migeon et al., 1999) revealed the presence of four turbidites (noted T1, T2, T3 and T4; Fig. 2A). Grey levels reflected the grain size of the material: an increase of the grey level corresponded to an increase in grain size. As reported by Gaudin et al. (2006), T4, T3, and T2 were interpreted as base cut-out Bouma sequences, whereas T1 is a classical Bouma sequence (Mulder et al., 2001). A visual examination of the core corroborated the presence of four sequences characterized by ~2 cm-thick ochre clay horizons overlying olive-green mud bodies with fine sandy bases (Fig. 2A and B). The colour variation is a consequence of diagenetic

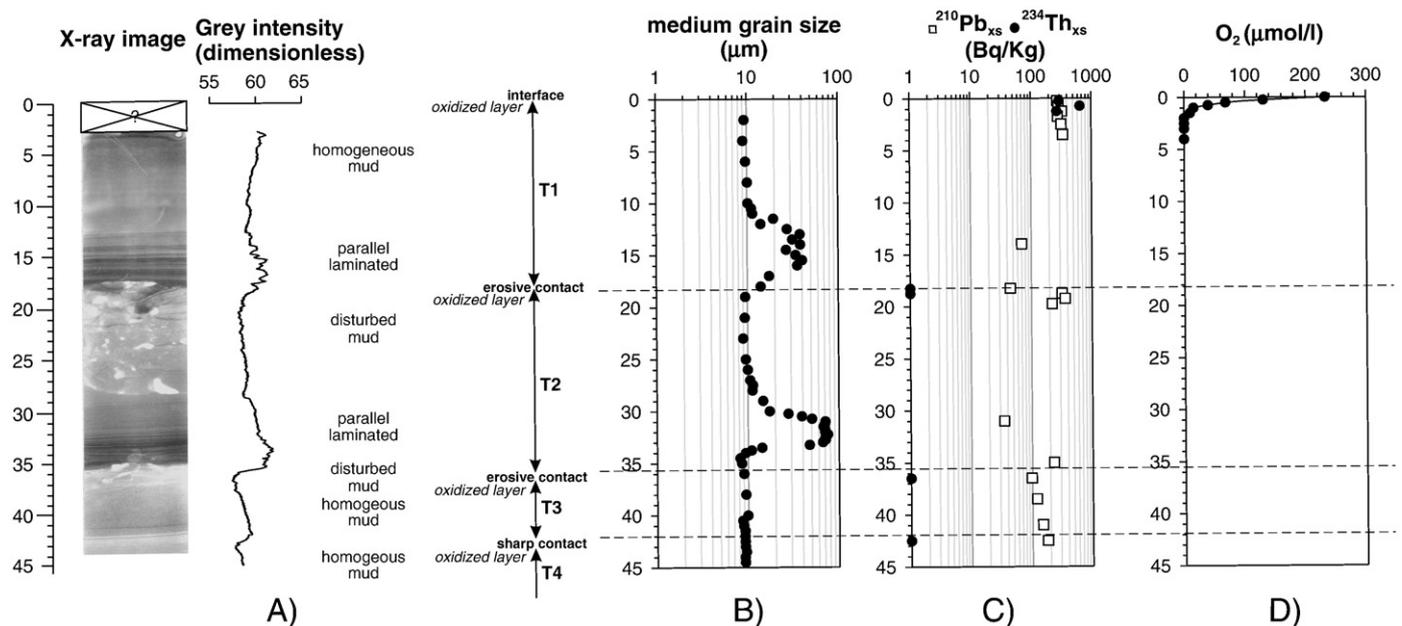


Fig. 2. Elemental composition of the studied core: A) X-ray image, grey intensity (dimensionless), and facies interpretation of the sedimentary core; B) medium grain size of the material (given in μm); C) ²¹⁰Pb_{xs} (open squares) and ²³⁴Th_{xs} (black dots) activities (given in Bq/kg), the detailed analytical methods to determine supported ²¹⁰Pb and ²³⁴Th were reported by Chaillou et al. (2002); and D) profile of dissolved oxygen obtained by microelectrode measurements. The dashed lines denote the boundary of each turbidite.

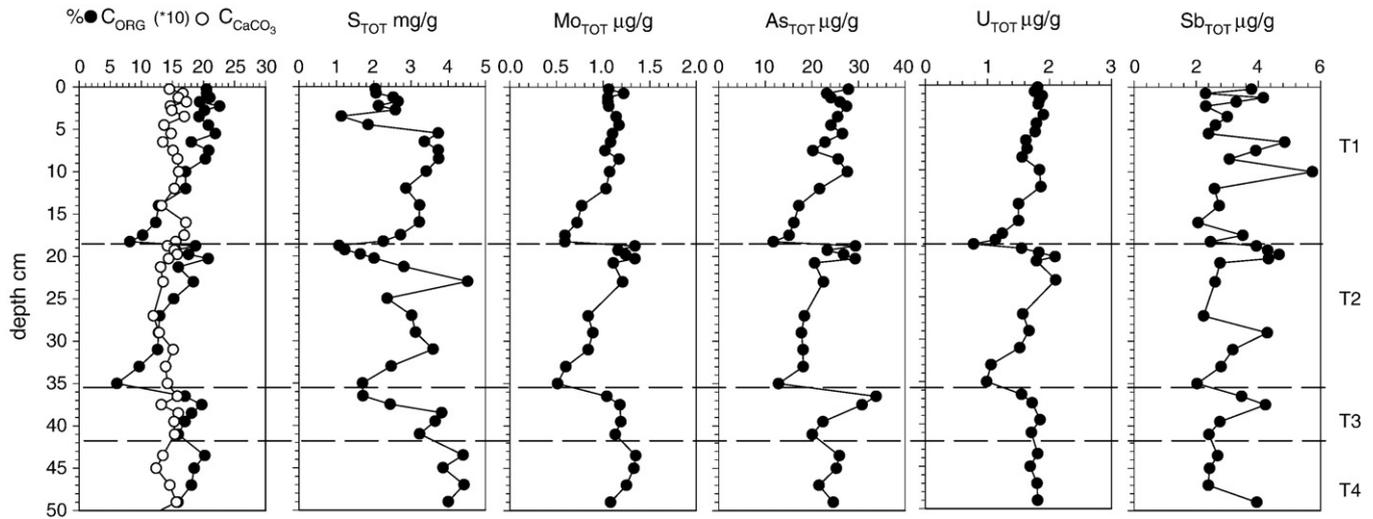


Fig. 3. Vertical distribution of C_{ORG} and C_{CaCO_3} and total S, Mo, As, U, and Sb. The dashed lines denote the boundary of each turbidite.

processes and metal-oxides content. As previously reported for distal turbidites (Wilson et al., 1985, 1986), the ochre-coloured clays are relicts of past oxic conditions when diffuse contact between oxygenated bottom waters and sediment was maintained.

The presence of excess ^{210}Pb activity ($t_{1/2}=22.3$ yr) at the top of each layer (Fig. 2C) indicated that the depositions occurred over the last 100 yr. There was no apparent continuous radioactivity gradient because of the fresh and homogeneous nature of the deposits. The measured $^{210}\text{Pb}_{\text{XS}}$ activity reflects the $^{210}\text{Pb}_{\text{XS}}$ inventory at the moment of the turbidite flow deposition rather than accumulation rates. The high excess ^{234}Th activity ($t_{1/2}=24$ days) at the SWI is consistent with the present-day hemi-pelagic sedimentation of particles. Unfortunately, short lived radionuclides do not allow us to date the layers.

Organic C (C_{ORG}) content ranged between 2 and 0.6 wt.% (Fig. 3). The down-core C_{ORG} distribution reflected grain size of the material distribution rather than mineralization processes. Due to its proximity to the coast, the Capbreton Canyon directly receives terrestrial inputs that accumulate in its head. The particle transport to the upper part of the canyon is dominated by gravity, mass, or turbidity flows (Mulder et al., 2001) and hemi-pelagic sedimentation is of minor importance. Recent works on amino acids have revealed that the residual C_{ORG} in these sediments is mostly refractory (Grémare et al., 2005). The lack of fresh organic matter likely limited the stimulation of microbial activities and the growth of macrobenthic fauna, explaining the absence of bioturbating structures in the X-ray image (Fig. 2A).

The studied sediment is characterized by homogeneous carbonate content (average content of $14.7 \pm 1.5\%$; Fig. 3, Electronic data). Therefore, the down-core distribution of trace-metals may probably reflect grain size variations and/or diagenetic processes, rather than the dilution by CaCO_3 .

3.2. Redox conditions

Dissolved O_2 was limited to the first 16 mm below the SWI (Fig. 2D) and ΣNO_3^- ($\text{NO}_3^- + \text{NO}_2^-$) was present in the uppermost 5 cm of the sediment (Electronic table). Dissolved Mn^{2+} , Fe^{2+} , and NH_4^+ , evidence of early stages in diagenesis, were detected in the core. The porewater composition did not reveal intense anoxic diagenesis, in contrast to that observed at other sites of the same continental margin (Hyacinthe et al., 2001; Chaillou et al., 2002). The limited fresh C_{ORG} input probably partially inhibited sulphide production. Due to the lack of porewater SO_4^{2-} data we cannot totally exclude sulphate reduction. However, the absence of both black coloured sediment and characteristic fumes of H_2S during HCl leaching suggested low production of

acid volatile iron sulphides. Accordingly, the high S_{TOT} content ($>30 \mu\text{mol/g}$, Fig. 3) probably reflected the S content of sediment prior to its destabilization and transport rather than authigenic production after deposition. Under less reducing conditions, dissolution of sulphide compounds may have occurred via the oxidation by O_2 , metal-oxides, and/or nitrate (Myers and Neilson, 1988; Jørgensen and Neilson, 2004). Nevertheless, we cannot exclude the formation of authigenic sulphide compounds in the bottom of the core and even deeper, as suggested by the slightly increasing S_{TOT} content observed in T3 and T4 (Fig. 3).

3.3. Iron and manganese

Concentrations of Fe- and Mn-oxides extracted by both ascorbate and HCl solutions (Fe_{ASC} , Fe_{HCl} , Mn_{ASC} and Mn_{HCl} , respectively; Fig. 4) were higher in the ochre horizons. Such local accumulations may be attributed to (i) purely diagenetic processes including the remobilization and the precipitation of metals near the redox front, and/or (ii) the accumulation of detrital particles under a hemi-pelagic sedimentation regime. Porewater Mn^{2+} and Fe^{2+} distributions were consistent with the first mechanism. High concentrations of Mn^{2+} just below the SWI (Fig. 4) were attributed to Mn-oxide reduction very close to the interface. Assuming that detrital input is negligible and that the porewater geochemical gradients are constant over time, one may use a simple diffusion model to estimate the time required to form the surficial Mn-oxide rich horizon. This estimate allowed dating the youngest turbidite (T1). We are aware of the paradox of using a steady-state model to describe a transient system. However, we assume that the time scale of turbidite emplacement is long relative to the reaction rates of Mn with potential oxidants. Moreover, in previous studies the assumption of steady-state conditions allowed describing Mn dynamics in natural and experimental turbidites (Anschutz et al., 2002; Chaillou et al., 2007).

The Mn^{2+} flux was estimated by Fick's First Law with $J = -\phi D_s (\delta C / \delta Z)$ where J is the flux, ϕ the porosity, $(\delta C / \delta Z)$ the concentration gradient, and D_s the bulk sediment diffusion coefficient corrected by tortuosity [i.e. $D_s = D_0 / \theta^2$, where θ is tortuosity and D_0 the molecular diffusion coefficient in water (Berner, 1980)]. D_0 values were obtained from the literature (Boudreau, 1997; Schulz, 2000) and θ^2 was assumed to equal $1 - \ln \phi^2$ (Boudreau, 1997). By using the Mn^{2+} concentration gradient between 2.5 and 4.5 cm depth (Fig. 4) and the mean porosity over that interval (Electronic table), we estimated an upward Mn^{2+} flux of $\sim 3 \text{ nmol/cm}^2/\text{day}$. Based on Mn_{ASC} concentrations and porosity, the estimated excess of Mn(III/IV)-oxides present within the uppermost

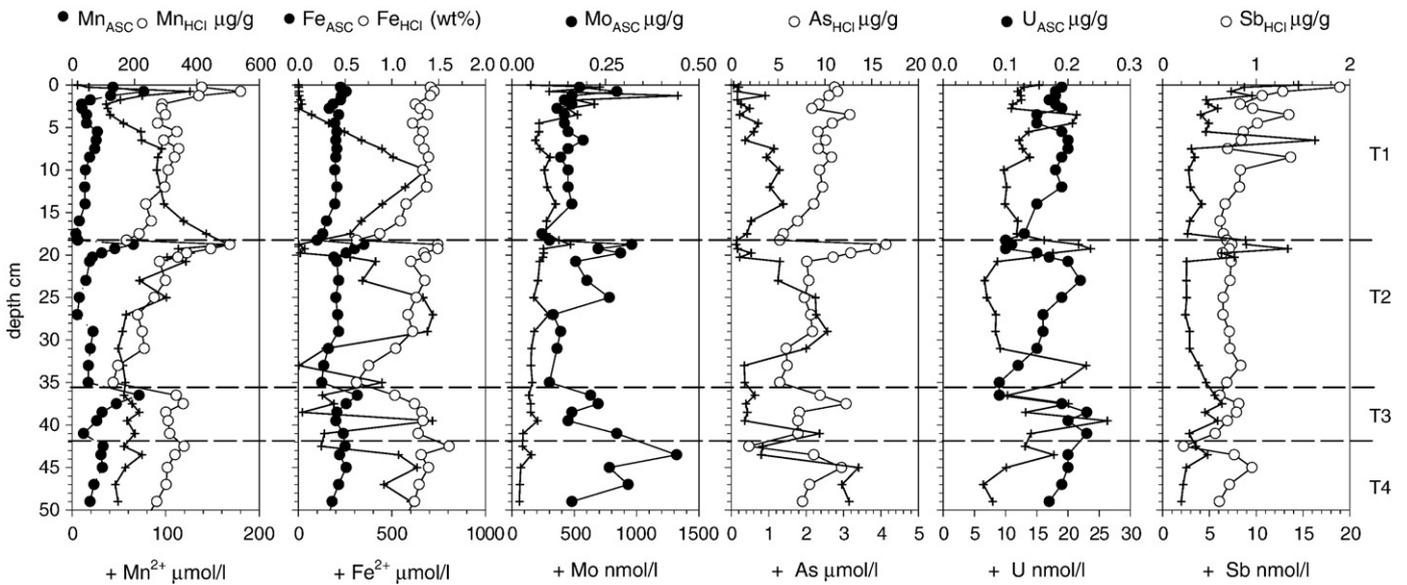


Fig. 4. Vertical distribution of reactive and porewater trace-metals. The dashed lines denote the boundary of each turbidite.

2 cm (in comparison with the underlying sediments, 0.5 $\mu\text{mol/g}$) was $\sim 2 \mu\text{mol/cm}^2$. The estimated Mn^{2+} flux can supply this excess over 22 months. This result is highly coherent with the time elapsed between the core sampling and the Martin Storm event which affected the western coast of France during December 1999 (i.e., ~ 18 months; Mulder et al., 2001; Anschutz et al., 2002; Gaudin et al., 2006).

The well-developed dissolved Fe gradient in porewaters is consistent with Fe-remobilization within the first centimetres (Fig. 4), upward transport by diffusion and precipitation of reactive Fe(III)-oxides at the surface. The profile of Fe^{2+} did not overlap the O_2 profile: Mn(III/IV)-oxides and NO_3^- probably acted as efficient oxidants for Fe^{2+} (Postma, 1985; Myers and Neelson, 1988; Hyacinthe et al., 2001). The low Fe_{ASC} enrichment observed in the uppermost 4 cm of the sediment was attributed to precipitation of fresh Fe(III)-oxides. In addition, detrital (i.e. non-authigenic) input of reactive Fe(III)-oxides formed in the water column cannot be excluded.

The three local maxima of Mn- and Fe-oxides observed deeper in the sediment (~ 18 – 20 cm, ~ 35 – 37 cm, and ~ 40 – 41 cm; Fig. 4) have probably the same origin as the surface enrichment. Their persistence under anoxic conditions may result from the lack of fresh organic matter that slowed down enzymatic reduction of Mn(III/IV)- and Fe(III)-oxides. At ~ 18 cm depth, however, the concomitant presence of high porewater Mn^{2+} concentrations and a Mn(III/IV)-oxide peak clearly indicated that Mn-oxides were reduced at the sampling time. In fact, Mn-oxide reduction is also supported by electron donors other than C_{ORG} such as NH_4^+ and sulphur species (Postma, 1985; Kostka and Luther, 1994; Hulth et al., 1999; Anschutz et al., 2005). The sporadic presence of ΣNO_3^- under oxygen-depleted conditions testifies of important anoxic reoxidation processes in these disturbed sediments. Weak ΣNO_3^- concentrations measured within the horizons rich in metal-oxides (Electronic data) are likely due to anoxic oxidation of NH_4^+ to NO_3^- by Mn(III/IV)-oxides (Hulth et al., 1999; Anschutz et al., 2000, 2005; Mortimer et al., 2004), which is in agreement with the NH_4^+ decrease observed at the top of each layer. However, the concentrations of ΣNO_3^- remained low ($< 1 \mu\text{mol/l}$; Electronic data), probably because of the multiple pathways to reduce ΣNO_3^- to N_2 under anoxic conditions (e.g. potential oxidants: C_{ORG} , Fe^{2+} , NH_4^+ , H_2S , AVS).

In contrast to Mn^{2+} , porewater Fe^{2+} was close to zero in the top layers of T2, T3, and T4. Oxidation of released Fe^{2+} by Mn-oxides (Myers and Neelson, 1988) is the most probable process to explain the observed removal of Fe from porewaters. This anaerobic oxidation

pathway favoured the replenishment of Fe(III)-oxides. The reduction of chemically reducible Mn/Fe-oxides is not complete after a few years, indicating slow dissolution kinetics despite reducing conditions. Similar results have already been reported for freshwater reducing sediments (Hyacinthe and Van Cappellen, 2004; Canavan et al., 2007).

3.4. Remobilization and precipitation of trace-metals

The total concentrations of particulate Mo, As, and U were strongly influenced by grain size of the material (Fig. 3). Trace metal reactivity in the turbidite layers was assessed from the vertical distributions of operationally defined reactive fractions: An ascorbate solution was used to extract the most reactive Mo and U phases formed by diffusive metal distribution in porewaters (Chaillou et al., 2002). Reactive As and Sb were extracted by 1 N HCl solution (Mucci et al., 2000; Keon et al., 2001; Chaillou et al., 2003). Although speciation and immobilization mechanisms of Sb in marine sediments are not well known, one might expect that Sb behaviour is somewhat similar to that of As, as both belong to the same column in the Periodic Table of Elements (Filella et al., 2002).

3.4.1. Metals with high affinity to Mn/Fe-oxides: Mo and As

The vertical distributions of particulate Mo and As followed similar patterns with high concentrations in the horizons rich in Mn/Fe-oxides (Figs. 3 and 4). Their porewater distributions, however, were significantly different, indicating two distinct behaviours in presence of metal-oxides.

Molybdenum release occurred in the first centimetres below the SWI. Porewater Mo concentrations increased sharply to reach values higher than seawater concentrations (i.e. $> 200 \text{ nmol/l}$; Fig. 4) at the depth, where porewater Mn concentrations were the highest. Deeper, dissolved Mo concentrations decreased except for a local peak at the top of T2. This distribution supports important Mo release into porewater in the zones of reductive Mn-oxide dissolution. Molybdate (MoO_4^{2-}), the soluble form of Mo in oxic water, is known to have high affinity with Mn-oxides in marine sediments (Bertine, 1972; Shimmiel and Price, 1986; Calvert et al., 1997; Erickson and Helz, 2000). Hence, Mo was linearly related to porewater Mn (Fig. 5A; $r^2=0.6$, $P<0.0001$), and was likely released into porewater when Mn(III/IV)-oxides were reduced. However, porewater Mo concentrations measured in the uppermost 3 cm of the sediment may not be explained by

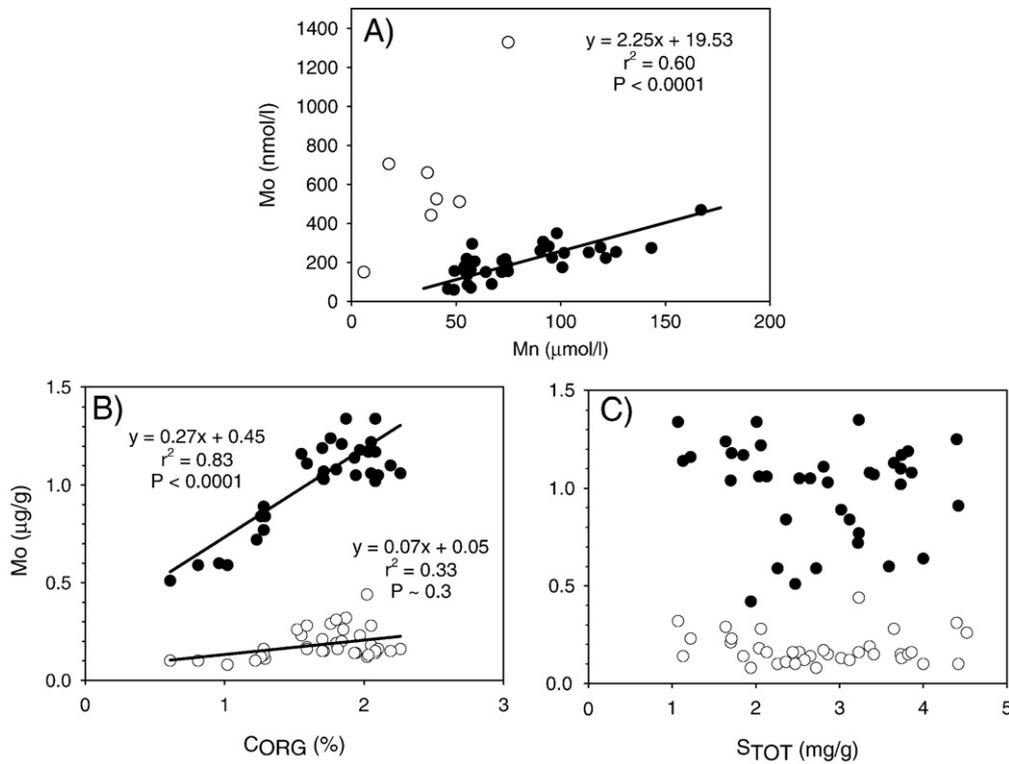


Fig. 5. Relationship between dissolved Mo and dissolved Mn within the four successive turbidites (A). The surficial data (0–3.5 cm; open dots) have not been taken into account for the linear regression analysis. The relationship between total Mo (filled dots) and reactive Mo (Mo_{ASC} open dots) with $CORG$ (B) and with $STOT$ (C). The results of linear regression analysis (analysis of variance; ANOVA) of the data are represented by the solid lines and the equations shown on each graph.

the same linear relationship (Fig. 5A, open dots). While Mn-oxides have been designed here to mainly explain the porewater Mo peaks, other sources can also supply the Mo pool. For example, organic matter has been recognized to be a host phase for sedimentary Mo in estuarine sediments (Malcolm, 1985; Audry et al., 2006), in anoxic marine environments (Algeo and Lyons, 2006) as well as in many ancient black shales (Lyons et al., 2003; Algeo, 2004; Algeo and Maynard, 2004; Wilde et al., 2004). The $Mo_{TOT}-CORG$ co-variance is evident in the studied sediment (Fig. 5B, $r^2 = 0.83$, $P < 0.0001$), implying that most sedimentary Mo is associated with residual organic matter. In euxinic basins, Algeo and Lyons (2006) proposed that Mo scavenging by sedimentary organic matter occurs rapidly at or close to the SWI. The lack of co-variation between Mo_{ASC} and $CORG$ (Fig. 5B, $r^2 = 0.17$, $P \sim 0.3$) supports the idea that Mo associated with the presumably residual organic matter is not released by ascorbate reduction. The absence of fresh organic matter probably limited reactive Mo scavenging and one can suppose that Mo was already associated with refractory organic matter as a relict of former diagenesis prior to the turbidite deposit. Dissolved Mo may diffuse towards the SWI as long as MoO_4^{2-} was not back-adsorbed onto Mn(III/IV)-oxides. Losses of Mo from energetic shelf sediment to seawater have already been reported by Breckel et al. (2005). Although the present dataset does not allow us to quantify Mo effluxes; we can expect that Capbreton Canyon sediments are a Mo source to seawater during surge flow events.

In coastal and margin environments, Mo authigenesis is controlled by authigenic sulphide phases (Shaw et al., 1990; Crusius et al., 1996; Zheng et al., 2000; Adelson et al., 2001; Sundby et al., 2004). Authigenic Mo previously formed at the original deposit (under more sulphidic conditions) may be remobilized under less reducing conditions. Oxygen and metal-oxides might act as efficient oxidants to Mo-S complexes (Myers and Nealson, 1988) and, hence, promote Mo release in Mn/Fe-oxide-rich horizons. At the bottom of the core, Mo_{TOT} and $STOT$ contents slightly increased and the porewater Mo concentrations

decreased. These observations suggest efficient anoxic Mo authigenesis in the sediment depth represented by the bottom of the core or even deeper.

In contrast to Mo, total porewater As ($As(III)+As(V)$) concentrations were clearly lower in the horizons rich in Mn/Fe-oxides than in the underlying sediment (Fig. 4). Porewater As low concentrations were concomitant with reactive As peaks (As_{HCl} , Fig. 4). This strongly suggests that As was transported to the sediment mainly associated with Fe- and/or Mn-oxides and then released to porewater by metal-oxide reduction. Several studies on coastal sediments have shown that Fe(III)-oxides control early diagenesis of As, when sediment chemistry is not dominated by Mn-oxides (Peterson and Carpenter, 1986; Mucci et al., 2000; Saulnier and Mucci, 2000; Chaillou et al., 2003). This point is supported by clear similarities in the vertical profile shapes of porewater As and Fe^{2+} . Arsenite ($As(III)$) being the dominant As species in anoxic porewaters (Andrea, 1979; Peterson and Carpenter, 1986; Chaillou et al., 2003), we assume that porewater As measured in the core is $As(III)$. In the presence of Mn-oxides, the oxidation from $As(III)$ to $As(V)$ may be faster than in the presence of O_2 and Fe-oxides alone (Oscarson et al., 1981; Rude, 1996). Therefore, the removal of $As(III)$ from porewaters at the SWI, may probably be attributed to its oxidation by Mn-oxides and subsequent adsorption onto authigenic Fe(III)-oxides. Accordingly, persistent Mn(III/IV)-oxides at the top of each turbidite are considered as a permanent oxidative barrier which promotes As adsorption onto Fe(III)-oxides, limiting As exchange between the different turbidite layers and/or its loss to the overlying bottom water.

Authigenic sulphide minerals play a major role in anoxic As authigenesis. Arsenic can precipitate as As-Fe-S minerals or form distinct As sulphides as As_2S_3 or AsS (Edenborn et al., 1986; Belzile, 1988; Widerlund and Johan, 1995; Huerta-Diaz et al., 1998; Saulnier and Mucci, 2000). The precipitation of authigenic As may be limited by the absence of efficient sulphide production in the studied sediment. Moreover, $As(III)$ -bearing sulphides from the original deposit (formed

during early diagenesis under more sulphidic conditions) may have been oxidized by O_2 , NO_3^- and/or metal-oxides, followed by trapping of As(V) by Fe(III)-oxides.

3.4.2. The downward transfer of U: a potential tool to date turbidites?

Uranium behaviour was very different from those of Mo and As. In fact, total and reactive U showed broad enrichments below horizons rich in metal-oxides (Figs. 3 and 4). For example, at T2, U_{ASC} content increased ~1 cm below the Mo_{ASC} and As_{HCl} maximum, i.e. in the zone of reductive Fe-oxide dissolution. Porewater data suggest the removal of dissolved U(VI) within the uppermost 3 cm, where Fe^{2+} is released. Seawater is a source of U as long as diffusion links porewater to the water column (Chaillou et al., 2002; McManus et al., 2005; Morford et al., 2005). All these observations support authigenic U accumulation below the metal-oxide-rich horizons suggesting that reduction of Fe (III)-oxides and U(VI) are coupled processes (Zheng et al., 2002).

An interesting aspect of the data set is the presence of dissolved U under anoxic conditions, where it would be supposed to be insoluble, i.e. in the ~4–6 cm, ~18–20 cm and ~33–36 cm depth ranges and deeper in the core (Fig. 4). The occurrence of high dissolved U concentrations has already been reported in several hemi-pelagic sediments (Kolodny and Kaplan, 1973; Cochran et al., 1986; Anderson et al., 1989; Chaillou et al., 2002). In most cases, the authors attributed this presence to air contamination during porewater sampling, inducing reoxidation of U(IV) to soluble U(VI). Although we cannot totally exclude such a sampling artefact, it seems unlikely that this would result in the observed well-developed peaks. Assuming that the presence of dissolved U in anoxic sediments reflects U(VI) production under anaerobic conditions in marine sediments, this could be due to oxidation of U(IV) to U(VI) by nitrogen species (Finneran et al., 2002a) and/or Fe(III)-oxides (Wielinga et al., 2000; Finneran et al., 2002b; Sani et al., 2004; Senko et al., 2005a,b). The mechanisms of this oxidation, observed in experimental bioremediation studies, are not well understood. The oxidation of U(IV) by Fe(III), produced by nitrite oxidation of Fe(II), might be important in natural environments (Senko et al., 2005b). The production of authigenic colloidal U(IV) phases, previously reported for microbial experiments (Gorby and Lovley, 1992; Fredrickson et al., 2000) could be an alternative mechanism explaining the high dissolved U concentrations. Mobile U(IV) species (that cross 0.2 μm pore size filter) would probably diffuse freely in marine sediments, favouring the U(IV) reoxidation by Fe(III)-minerals and the uranite precipitation in distinct horizons. This implies that high concentrations of dissolved U and increasing concentration of solid U can be concomitant, as observed in the bottom of the core (Fig. 4) and elsewhere in undisturbed marine sediments (Chaillou et al., 2002).

Uranium distribution is in agreement with downward diffusion of reoxidized U and immobilization below the Fe(III)/Fe(II) front, as observed in distal turbidites (Colley and Thomson, 1985; Thomson et al., 1998a,b). Balancing the amounts of particulate U “lost” by reoxidation of U(IV) (noted “–”) and U “gained” by the downward migration (noted “+”), we estimated the excess of U supplied by the seawater. Assuming U flux at the SWI is constant over time we could roughly date each turbidite.

Although constant U flux at the SWI is probably an oversimplified assumption, the main uncertainty in this approach seems to be related to the value of the diffusion coefficient (D_s). Previous work (Chaillou et al., 2002; McManus et al., 2005) used the coefficient given by Li and Gregory (1974) to describe UO_2^{2+} diffusion (i.e. D_s corrected for the temperature = 1.22×10^{-6} cm^2/s). However, in seawater the U(VI) ion is more likely associated to carbonate complexes ($UO_2(CO_3)_3^{4-}$) which probably have a larger diffusion coefficient. As proposed by Morford et al. (2007), diffusion coefficient for MoO_4^{2-} could be more appropriate to describe U diffusion (i.e. D_s corrected for the temperature = 2.37×10^{-6} cm^2/s). From the downward concentration gradient in the uppermost cm (4.6 $pmol/cm^4$) and Fick's First Law, the estimated downward U fluxes were ~140 and ~270 $pmol/cm^2/yr$, depending on

the diffusion coefficient applied. These results highlight the need for improving our knowledge on U diffusion coefficient. In spite of this important difference (factor two), the obtained fluxes are in agreement with those previously calculated in the adjacent sediment margin (Chaillou et al., 2002), and are of the same order of magnitude as fluxes reported for other well-oxygenated sediment systems (Zheng et al., 2002; McManus et al., 2005).

The approach needs reliable values for the diffusion coefficient and precise estimates of the “gained” (or “lost”) fraction by subtracting “background” from the measured reactive concentration. The lowest U_{ASC} concentration (i.e. 0.17 $\mu g/g$ for T1 and 0.16 $\mu g/g$ for the other layers) was considered as the background content of the transported sediment slurry. For T1, the “gained” is equivalent to the “lost” fraction (+0.042 μg vs. –0.043 μg), suggesting that U diffused from the seawater did not influence the U pool at the sampling time. For T2 and T3, the “lost” represented ~20% of the “gain” (+0.315 μg vs. –0.069 μg and +0.262 μg vs. –0.045 μg , respectively), indicating that the U pool was mainly controlled by the time elapsed between turbidite deposition events. Assuming a constant flux of 140 $pmol/cm^2/yr$, the excess of U “gained” could be supplied within 7.5 and 6.5 yr for T2 and T3, respectively. These results suggest that T2 would have been deposited in ~1992 and T3 in ~1986. Based on the second calculated flux (i.e. using a diffusion coefficient of 270 $pmol/cm^2/yr$), the deposits would be younger, i.e., ~1995 for T2 and ~1992 for T3. Both results obtained from this age model support the idea that turbidity currents are frequent in the Capbreton Canyon (one event per 10 yr on average; Mulder et al., 2001).

3.4.3. The case of Sb

Little is known on the processes controlling the transformation and transport of Sb in natural systems. In most studies, the Sb behaviour is assumed to be somewhat similar to that of As (Montserrat et al., 2002, and references therein). In our study, apparent Sb behaviour was very different from that of As. The total solid Sb data are scattered and revealed no clear trend over depth (Fig. 3), which cannot be explained. In contrast, the reactive Sb_{HCl} fraction showed a less noisy profile with concentrations representing more than 30% of Sb_{TOT} .

No clear relation was observed between Sb and major diagenetic elements. In T1, association of Sb_{HCl} with metal-oxides could explain the well-developed enrichment observed in the first centimetres below the SWI, which is consistent with adsorption studies (Thanabalasingam and Pickering, 1990) and selective extraction analyses on sediment (Brannon and Patrick, 1985). This potential association is only observed in the most recent turbidite. The shape of the peak, however, is somewhat different from that of reactive Mn- and/or Fe-oxides. Moreover, porewater data did not reveal any Sb release in the depth-range of reductive metal-oxide dissolution. All these observations support the idea that Sb is mainly delivered to sediment by sinking particles formed in oxic water (Andrea and Froelich, 1984; Cutter, 1991). Interestingly, the porewater Sb profile is similar to that of U suggesting Sb removal at few cm below the SWI, which would imply that seawater is an Sb source to sediment. The high concentrations of dissolved Sb measured at the top of T2, T3, and T4 indicated local reoxidation and/or dissolution of Sb compounds. Trivalent Sb can rapidly (i.e. within few days) be oxidized by Mn and Fe-oxides to Sb(V) (Belzile et al., 2001). Antimony released into porewater seems to be immobilised just below the metal-oxide front. The vertical relocation of Sb under anoxic conditions has already been reported for distal turbidites (Thomson et al., 1993, 1998a,b), but the exact mechanism of Sb immobilization remains unknown.

Based on the downward gradient of porewater Sb in the upper sediment layer (~9.62 $pmol/cm^4$), the average porosity (79%) and D_s (2.46×10^{-6} cm^2/s), the estimated Sb flux into the sediment is 591 $pmol/cm^2/yr$. Assuming a constant gradient over time, this flux would represent diffusive input of ~108 ng/cm^2 of Sb since the last turbiditic event, which is very low compared to the solid Sb “gained”

in the 2–7 cm depth-range of T1 (~525 ng/cm²). Therefore, reactive Sb in the studied sediments was mainly attributed to settling particles and Sb compounds transported by the sediment slurry.

4. Conclusions

The physical reworking of seabed, which is common on continental margins, may hamper the attempts to reconstruct paleoenvironmental changes from the record of authigenic Mo, As, Sb and U. The successive deposition of recent turbidites on continental margin sediments strongly influences the behaviour of trace-metals, causing rapid metal migration and/or immobilization, as observed for distal turbidites. The down-core distributions of Mn, Fe, Mo, U, As and Sb mainly depend on ongoing diagenesis and reflect the coupled transport-reaction processes.

The formation and the persistence of horizons rich in reactive Mn (III/IV)- and Fe(III)-oxides rather than diffusion of oxygen into the turbidite mainly control the oxidation of authigenic trace-metals previously formed at the original deposit. Low sulphide production in these sediments limits the formation of authigenic Mo and As, that remain associated with Mn/Fe-oxides. Uranium and Sb are immobilized below the Fe-dissolution front. The exact mechanism of Sb immobilization are not known, but it is most certainly different from that of As.

The profile shapes of dissolved and particulate Mn and U may be used to estimate the age of the turbidite deposits, which cannot be determined by conventional radionuclide methods. Based on a simple diffusive model applied to Mn the age of the most recent deposit (noted T1) was estimated ~22 months, which is close to the time elapsed between the core sampling and the last known turbiditic event in the Capbreton Canyon (i.e., Martin Storm, ~18 months). Using the U data set, we obtained age estimates for 2 older turbidite layers: 8–14 yr for T3 and 4–7 yr for T2, depending on the diffusion coefficient applied. Reliability and precision of this new approach depend on knowledge of diffusion coefficients that needs to be improved, particularly for U.

Acknowledgements

We thank the crew of the “Côte de la Manche” and the participants of the Sedican cruises for help in the field. We thank C. Bossy and A. Caule for As and Sb analyses. The manuscript has benefited from the reviews of two anonymous referees, as well as from the editorial handling of G.J. De Lange. This research was funded by the program PROOF of the Institut National des Sciences de l'Univers-CNRS. This is a contribution of the UMR 5805 EPOC.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.margeo.2008.06.002.

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