Occurrence of thin, metal-rich layers in deep-sea sediments: a geochemical characterization of copper remobilization

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Abstract—Distinctly coloured trace metal enriched fronts with a six-fold Cu-enrichment occur in the interbedded pelagic-turbiditic sediments from the Madeira Abyssal Plain. To decipher their mode of formation, two sequential extraction techniques, an acid-gradient and a “Tessier-type” scheme, were applied. Two different front types could be distinguished: Type-1 fronts are mostly black and enriched in Co, Zn, Ni and Cu, and associated with the oxidation fronts that developed after deposition of turbidites. Type-2 fronts are purple, extremely enriched in Cu, and associated with sulphur. These fronts are sometimes found in relation with a relict oxidation front, but often show no clear relation with lithology. Two different modes of formation are postulated. (1) The transition-metal enrichment in the type-1 fronts is typical for a manganese-oxide association often found in marine sediments. After the dissolution of manganese-oxide during sub-oxic diagenesis, the transition metals were liberated and subsequently relocated and precipitated in response to a redox-gradient. (2) The Cu-S association in type-2 fronts is also formed during sub-oxic diagenesis. The main process leading to the formation of this Cu-S enrichment is the mobilization of inherited Cu-S compounds from organic-rich turbidites. The accumulation of these compounds is possibly related to redox changes at relict oxidation fronts and to gradual, probably slowly evolving, redox changes that occur at present.

INTRODUCTION

TRACE metal behaviour in pelagic deep-sea sediments has received increasing attention, especially since the discovery of Mn-nodules covering large parts of the deep-sea floor. These investigations show that the flux of metals to the deep-sea sediment is mainly dependent on the organic-C and particle flux. In the sediment, the distribution of Mn and associated trace elements is dependent on redox conditions (PEDERSEN *et al.*, 1986; SHAW *et al.*, 1990). Oxidation of organic matter by the subsequent oxidants oxygen, nitrate, manganese, iron and sulphate determines the sediment chemistry directly and indirectly. In general, pore water profiles indicate that Cu concentrations are the highest at the sediment–water interface and rapidly decrease with depth. These profiles are explained by the degradation of the organic-Cu carrier during early diagenesis; this results in a release of Cu into the bottom-water (e.g. HEATH and DYMOND, 1977; HEIN *et al.*, 1979; CALLENDER

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and BOWSER, 1980; ELDERFIELD, 1981; KLINKHAMMER *et al.*, 1982; GRAYBEAL and HEATH, 1984; LYLE *et al.*, 1984; PEDERSEN *et al.*, 1986; HEGGIE *et al.*, 1987; CHESTER *et al.*, 1988; SHAW *et al.*, 1990). Manganese pore-water concentrations often show an increase with depth (e.g. FROELICH *et al.*, 1979; DE LANGE, 1986) due to the microbially mediated oxidation of organic matter by solid phase Mn.

In the past, steady state was assumed for most deep-sea sediments. Steady state conditions develop when sedimentation rate and organic-C content of the settling particles remains constant (FROELICH *et al.*, 1979). However, recent investigations show that climatically induced variations of organic-C fluxes (THOMSON *et al.*, 1984; PEDERSEN *et al.*, 1986; FINNEY *et al.*, 1988; WALLACE *et al.*, 1988) can cause non-steady state diagenesis in deep-sea sediments. At various depths Mn-enrichments were found, related to variations in redox conditions. Similarly, in basin-plains, mass-flows from the shelf to the deep-sea can deposit organic- (and metal-) rich sediment at deep-sea sites. Such a sudden deposition of organic-rich material in an "oxic" environment with a low sedimentation rate initiates a sharp oxidation front as O₂-rich bottom-water diffuses into the sediment (e.g. WILSON *et al.*, 1985; DE LANGE, 1986). Elements mobile under oxidized conditions accumulate below the redox boundary (U, V and Zn) during the development of such a progressive oxidation front (JARVIS and HIGGS, 1987; THOMSON *et al.*, 1990; COLLEY and THOMSON, 1990). Fe and Mn, mobilized during anoxic and sub-oxic conditions, subsequently scavenge Ni and Co and to a lesser extent Cu. Another result of the emplacement of an organic-rich turbidite is that the underlying sediment becomes reduced and redistribution of transition metals occurs. This can result in the formation of reduction haloes and local trace metal enrichments (HARTMANN, 1979; JARVIS and HIGGS, 1987; THOMSON *et al.*, 1989).

We investigated the Madeira Abyssal Plain (MAP) sediments which are composed of three different types of turbidites, namely: organic-rich, volcanic and calcareous turbidites (DE LANGE *et al.*, 1987). These distal turbidites are very homogenous and fine grained. By their nature, these remarkably homogenous turbidites are extremely suited to study the effects of oxidation and the subsequent diagenetic alterations (e.g. WILSON *et al.*, 1986; PRAHL *et al.*, 1989; THOMSON *et al.*, 1989). Oxidation of the top of these turbidites caused drastic colour changes of the sediment, mostly from brown-pale green (oxidized) to dark green (reduced) (MIDDELBURG and DE LANGE, 1988). These colour changes are often accompanied by black or purple diffusive fronts above and below the oxidation front. In addition, some black and purple fronts do not seem to be associated with the brown-green colour transition (JARVIS and HIGGS, 1987).

In this study two sequential extraction techniques were used to investigate the pathways of the trace metal enrichments in MAP sediments. Special attention is given to the characterization of two of these coloured fronts that have developed above and below an oxidation front and one very pronounced front not associated with a colour transition.

MATERIALS AND METHODS

The MAP is a typical basin parallel to the continental margin and enclosed by the African and the Madeira continental rise in the east and abyssal seamounts in the west (Fig. 1).

The basin is filled with thick, ponded sediments delivered by distal turbidites, with a thickness ranging from a few centimetres to several metres and an average carbonate content of 50–60%. Due to the distal and non-turbulent nature (McCAYE and JONES,

Fig. 1. Map of the Madeira Abyssal Plain and the locations of the cores.

1988) the turbidites are ungraded, homogeneous, fine grained and pertain predominantly to the E-division of the Bouma turbidite facies (BOUMA, 1962). The base occasionally grades toward the D-division (WEAVER and KUIJPERS, 1983). Based on their provenance and composition, three major types of turbidites can be distinguished. These are organic-rich turbidites, turbidites with a volcanic component, and calcareous turbidites (DE LANGE *et al.*, 1987). The turbidites are intercalated with thin pelagic intervals that can be correlated by their coccolith distributions over very large distances (WEAVER and KUIJPERS, 1983; Fig. 2.).

Results will be presented from two cores, namely MD10 and PC5. The Stacor piston core MD10 was collected during the 1985 ESOPE cruise with the R.V. *Marion Dufresne* and is described in detail elsewhere (SCHÜTTENHELM *et al.*, 1989). Piston core PC5 was collected during the 1986 R.V. *Tyro* cruise. Samples were obtained from the organic-rich *f*-turbidite and calcareous *l*-turbidite (turbidite codes after WEAVER and KUIJPERS, 1983).

The samples selected in core PC5 are located in the *f*-turbidite (135 ky; 50–60% CaCO_3) in the region of a sharp colour change at a depth of 741 cm from pale green at the top towards dark green at the bottom. This depth represents the depth of O_2 diffusion after deposition. The O_2 penetration stopped after the deposition of a new turbidite and the diagenetic conditions changed to sub-oxic. Due to the development of the progressive

Fig. 2a and 2b. Stratigraphic column of core MD10 with expanded *l*-turbidite and stratigraphic column of the *f*-turbidite of core 86PC5.

oxidation front in the *f*-turbidite, the organic matter content above the colour boundary is only 0.14%, whereas below the boundary the normal value of 1% C_{org} is found (PRAHL *et al.*, 1989). The samples were collected at a depth of 720–722 cm from a thin laminar diffusive black–purple coloured front located above the paleo-oxidation front (front 1) and about 6 cm below the paleo-oxidation front at 746–748 cm (front 2) (Fig. 3). These fronts are not isolated curiosities observed only in core PC5, but are found throughout the MAP, often in the region of paleo-redox fronts.

The calcareous turbidite *l* (~300 ky) in core MD10 (80–90% $CaCO_3$) is grey at the top (1925 cm below core top) and gradually changes into grey–green at the bottom (2012 cm below core top). The samples were taken from a distinct, intense black–purple coloured

Fig. 3. Concentrations from respectively Cu, Co, Ni, S, Fe and Zn versus depth of front-1 in the *f*-turbidite. The hatched areas display the visible colour change to black-purple.

front, located 21 cm below the top of the turbidite. The edges of the coloured front were faint. The purple and black colours of all the fronts rapidly disappeared on exposure to air.

On board ship, the *f*-turbidite samples were taken, as soon as possible after recovery of the core PC5, with a bone spatula from the selected purple and black coloured fronts at mm scale intervals. For the samples of the *l*-turbidite in core MD10, samples were taken within a few months after recovery of the core. The core was always stored at 4°C, within hermetically closed D-tubes. After opening of the D-tubes and removing of 10–15 mm from the surface, the front was clearly visible and was subsequently sampled. All samples were transferred into snap-cups that were closed under a N₂ atmosphere and stored at –20°C.

First we applied a modified “Tessier-type” extraction scheme. This extraction scheme attempts to distinguish between the main mineralogical phases (absorbed/pore-water, carbonate, easy reducible Fe/Mn oxides, Fe oxides, pyrite and organic matter, residual

and silicates) in the sediment. Our results of the *f*-turbidite indicated (see Results section) that the diffusive colour band mainly showed increases in Cu and S, released during the first extraction steps. Therefore, for analyses of the *l*-turbidite samples of the in core MD10 we applied a more sensitive extraction scheme. This scheme was adapted from SUESS (1979) and MIDDELBURG (1991). This extraction procedure was developed specifically for the determination of authigenic mineral phases in anoxic sediments. It therefore might be useful for the extraction of reduced compounds from sub-oxic sediments. Both extraction procedures and the analytical details are briefly summarized in the next sections.

"Tessier-type" extraction

One to two grams of wet sample were transferred to 50 ml Teflon (FEP) airtight centrifuge tubes in a nitrogen gas (99.9995% N₂) filled glove-bag and weighed accurately. During extraction the solid-solution ratio was always >20. Corrections for water content were made by Cl⁻ analyses of the first extractant (NH₄Ac) assuming that all Cl⁻ was derived from seawater. Prior to contact with the samples, the chemical extractants of the first four extraction steps were thoroughly deoxygenated through bubbling with purified N₂ gas for several hours. To avoid unintended oxidation during mechanical shaking and sample handling all extractions and handling until step 5 were performed inside a glove-box system (DE LANGE, 1986) under nitrogen atmosphere (O₂ < 0.0002%).

Following each extraction step the well-closed tubes were centrifuged outside the glove-box and the supernatant was carefully removed and acidified with an appropriate amount of HCl inside the glove-box. No leakage of the tubes was observed during evacuating the airlock. After each extraction step the samples were washed with redistilled water to remove excess extractant (except extraction step 6) and added to the already obtained supernatant. The final residue (step 6) was quantitatively transferred into a Teflon vessel and dissolved in a HClO₄/HF/HNO₃ mixture, followed by evaporation to dryness. The final solutions were made up in 50 ml 1 N HCl. On the basis of a comparison between the sum of all extractions and the independently determined total concentrations, the total weight-loss of sample material was always found <20%. The extraction scheme is summarized in Table 1.

Table 1. *Tessier-type extraction scheme*

Fraction	Extractant	pH	Time (h)	Components
Exchangeable	1 N NH ₄ OAc	8.2	18	Pore-water cations
Carbonatic	1 N NaOAc	5.0	5	Carbonates
Easily reducible	0.1 N NH ₂ OH.HCl + HNO ₃ *	2.0	7	Mn-oxides and Fe-hydroxides
Moderate reducible	0.1 N NH ₄ -oxalate	2.5	5	Amorphous Fe-oxides, amorphous clay-minerals
Sulphidic/organic	30% H ₂ O ₂ + HNO ₃ * extracted after evaporation with 1 N NH ₄ OAc	2.0 7	3*2	Organic matter and mono sulfides
Residual	HF/HClO ₄ /HNO ₃ residue dissolved in HCl			Pyrite and crystalline Fe-minerals silicates

*HNO₃ is added to destroy the excess reducing agent.

Acid gradient extraction

The samples of the *l*-turbidite were subjected to an acid-gradient extraction (Suess 1979; Middelburg, 1991). No precautions were taken to avoid the contact of oxygen with the samples.

About 1 g of a wet fresh sample was weighed in 50 ml Teflon (FEP) airtight centrifuge tubes. After each extraction step the samples were centrifuged and the supernatants were carefully removed. This was followed by washing with distilled water to remove excess extractant. The supernatants of extraction steps 9 and 10 were transferred in a Teflon beaker and evaporated to dryness, and the final solutions were made up in 1 N HCl. The remaining sediment after step 11 was completely digested by a similar procedure used above. Reagent, concentration, duration and characterization of each extraction step are summarized in Table 2.

Total concentrations

The sums of the concentrations from the extractions were compared with the total concentrations determined independently. For the samples of the *l*-turbidite sufficient material remained for comparison. Due to the higher sample resolution in the *f*-turbidite, new samples, taken adjacent to the samples used for extraction, were used for this comparison. Total weight loss of sample material during the extraction procedures were estimated to be <10%. Background concentrations were derived from representative bulk samples taken in the middle of the reduced and oxidized part of the *f*-turbidite. To determine the total concentration, the samples were dried for 24 h at 105°C and thoroughly ground in an agate mortar prior to dissolution in an HClO₄, HNO₃, HF acid mixture. The final residue was taken up in 1 N HCl.

All elements used in this study (Ca, Al, Fe, S, Cu, Co, Mn, Zn and Ni) were measured with an ARL 34.000 Inductively Coupled Plasma emission spectrometer. Analytical precision and accuracy were determined by replicate analyses of some samples, an international standard (SO-1) and several house standards. The relative standard deviations of SO-1 (*n* = 15) were smaller than 2% for all elements, and accuracy was better

Table 2. Acid gradient extraction scheme

Step	Extraction solvent	Time (h)	Fraction
1	Quartz-subboil dest. H ₂ O	8	Porewater + exchangeable
2	NaAc/HAc (pH 5)	16	Carbonates + exchangeable
3	NaAc/HAc (pH 4)	8	Carbonates
4	HAc (0.5 N)	16	Carbonates
5	HCl (0.1 N)	8	Carbonates + Fe and Mn (hydr)oxides
6	HCl (0.5 N)	16	Fe-oxides
7	HCl (1 N)	8	Fe-oxides and sulfides
8	HCl (6 N)	16	Sulfides + crystalline Fe-oxides and Fe-silicates
9	HF (20%)	16	Fe-silicates and clay minerals
10	HNO ₃ (60%)	16	Pyrite
11	HF/HNO ₃ /HClO ₄		residual

than 4%. The bulk composition of the turbidites from the PC5 core are from a companion study (DE LANGE, in preparation).

It should be noted that the applied extraction methods are operationally defined. Therefore, the subsequent sequentially extracted fractions only partially represent different sedimentary phases. For example, in the Tessier-type scheme, no difference can be made between organic fractions and mono- or disulphide fractions (Table 1; TESSIER *et al.*, 1979; VAN VALIN and MORSE, 1982; RAPIN and FÖRSTNER, 1983; MARTIN *et al.*, 1987). Also, liberation of elements during a certain extraction step followed by adsorption by Fe-hydroxides or clay minerals will lower the recovery of these elements during that step. Moreover, during the acid-gradient extraction, oxidation of the samples could have caused a shift from a sulphide fraction to a more easily extractable fraction (KERSTEN and FÖRSTNER, 1987). Buffering of the pH due to the dissolution of carbonates in the first three steps of the acid gradient extraction caused a low specificity towards carbonate related fractions.

In general, care must be taken when interpreting the results of a sequentially performed extraction.

RESULTS

f-turbidite

Major elements. Major element (Ca, Al, Fe) concentrations display small variations over the coloured front. However, the concentration levels between front 1 and front 2 differ slightly (Table 3). The carbonate content of front 1 is approximately 5% lower than that of front 2. The lower carbonate content of the oxidized part is caused by dissolution of carbonate during (oxic) decomposition of organic matter. Due to the closure effect, Fe (Fig. 3) and Al concentrations are opposite to the carbonate content. The extraction results are summarized in Table 4.

Iron is mainly present in the residual fraction ($Fe_{res} > 90\%$). Reactive Fe (easily-moderate reducible fraction) equals about 10% of the total Fe concentration. (Table 4).

The Mn content is low (400 ppm). Most Mn (80%) is extracted in the "carbonate fraction" (1 N NaOAc, pH 5). This suggests that Mn exists rather than as a carbonate phase than as a Mn-oxide phase (e.g. BOYLE, 1983; THOMSON *et al.*, 1987). Manganese-oxides in this scheme would be extracted with the Chester-Hughes reagent (0.1 N $NH_2OH \cdot HCl$). The recovery of Mn for this fraction, however, is only about 40 ppm.

Trace elements. The concentration of some trace elements (Ni, Co) is constant with depth in front 2 but shows some variation in front 1 (Figs 3 and 4). In front 1, the highest

Table 3. Main composition of the coloured fronts in the *f*- and *l*-turbidite

	Ca (%) $\pm$ S.D.	Al (%) $\pm$ S.D.	Fe (%) $\pm$ S.D.
Front 1	20.3 $\pm$ 0.5	4.7 $\pm$ 0.1	2.6 $\pm$ 0.07
Front 2	21.4 $\pm$ 0.5	4.3 $\pm$ 0.1	2.1 $\pm$ 0.06
<i>l</i> -turbidite	35.2 $\pm$ 0.5	1.7 $\pm$ 0.05	0.9 $\pm$ 0.02

concentrations are found in the middle of the coloured front. Cu shows distinct peaks in both coloured bands and is up to three times enriched in front 2 (Fig. 4).

The concentration of S almost doubles in front 2 (Fig. 4). The increased concentrations of S in the front correspond with the background values as derived from the reduced bulk-samples. The recovery of sulphur of the organic and pyrite fraction (30% H₂O₂) does not contribute much to the total S concentration. The specificity of this step with respect to

Table 4. Summarized results of Tessier-type extraction. The selected intervals are above, inside and below the fronts, respectively. Concentrations in ppm; Depth in cm

		86pc5, f-turbidite, front 1			86pc5, f-turbidite, front 2		
		Depth 719.1–720.1	Depth 720.4–721.0	Depth 721.3–722.3	Depth 745.5–746.0	Depth 746.1–746.5	Depth 746.8–748.7
Fe	Exchangeable	9	5	6	4	14	7
	Carbonatic	50	21	16	10	101	102
	Easily reducible	740	666	486	442	1114	1284
	Moderate reducible	3014	3061	2745	2506	3246	2476
	Organic/sulphidic	30	21	53	14	27	15
	Residual	25,118	28,081	26,139	21,478	22,158	20,445
S	Exchangeable	1950	1610	1515	1342	2248	2687
	Carbonatic	0	0	57	0	0	31
	Easily reducible	0	0	0	0	0	0
	Moderate reducible	413	70	63	179	713	86
	Organic/sulphidic	60	11	0	141	196	227
	Residual	255	156	207	327	691	1333
Ni	Exchangeable	0	6	2	2	2	0
	Carbonatic	3	7	5	3	6	5
	Easily reducible	2	10	6	3	3	3
	Moderate reducible	5	5	5	9	6	5
	Organic/sulphidic	4	1	1	2	1	2
	Residual	25	22	24	21	21	25
Co	Exchangeable	0	0	0	0	0	0
	Carbonatic	1	4	2	0	2	1
	Easily reducible	3	6	4	3	5	4
	Moderate reducible	3	3	4	3	3	3
	Organic/sulphidic	2	1	2	1	2	1
	Residual	7	8	8	7	7	7
Cu	Exchangeable	15	63	32	0	21	0
	Carbonatic	12	35	24	0	25	2
	Easily reducible	6	21	27	1	19	3
	Moderate reducible	19	14	15	20	34	17
	Organic/sulphidic	1	0	0	0	1	1
	Residual	15	12	12	23	20	28
Zn	Exchangeable	1	1	0	0	1	2
	Carbonatic	5	5	2	3	7	8
	Easily reducible	7	6	4	11	14	15
	Moderate reducible	18	14	21	19	21	20
	Organic/sulphidic	9	4	10	4	6	5
	Residual	45	48	50	42	46	45

Fig. 4. Concentrations from respectively Cu, Co, Ni, S, Fe and Zn versus depth of front-2 in the *f*-turbidite. The hatched areas display the colour change to black-purple.

pyrite is not very high. If pyrite is present, most will be extracted in the residual step (TESSIER *et al.*, 1979). In the lower part of front 2 about 50% is extracted in the residual and organic matter (pyrite) step (Table 4). Therefore, the increase found in total S is possibly due to an increase in pyrite. Note that the highest S concentration corresponds to the highest Cu concentration. This increase in S is closely matched by a small increase in (residual) Zn, but not by Co and Ni. The distribution of the trace elements Ni, and Co in the different fractions does not show much variation. Note that for these trace elements a large amount is found in relatively reactive fractions (Table 4).

Surprisingly, the Cu distribution over the various fractions changes significantly in the coloured fronts (Fig. 6a and b). The Cu concentration remains constant, only in the residual and oxide fractions. In contrast, the Cu concentration in the exchangeable, carbonate and easy reducible fractions demonstrates a 10-fold increase relative to the concentration in the samples taken outside the coloured front, especially in front 2 (Fig.

Fig. 5. Concentrations from respectively Cu, Co, Ni, S, Fe and Zn versus depth of the front in the *l*-turbidite.

6a; Table 4). The “excess” Cu concentration (Cu concentration in the peak minus the Cu concentration outside the coloured front) is about 130 ppm.

l-turbidite

The concentrations of Co, Ni and Zn are constant nearly across the coloured front, whereas those of Cu and S display distinct enrichments (Fig. 5). Cu is about six times enriched compared with the lowest value in this interval and S about four times. A clear linear relation is observed between the Cu and S enrichments (Fig. 7). The distribution of Cu in the *l*-turbidite follows the same pattern as that found in the *f*-turbidite. In the refractory fractions, residual and oxides fractions, Cu is constant. In the front, which is represented by sample 55.157, Cu is enriched in the exchangeable–carbonate–easily destructible oxides fractions. The enrichment of Cu can be attributed almost entirely to the increase of Cu in the exchangeable–easily soluble oxides–carbonate fractions. Also the concentration of S is higher in the exchangeable–pore-water fraction in the front (Fig. 8). The Cu concentration of the mild extracted fraction is about 7.9 mmol kg^{-1} . The excess S concentration is about $15.6 \text{ mmol kg}^{-1}$. The ratio Cu:S is 0.51.

Due to the high carbonate content ($\text{CaCO}_3 > 80\%$) the first five steps are dominated by a carbonate phase. The high carbonate content probably overloaded the buffer capacity

Fig. 6. The cumulative distribution of Cu from respectively front 1 and 2 in the *f*-turbidite. The arrow indicates the samples with in the front. Note that the samples are not equally spaced. The numbers at the hatches in the legend box correspond to the different extracted steps. 1 = NH_4Ac ; 2 = NaAc ; 3 = $\text{NH}_2\text{OH}.\text{HCl}$; 4 = $\text{NH}_4\text{-oxalate}$; 5 = $\text{H}_2\text{O}_2/\text{HNO}_3$; 6 = HF/HClO_4 . For a complete extraction scheme the reader is referred to Table 1.

during each of these extractions, raising the pH. The selectivity of the first quartz distilled water step towards exchangeable phases is probably low and only dissolved phases (salts) are extracted. Therefore an overlap between exchangeable sorbed phases and carbonate related phases is suspected in step 2.

The HNO_3 step designed for extraction of pyrite (LORD, 1983) has a low recovery for most elements, suggesting the absence of pyrite.

DISCUSSION

Two different front types can be distinguished. The first type, exemplified by the front above the redox-front in the *f*-turbidite, is enriched in various trace elements and does not show an association with S. The second type, represented by the fronts in the *l*-turbidite

Fig. 7. Cu versus S from the front in the *l*-turbidite.

Fig. 8. Cu and S release during the successive extraction steps of sample 55.157. The numbers correspond to the extractions steps as summarized in Table 2.

and that below the colour change of the redox front in the *f*-turbidite, is extremely enriched in Cu and associated with S, but is almost not enriched in other trace metals.

In the interpretation below, we first describe the general diagenetic processes that occur during the emplacement of a turbidite. Subsequently, we discuss the impact of these processes on the distribution of Cu. The point we make is that the front type-1 is a remnant of the paleo-oxidation front whereas front type-2 is caused by accumulation of easily extractable and oxidizable Cu-S compounds.

Formation of front type-1

During pelagic sedimentation the rate of accumulation of organic matter is low and all but the most refractory organic matter is oxidized quickly after deposition. Consequently, O_2 supplied by diffusion from the bottom-water may persist in the pore water down to considerable depths resulting in an *oxic* sediment.

After emplacement of a (organic-rich) turbidite, oxidation of excess labile organic matter by bottom-water O_2 diffusing downward from the sediment-water interface ("burn-down") can lead to a sharp colour change as observed in the *f*-turbidite. After O_2 is exhausted, nitrate, manganese and iron are subsequently used as oxidants in the bacterially mediated decomposition of organic matter.

As a result of the continuous supply of dissolved Fe and Mn from the underlying reduced sediment and the downward migration of the oxidation front, Fe and Mn enrichments are formed near this front. This also may lead to enrichments of elements such as Ni, Co, Zn and Cu that are involved in the Mn-cycle and easily scavenged by Fe-hydroxides (WILSON *et al.*, 1986; WALLACE *et al.*, 1988). Elements that were previously fixed in the reduced upper part of the turbidite, such as U, V and Cu (COLLEY and THOMSON, 1985; THOMSON *et al.*, 1990), will be released as the oxidation front passes, and will accumulate just below the redox-boundary.

At deposition of the next turbidite the penetration of O_2 stops and the underlying sediment becomes more reduced. Since the organic matter of turbidites is mostly reworked, the underlying sediments will not acquire sulphate reduction but will become post-oxic or sub-oxic. The previously formed Fe and Mn enrichments at the (old) redox-boundary and their associated trace metals will slowly dissolve and redistribute. If the duration of post-oxic conditions is long enough, all the Fe and Mn enrichments will

disappear (FINNEY *et al.*, 1988). Mn is easily adsorbed to carbonates (BOYLE, 1983) and will be decoupled from Co, Ni and Cu that do not have such a high affinity with carbonates.

Redistribution probably takes place along redox-gradients. Because the studied coloured fronts are equilinear to the sediment–water interface, the redox-gradient is coupled to a large scale, long term diagenetic process. The Cu, Ni, Co and Zn enrichments in the fronts (Fig. 3) are explained by increases of these elements in the exchangeable, carbonate and easily-reducible Fe-hydroxides fractions. Therefore, redox-driven, non-specific sorption to clays, calcite and, most of all, hydroxides is likely to be the most important process controlling the formation of type-1 fronts.

Formation of front type-2

In the MAP sediments, Cu is delivered by organic-rich turbidites that inherited their Cu-organic complexes content from the shelf sediments (CHESTER *et al.*, 1988). Consequently, the organic carrier survives destruction at the sediment–water interface. During the burn down stage of the turbidite some Cu is probably liberated due to the degradation of the organic carrier. Subsequently, Cu can be involved in the Mn-cycle or is released into the pore-water. Some Cu will remain in the anoxic (organic-rich) part of the turbidite. After liberation by the oxidation front, this Cu can be adsorbed to authigenic clays or react with sulphides. Additionally, Cu can be complexed again with organic matter and as a result accumulate below the redox-boundary, like U and V (WALLACE *et al.*, 1988; COLLEY and THOMSON, 1985, 1990). However, this is probably not the main process for Cu enrichment in type-2 fronts. The fact that Cu is the only trace element that is enriched (Figs 4 and 5), and the association of Cu with S suggests an additional phase in the Cu diagenesis. The molar Cu:S ratio of 1:2 suggests that authigenic Cu–S precipitation might explain the formation of type-2 fronts. In oxic seawater, concentrations of 3–10 nM of HS^- have been measured (LUTHER and TSAMAKIS, 1989). SHAW *et al.* (1990) reported values of dissolved Cu up to 115 nM in marine sub-oxic pore-waters, although in most cores that they investigated, Cu concentrations decreased rapidly with depth to 0–10 nM. Using a $[\text{HS}^-]$ of 100 μM (10 times oxic seawater) and a $[\text{Cu}^{2+}]$ of 100 nM we calculated a near-saturation with respect to CuS_2 using the CHARON program (N. M. DE ROOIJ, Delft Hydraulics Laboratory). However, the concentrations that we assumed are likely to be much lower, especially that of Cu. In seawater over 90% of the “dissolved” Cu is complexed with organic ligands lowering the activity of Cu (DONAT and VAN DEN BERG, 1992). Dissolved organic-C levels in sub-oxic pore-waters are usually more than 10-fold that of seawater. It seems therefore that the formation of authigenic Cu-sulphide in these sub-oxic sediments is not a viable explanation for the observed relation between Cu and S. This implies that Cu–S association must have existed before the formation of the fronts and has accumulated at the present locations of the fronts.

The extent of mobilization of the Cu–S association is not limited to an organic-rich turbidite, as demonstrated by the Cu–S (Fig. 5) enriched front in the *l*-turbidite. The source of the Cu–S association of the coloured front in the *l*-turbidite is probably not the *l*-turbidite itself. This calcareous turbidite is not comprised of (organic-rich) shelf sediments, but has an oceanic western origin where sulphate reduction does not occur (DE LANGE *et al.*, 1987; SCHÜTTENHELM *et al.*, 1989). The origin of the Cu–S association therefore must lie in adjacent organic-rich (Cu-bearing) turbidites. The nearest organic-rich turbidite is the *l*₁-turbidite that is found 80 cm below the *l*-turbidite (MIDDELBURG

Fig. 9. pe versus depth from core 85MD10. The hatched area represents the coloured front in the l -turbidite.

and DE LANGE, 1988). This implies that the mobilization distance of the Cu-S association is at least 80 cm (Fig. a). Transport of the Cu-S association could occur *via* intermediate organic (S) components, enhanced by the high affinity of Cu for organic compounds (RASHID, 1985). Indeed, the extraction of Cu and S under mild conditions (Figs 6 and 8) and the rapid disappearance of the colour of the front suggests a labile organic or easily oxidizable Cu compound. The performed extractions, however, do not allow the identification of the exact composition and nature of the Cu-S association.

Accumulation of Cu. An indication that relict oxidation fronts could be a source for this accumulation is given by the change in S in front 2 of the f -turbidite. Although the colour change in the sediment is governed by the Fe^{III}/Fe^{II} ratio (LYLE, 1983; DE LANGE, 1988), the extent of the progressive oxidation front may have been deeper. In the initial stage of "burn-down", oxidation of the organic matter and other reduced compounds occurs at a sharp oxidation front, mainly by O_2 . The classical redox sequence (FROELICH *et al.*, 1979) is not observed, as all reactions takes place in a very thin interval. As the front moves down, the flux of oxidants is compensated by the reduced compounds, and the burn-down process will be decelerated. Consequently, the process will incline towards a new steady state situation. As a result, the front will become stretched and the different reactants (Fe, Mn, NO_3 , O_2) will be separated according to their redox potential. The oxidation of organic matter and reduced Fe can take place at a higher level than the oxidation of pyrite.

The stepwise increase of S (and Zn, Fig. 4) below the paleo-oxidation front suggests that the oxidation of pyrite occurred deeper than the colour change caused by the transition of $\text{Fe}^{\text{III}}\text{--Fe}^{\text{II}}$. These changes in p_e probably are sufficient to accumulate the Cu–S association in distinct bands in the region of paleo-oxidation fronts.

The Cu–S association in the *I*-turbidite probably also accumulated in response to a redox-gradient. The p_e against depth profile (Fig. 9) displays a conspicuous peak at a depth of about 21 m. Remarkably, the Cu-enriched front lies just above this peak, at the steepest incline of this p_e gradient. Although the formation of such redox boundary under sub-oxic conditions is yet unclear, these coloured, Cu-enriched layers may be very sensitive indicators for redox changes.

Summarizing, sub-oxic diagenesis can play a very important role in the Cu cycle and could be the most important stage for accumulation of Cu in marine sediments. It is remarkable that even under sub-oxic conditions in deep-sea sediments significant metal enrichments are formed that persist in a labile phase over a long period and over a large area. However, many questions remain unsolved. Future research must be able to: (1) identify the exact nature of the Cu carriers and (2) estimate the importance of sub-oxic diagenesis for the accumulation of Cu-rich phases.

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