10. DEVELOPMENT OF REDUCTION HALOES UNDER CALCAREOUS AND VOLCANICLASTIC TURBIDITES IN THE LAU BASIN (SOUTHWEST PACIFIC)¹

J. Thomson,² R.G. Rothwell,² and N.C. Higgs²

ABSTRACT

The sediment column overlying basement in the Lau Basin consists of a sequence of volcanoclastic turbidites interbedded with hemipelagic clayey nannofossil mixed sediments, overlain in turn by a sequence of hemipelagic clayey nannofossil oozes containing sporadic calcareous turbidites. The clayey nannofossil oozes and mixed sediments are pervasively stained by hydrothermally derived iron and manganese oxyhydroxides. Sharply defined, lighter colored bands occur in the hemipelagic sediments, immediately beneath some (but by no means all) volcanoclastic and calcareous turbidites. These are identified as reduction haloes, of a type previously identified in quite different turbidite/pelagic sequences. The haloes are attributed to the burial of labile surficial C_{org} by turbidites, followed by the remineralization of this C_{org} with Mn and Fe oxyhydroxides as electron acceptors. The resultant characteristic Mn and Fe concentration/depth profiles are described, and a model is proposed for their development. The color alteration of the halo is ascribed to the removal of Mn oxyhydroxides, because, although the Fe content fluctuates through the haloes, this does not appear to affect their color. Other elements (Co, Cu, and Ni) are also at low concentration levels in the haloes like Mn, consistent with remobilization and migration out of the halo section, although the profile shapes are not identical with those of Mn. The behavior of V is distinctive in that it appears to have migrated into the haloes to be enriched there. Haloes are unlikely to form if turbidite emplacement is erosive and removes the near-surface layer, which generally is the most fluid part of the sediment and contains the highest levels of reactive C_{org} to drive the reduction process. Conversely, the presence of a halo implies that emplacement of the overlying turbidite did not significantly erode the pre-existing sediment/water interface.

INTRODUCTION

Deep-sea cores often reveal that turbidites are an important component of basin plain sediments; indeed, such redeposited sediments can dominate sediment accumulation over long periods of time. Thus, turbidite sedimentology is an active research area, but little account is generally taken of postdepositional, early diagenetic effects. Such geochemical reactions can produce readily recognizable alterations, particularly to sediment color, which can be a useful diagnostic tool in core interpretation. One example is the progressive oxidation front, in which bottom-water oxygen modifies the tops of turbidite units and causes marked color changes (Jarvis and Higgs, 1987; Thomson et al. 1987).

A different observation frequently made during shipboard core description of cores from the Lau backarc basin on Ocean Drilling Program (ODP) Leg 135 was the presence of lighter colored bands immediately beneath some turbidite units. These lighter colored sediments, which had a very sharp lower boundary, were not present elsewhere in the same cores, and were reminiscent of the "reduction haloes" investigated in Atlantic brown clays by Thomson et al. (1989). It is important to identify features that are the result of diagenetic reactions rather than primary sedimentary features for core description and stratigraphic assessment. Consequently, we report an investigation into the nature of these lighter colored bands and their significance.

SEDIMENTATION IN THE LAU BASIN

The western Lau Basin, between the central and eastern Lau spreading centers and the Lau Ridge, contains several small, elongate, fault-bounded, sediment-filled sub-basins. Sites 834 and 835 were drilled in two of these basins between 100 and 200 km east of the axis of the Lau Ridge, whereas Sites 836, 837, 838, and 839 were drilled

in small basins much closer to the East Lau Spreading Center (ELSC; Fig. 1). The sediment column overlying the basement basalts at all sites consists primarily of a lower sequence of volcanoclastic turbidites interbedded with hemipelagic clayey nannofossil mixed sediments and nannofossil clays; this in turn is overlain by an upper sequence of hemipelagic clayey nannofossil oozes that sometimes contain calcareous turbidites. The thicknesses of both the volcanoclastic turbidite sequence and the overlying clayey nannofossil ooze sequence are variable.

The clayey nannofossil oozes and mixed sediments at all sites are pervasively stained reddish brown to yellowish brown by hydrothermally derived iron and manganese oxyhydroxides. These occur as small aggregates within the sediments and as surface coatings around the sedimentary grains. Hydrothermally derived iron and manganese oxyhydroxides are widely distributed throughout the sediments of the Lau Basin (Cronan et al., 1986; Hodgkinson et al., 1986; Reich et al., 1990). Typically, the clayey nannofossil oozes are stained brown to dark yellowish brown, having Munsell color values and chromas within the hue 10YR. Typical colors are moderate (10YR 5/4) to dark yellowish brown (10YR 4/2).

Frequently, bands of lighter color occur in the clayey nannofossil sediments directly beneath turbidite bases. These lighter colored bands occur under both calcareous and volcanoclastic turbidites, but they are not universal, frequently being quite rare in many of the interbedded turbidite/hemipelagite sequences. They occur at all the backarc sites, although they are more common in the sediment sequences at Sites 837 and 839. Typical colors of these lighter bands are moderate yellowish orange (10YR 6/6 to 10YR 6/4) to moderate yellowish brown (10YR 5/4). Their lower boundaries with the darker clayey nannofossil ooze are sharp and the bands contrast with the underlying sediment, varying in thickness from a few millimeters up to 88 cm. The thickness of these lighter bands is independent of the thickness of the overlying turbidite and of the thickness and coarseness of any basal sand. Even under very thick turbidites, they are never more than 1 m thick.

These lighter colored bands present beneath turbidites are strongly reminiscent of the "reduction haloes" investigated in Atlantic brown clays by Thomson et al. (1989). The sediment types in these two cases

¹ Hawkins, J., Parson, L., Allan, J., et al., 1994. *Proc. ODP, Sci. Results*, 135: College Station, TX (Ocean Drilling Program).

² Institute of Oceanographic Sciences, Brook Road, Wormley Near Godalming, Surrey GU8 5UB, United Kingdom.

Figure 1. Location of ODP sites drilled in the Lau Basin, Western Pacific, during Leg 135. Also shown are the main geological features of the Tonga Trench and Lau Basin system. Islands shown are Tongatapu (T), 'Eua (E), Vava'u (V), Niufo'ou (NF), 'Ata (A), and Upolu (U). Locations of the Central Lau (CLSC) and East Lau (ELSC) spreading centers, Valu Fa Ridge (VF), Mangatolu Triple Junction (MTJ), and Zephyr Shoal (Z) are also shown.

are entirely dissimilar, however. The brown clay reduction haloes occurred in the sediments of the Nares Abyssal Plain, which comprise slowly accumulated brown clays interbedded with turbiditic grey clays. Both clay types had a similar mineralogical composition with a negligible carbonate content, and the color differences were found to be the result of different Mn and Fe contents and redox status. Such clays are quite unlike the Lau Basin sediments, which are considerably more complex compositionally. Thomson et al. (1989) ascribed the reduction haloes in the Nares sediments to the burial of labile surficial C_{org} by turbidites, followed by the oxidation of this C_{org} with Mn and Fe oxyhydroxides as electron acceptors after the original pore-water oxygen was exhausted. This process will be discussed in more detail below, but it seems likely that the burial of the labile C_{org} at former sediment surfaces by turbidites is the link in the two contrasting situations. For different reasons, the nonturbiditic sediments of both areas have substantial Mn and Fe oxyhydroxide contents to act as electron acceptors. This study was undertaken to investigate this interpretation and the pattern of diagenetic relocation of elements within the haloes.

METHODS

Two vertical profiles through the lighter colored bands beneath a calcareous turbidite (in Section 135-834A-2H-1; Fig. 2) and a volcanoclastic turbidite (in Section 135-837A-8H-2; Fig. 3) were sampled. Each example was sampled from above the base of the turbidite, through the lighter colored band, and down into the darker clayey nannofossil ooze below. In both cases, the turbidites were chosen for their relative thickness (>3.5 m) and for the thickness of the lighter colored bands beneath them (15–20 cm).

For each profile, 25 samples were taken, about 1–2 cm apart, using 5-ml capacity syringes of 1-cm diameter to extract 2-cm³ samples of wet sediment, which gave a dry sample mass of approximately 1 g. Thus, sampling was at the maximum allowed ODP sampling density (50 cm³/m removed from the core). The samples were dried at 110°C and ground manually in agate. Aliquots of 0.5 g were dissolved in HF/HClO₄, heated to near dryness, redissolved in 5 ml 5N HNO₃, and diluted to 50 ml with double distilled water for simultaneous ICP-AES analysis (Totland et al., 1992). The elements Al, Fe, Mn, Mg, Na, K, Ti, Co, Cu, Ni, Sc, Sr, V, Y, Zn, and P were determined. Precision ranged from 2% to 5% for all elements except P₂O₅ and Sc (6%). Accuracy was assessed by analysis of USGS standard basalt BHVO-1 (see Table 2). Calcium carbonate analyses were performed using the Coulometrics analyzer on the CO₂ released from 25-mg samples by acid treatment. Precision for carbonate analysis was better than 1% relative.

RESULTS AND DISCUSSION

The two core sections investigated (Figs. 2 and 3) show minor coring distortion of the interface between the base of the turbidite and the top of the underlying sediment; in both, the lower limit of the light-colored sediment is sharply defined. The lighter color of the calcareous turbidite in Section 135-834A-2H-1 contrasts with the darker color of the volcanoclastic turbidite in Section 135-837A-8H-2. Compositionally, the hemipelagic clayey nannofossil ooze beneath the basal turbidite foraminiferal sand in Section 135-834A-2H-1 consisted of about 35%–40% clay, 5% foraminifers, and the remainder, calcareous nannofossils. The color of the lighter colored band directly beneath the calcareous turbidite in this core is very dark yellowish orange (10YR 5/6), whereas the clayey nannofossil ooze directly beneath the lighter colored band is very dark yellowish brown (10YR 3/4) (Fig. 2). In Section 135-837A-8H-2, the hemipelagic sediment directly below the volcanoclastic turbidite base consists of up to 50% clay and 5% foraminifers. The rest is composed of calcareous nannofossils and is considered to be a mixed sediment, according to the classification of Mazzullo et al. (1987). The lighter colored band in

Figure 2. Lighter colored band beneath a thick calcareous turbidite in Section 135-834A-2H-1. The lighter colored band is dark yellowish orange (10YR 5/6) and contrasts with the much darker dark yellowish brown (10YR 3/4) clayey nannofossil ooze below. The lighter colored band is 19 cm thick.

Figure 3. Lighter colored band beneath a thick volcaniclastic turbidite in Section 135-837A-8H-2. The lighter colored band is yellowish brown (10YR 6/4) and contrasts with the much darker dark yellowish brown (10YR 4/3) clayey nannofossil ooze below. The lighter colored band is 22 cm thick.

this core is light grayish orange (10YR 6/4), whereas the nannofossil clay mixed sediment directly below the lighter colored band is very dark yellowish brown (10YR 4/3) (Fig. 3).

Selected major and minor element concentration/depth profiles corresponding to the core sections of Figures 2 and 3 are shown in Figures 4 and 5, and the complete data for all the elements measured are listed in Tables 1 and 2. The differences in the composition of the two turbidites in comparison with the underlying pelagic sediments are clear, with CaCO_3 dominating the composition of the high magnesian calcite turbidite in Section 135-834A-2H-1 (Fig. 4), and high Al_2O_3 (and TiO_2) characterizing the volcaniclastic turbidite in Section 135-837A-8H-2 (Fig. 5). The turbidite in Section 135-837-8H-2 shows some fluctuation in Al_2O_3 content, consistent with basal grading, as well as increased Fe_2O_3 coincident with the blue/black stain at 46–52 cm (66.94–67.00 mbsf) at the base of this turbidite (Fig. 5).

The underlying hemipelagic sediments in both cases contain around 50%–60% CaCO_3 , and both also show compositional fluctuations (range: 48%–82% CaCO_3) with depth. These carbonate/noncarbonate fluctuations are a complication over the previously studied Nares cases (Thomson et al. 1989), where the pelagic clays were essentially carbonate-free and the geochemically inert elements had a uniform content. Some sediments can be approximated as a two-component system comprising biogenic CaCO_3 and clay, and in such cases carbonate fluctuations can be overcome by expressing data on a carbonate-free basis because biogenic carbonate is essentially pure CaCO_3 . This technique is not appropriate here because the hemipelagic Lau Basin sediments also contain a third (hydrothermal) component. A further uncertainty for interpretation of the Lau Basin sediments is that the two sections investigated are only 30% sampled ($25 \times 1\text{-cm}$ samples in 80 cm), whereas the previous work (Thomson et al. 1989) sampled in contiguous 1-cm increments and observed that redox-sensitive elements showed considerable local detail in their redistributions. The approach taken in the interpretation of the redox-sensitive element data of Sections 135-834A-2H-1 and 135-837A-8H-2, therefore, is to seek similarities first between their element concentration/depth profiles, and second with the three examples from the Nares Abyssal Plain previously investigated (Thomson et al., 1989).

Behavior of Mn and Fe

Marked similarities are present between the profile shapes of Mn and Fe through the light-colored sediments in the two Leg 135 examples.

1. For example, consistently low Mn levels are present throughout the light-colored sediments in comparison with the underlying hemipelagic sediments. The slight increase in Mn content with depth in the light colored sediments in Section 135-834A-2H-1 is a consequence of the decreasing calcium carbonate content with depth (Fig. 4), whereas the Mn and carbonate contents in the light colored interval of Section 135-837A-8H-2 are essentially invariant (Fig. 5).

2. In addition, a more complex Fe shape occurs in the light-colored sediments, with low values immediately below the turbidite, increasing with depth through a maximum, and then decreasing within the light-colored sediments. The Fe levels of the maxima in the light colored sediments are the highest observed in the two core sections (Figs. 4–6).

These general profile shapes for Fe and Mn are identical with those observed previously in the three Nares Abyssal Plain examples investigated (Thomson et al., 1989), and this is taken as justification for referring henceforth to the light-colored sediments as *reduction haloes*. The model developed from the Nares examples envisaged that, in the absence of O_2 after turbidite emplacement, all available Mn oxyhydroxide near the sediment/water interface was used first for labile C_{org} remineralization. This mobilizes Mn as Mn^{2+} , which is then free to diffuse in pore-water solution. Residual labile C_{org} present at

Figure 4. CaCO₃ and geochemical profiles for Al₂O₃, Fe₂O₃, MnO, Co, Cu, Ni, and V through the base of the calcareous turbidite, reduction halo, and underlying clayey nannofossil ooze in Section 135-834A-2H-1 (8.2–9.0 mbsf).

Figure 5. CaCO₃ and geochemical profiles for Al₂O₃, Fe₂O₃, MnO, Co, Cu, Ni, and V through the base of the volcaniclastic turbidite, reduction halo, and underlying clayey nannofossil ooze in Section 135-837A-8H-2 (66.8–67.6 mbsf).

Table 1. Results of geochemical analyses by ICP-AES through reduction halos in Section 135-834A-2H-1.

Core, section, interval (cm)	Depth (mbsf)	Major elements								Trace elements								
		CaCO ₃ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MnO (%)	MgO (%)	Na ₂ O (%)	K ₂ O (%)	TiO ₂ (%)	Co (ppm)	Cu (ppm)	Ni (ppm)	Sc (ppm)	Sr (ppm)	V (ppm)	Y (ppm)	Zn (ppm)	P ₂ O ₅ (%)
135-834A-																		
2H-1, 70-71	8.30	92.1	0.75	0.48	0.12	2.66	1.19	0.09	0.03	13	21	6	2	2727	3	7	35	0.15
2H-1, 73-74	8.33	91.7	0.78	0.39	0.12	2.72	1.60	0.12	0.03	6	12	4	2	2600	3	7	21	0.16
2H-1, 77-78	8.37	93.4	0.65	0.30	0.12	2.92	1.22	0.10	0.03	4	9	4	1	2565	<LD	5	13	0.17
2H-1, 80-81	8.40	92.3	0.79	0.44	0.13	2.74	1.43	0.12	0.04	6	17	6	2	2435	12	6	15	0.17
2H-1, 83-84	8.43	91.8	0.91	0.46	0.12	2.90	1.20	0.10	0.04	3	15	5	2	2538	16	7	24	0.15
2H-1, 85-86	8.45	93.4	0.77	0.41	0.11	2.97	1.17	0.08	0.04	4	12	5	2	2648	15	6	26	0.15
2H-1, 88-89	8.48	91.4	0.84	0.41	0.11	2.76	1.24	0.08	0.04	8	12	5	2	2421	21	6	16	0.15
2H-1, 91-92	8.51	90.9	0.73	0.38	0.11	2.70	1.19	0.09	0.03	5	15	5	2	2448	12	7	18	0.16
2H-1, 93-94	8.53	92.0	0.79	0.51	0.11	2.70	1.17	0.07	0.04	4	30	6	2	2610	15	7	32	0.16
2H-1, 95-96	8.55	81.9	2.07	2.07	0.20	2.26	1.82	0.23	0.10	8	48	24	5	2014	119	26	47	0.20
2H-1, 97-98	8.57	81.6	2.02	2.29	0.21	2.02	1.87	0.23	0.09	7	50	26	6	2323	130	28	61	0.21
2H-1, 100-101	8.60	74.1	2.77	3.29	0.27	1.73	2.21	0.31	0.13	12	115	37	8	1494	152	40	57	0.23
2H-1, 103-104	8.63	65.5	3.82	5.09	0.34	1.43	2.65	0.44	0.17	21	52	50	10	1085	152	49	76	0.27
2H-1, 106-107	8.66	71.0	3.68	5.43	0.35	1.27	3.08	0.52	0.15	13	35	61	9	1133	153	50	76	0.30
2H-1, 108-109	8.68	66.0	3.15	5.66	0.37	1.30	2.46	0.43	0.14	10	29	56	9	1076	116	54	84	0.28
2H-1, 110-111	8.70	64.5	3.58	6.92	0.44	1.45	2.51	0.46	0.17	17	31	65	10	1109	112	61	101	0.32
2H-1, 112-113	8.72	63.7	3.61	5.92	0.40	1.16	3.41	0.49	0.15	15	41	71	8	1037	84	53	92	0.32
2H-1, 114-115	8.74	67.1	3.52	4.57	1.44	1.14	2.67	0.33	0.16	39	177	76	10	1305	78	62	84	0.33
2H-1, 116-117	8.76	60.6	3.60	4.34	1.67	1.08	2.67	0.34	0.16	48	181	79	9	1133	63	62	77	0.33
2H-1, 118-119	8.78	65.8	3.75	4.47	1.70	1.14	2.70	0.34	0.17	44	163	80	10	1164	65	66	82	0.34
2H-1, 123-124	8.83	63.4	4.31	4.96	1.87	1.11	3.48	0.42	0.19	53	195	98	10	1086	101	62	89	0.38
2H-1, 126-127	8.86	64.5	3.67	4.76	1.94	1.13	2.66	0.32	0.17	45	159	86	10	1279	92	69	87	0.35
2H-1, 128-129	8.88	64.8	3.82	5.23	1.88	1.23	2.75	0.35	0.17	39	164	87	10	1154	90	70	114	0.37
2H-1, 131-132	8.91	63.8	3.91	5.32	1.84	1.28	2.58	0.33	0.19	48	155	81	11	1137	89	69	95	0.37
2H-1, 134-135	8.94	64.9	3.95	4.76	1.55	1.14	3.13	0.35	0.17	55	166	83	10	1106	102	62	90	0.37

Note: <LD = less than limits of detection.

Figure 6. Quantitative color log through the interval 135-837A-8H-2 (20-115 cm) showing variation in intensity in the red video primary (700 nm), made using the CIE LAB color system, with MnO and Fe₂O₃ profiles plotted alongside. Note that changes in Mn concentration broadly correlate with variations in color intensity in the halo and underlying clayey nannofossil ooze, with low manganese values correlating with lighter color and high manganese values correlating with darker color. Variations in Fe content appear to be unrelated to variations in color, except in the base of the turbidite where a short interval of darker color correlates with increased Fe content.

the top of the buried former sediment surface, was then further remineralized by Fe oxyhydroxide reduction. This accounts for the low Fe levels observed immediately below the turbidites.

The final step of the model is that Fe²⁺ downward diffusion and reaction with Mn (IV) oxyhydroxide (Postma, 1985), mobilized further Mn²⁺ in the lower parts of the haloes. This exchange of solid phase Mn by Fe is the reason for the Fe maxima observed within the reduction halo and is the cause of the sharp color change at the base

of the halo. This color alteration of the haloes is ascribed to the lack of Mn oxyhydroxide because, although the Fe level fluctuates through the haloes, this does not appear to affect their color (Fig. 6). From the Fe and Mn profiles of the Nares Abyssal Plain haloes, it was possible to reconstruct profiles of the labile C_{org} at the buried sediment surface because of the homogeneity of the sediments. These profiles were of a reasonable magnitude and shape in comparison with modern surface sediments in that area. In the present cases, compositional fluctuations

Table 2. Results of geochemical analyses by ICP-AES through reduction halos in Section 135-837A-8H-2.

Core, section, interval (cm)	Depth (mbsf)	Major elements								Trace elements								
		CaCO ₃ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MnO (%)	MgO (%)	Na ₂ O (%)	K ₂ O (%)	TiO ₂ (%)	Co (ppm)	Cu (ppm)	Ni (ppm)	Sc (ppm)	Sr (ppm)	V (ppm)	Y (ppm)	Zn (ppm)	P ₂ O ₅ (%)
135-837A-																		
8H-2, 34-35	66.84	6.8	11.79	3.25	0.14	1.43	5.04	1.20	0.53	70	27	20	16	174	64	46	74	0.12
8H-2, 36-37	66.86	6.7	12.20	3.35	0.13	1.48	4.85	1.15	0.52	38	28	6	16	187	65	41	75	0.14
8H-2, 40-41	66.90	7.9	12.47	3.69	0.14	1.72	4.58	1.05	0.55	42	31	8	17	202	69	40	72	0.14
8H-2, 44-45	66.94	8.9	11.97	5.16	0.16	2.12	4.16	1.04	0.61	34	41	15	19	197	126	39	77	0.15
8H-2, 47-48	66.97	6.0	16.24	5.31	0.16	2.58	4.89	0.95	0.70	248	66	14	23	205	143	33	86	0.19
8H-2, 51-52	67.01	7.3	12.56	4.23	0.18	1.96	4.27	1.00	0.59	49	42	9	19	189	85	37	77	0.15
8H-2, 54-55	67.04	7.1	14.07	4.71	0.16	2.36	4.09	0.86	0.62	76	61	14	22	205	109	34	77	0.16
8H-2, 56-57	67.06	53.2	6.42	4.90	0.38	2.12	3.05	0.66	0.35	16	47	53	17	828	411	51	88	0.28
8H-2, 59-60	67.09	52.0	6.43	6.72	0.41	2.28	2.97	0.69	0.34	20	56	77	17	853	270	52	112	0.32
8H-2, 63-64	67.13	52.0	6.12	7.26	0.41	2.35	2.75	0.70	0.34	24	57	79	16	846	190	52	109	0.33
8H-2, 66-67	67.16	50.7	6.36	7.43	0.38	2.23	3.18	0.77	0.33	19	66	81	16	817	185	49	112	0.35
8H-2, 69-70	67.19	48.1	6.29	8.33	0.45	2.49	2.82	0.70	0.36	19	71	79	18	1010	195	57	128	0.37
8H-2, 72-73	67.22	52.4	6.37	7.52	0.41	2.18	3.03	0.71	0.35	15	75	73	17	884	130	53	117	0.36
8H-2, 74-75	67.24	50.0	6.30	7.08	0.41	2.07	2.97	0.67	0.35	14	127	69	16	842	107	50	122	0.35
8H-2, 77-78	67.27	52.1	6.87	6.64	0.91	2.15	3.23	0.66	0.37	24	238	82	18	929	117	55	120	0.38
8H-2, 82-83	67.32	48.8	6.79	6.78	1.06	2.23	3.11	0.66	0.38	29	236	86	17	879	118	51	134	0.37
8H-2, 85-86	67.35	52.4	7.57	6.25	1.03	1.98	3.97	0.76	0.38	32	261	92	16	917	130	53	113	0.39
8H-2, 88-89	67.38	52.1	6.23	6.10	1.25	2.07	2.93	0.66	0.35	38	208	90	16	912	91	54	105	0.36
8H-2, 91-92	67.41	53.8	6.35	6.42	1.38	2.27	2.91	0.79	0.35	47	198	101	17	1076	117	57	108	0.38
8H-2, 93-94	67.43	54.5	5.62	6.06	1.54	2.15	2.60	0.72	0.33	57	183	108	16	961	87	55	102	0.37
8H-2, 96-97	67.46	58.0	5.43	5.31	1.48	1.96	2.80	0.75	0.29	58	165	108	14	965	69	50	97	0.36
8H-2, 101-102	67.51	59.8	5.26	5.39	1.51	2.04	2.59	0.67	0.30	53	148	102	15	1014	67	50	95	0.37
8H-2, 103-104	67.53	61.1	5.12	4.98	1.48	1.84	2.80	0.69	0.29	61	147	93	13	957	83	43	92	0.38
8H-2, 106-107	67.56	62.3	5.10	4.78	1.24	1.82	2.51	0.55	0.29	37	126	76	14	982	69	43	81	0.35
8H-2, 108-109	67.58	66.2	4.94	4.83	1.26	1.85	2.44	0.45	0.29	33	127	72	15	1007	75	44	90	0.34
USGS BHVO-1			13.85	11.24	0.17	6.36	1.80	0.56	2.75	48	135	118	34	285	303	28	117	0.33
"Recommended" value			13.80	12.23	0.168	7.23	2.26	0.52	2.71	45	136	121	31.8	403	317	27.6	105	0.27

Note: "Recommended" value taken from Govindaraju (1989).

make it difficult to estimate the initial levels of Mn and Fe that are necessary to perform a reconstruction of C_{org} profiles. From the profile shapes, however, it is likely that $>0.5\%$ MnO has been mobilized throughout the haloes, and that the Fe maxima represent an additional 2% Fe₂O₃ added by Fe³⁺ precipitation from Fe²⁺.

A major contrast between the Mn profiles observed immediately above and below the haloes in the Leg 135 examples and those from the Nares Abyssal Plain arises because of the different thicknesses of the overlying turbidites. The Mn²⁺ remobilized to pore-water solution will tend to diffuse upward and downward out of the halo regions, with the relative fluxes partitioned according to the gradients in pore-water Mn²⁺ concentration. Much of the Mn remobilized from the haloes in the Nares cases was relocated into the lower reaches of the turbidites, where it was evident as dark laminae. This was caused by reprecipitation of Mn²⁺ by bottom-water oxygen diffusing downward through the short (decimeter thick) turbidites investigated there. In the Lau Basin examples, thick turbidites were selected for investigation, so that oxidation of the turbidite surface was occurring 3.5–5 m above the haloes. These distances are so long that only small upward fluxes of Mn²⁺ could have been involved before oxic conditions were encountered (concentration gradient $\delta c/\delta x$ small for Mn²⁺ in solution because x is large). Therefore, no Mn enrichments were observed in the lower reaches of the Lau Basin turbidites, and larger enrichments of Mn are found just below the haloes in both cases ($1.5\%–2\%$ MnO) than in the Nares cases ($<0.4\%$ MnO). The mechanism of removal of Mn²⁺ from solution to the solid phase in the downward direction, which is necessary to provide a sink to establish a pore-water Mn²⁺ gradient, is not certain. The sink may be absorption of Mn²⁺ by pre-existing Mn oxyhydroxide, which is an effective scavenger for many cations (Means et al., 1978; Kadko et al., 1987).

Congener Elements

In slowly accumulated sediments, a number of elements are found enriched along with Mn oxides and oxyhydroxides. The elements

most regularly identified are Co, Cu, and Ni (Krishnaswami, 1976; Li, 1981; Thomson et al., 1984; Kadko, 1985; Piper, 1988). Several other elements (e.g., Ce, Mo, Sb, V, and Zn) are likely to be similarly enriched in this hydrogenous or authigenic fraction, but either the enrichment is less marked or the element is less frequently measured (Piper et al., 1987; Thomson et al., 1984, 1989). Hodgkinson et al. (1986) have shown that the sediments of the Lau Basin contain a hydrothermal component that is enriched in Mn, Cu, Zn, Pb, and P and to a lesser extent Fe, Co, and V.

It might be expected *a priori* that when the Mn and Fe oxyhydroxides originally present in the solid phase of the halo regions are reduced to the solution phase after turbidite emplacement, then the congener elements will be similarly mobilized. This was observed in the Nares cases and is also evident in the Lau Basin reduction haloes. Thus, Co and Cu are generally at low values in the haloes in comparison with the underlying pelagic sediments, consistent with a downward movement similar to that of Mn (Figs. 4–5), although a local peak in Cu occurs within the halo in Section 135-834A-2H-1. Nickel also has generally lower values in the haloes, but the lowest values are just under the former sediment surface and a marked gradient in Ni content with depth is present in the halo in Section 135-834A-2H-1. None of these three elements have exactly the same shape of profile as Mn, demonstrating that the individual elements have characteristic responses to the diagenesis responsible for halo formation. Cobalt, Cu, and Ni were similarly found to be depleted in the Nares examples, but in those cases clear evidence also existed of immobilization at the base of the turbidites along with Mn, which is not seen here for the reasons already discussed.

The behavior of V (which was not measured in the Nares examples) is distinctive in that it is enriched in the solid phase in both haloes. Downhole bulk geochemistry data for all the backarc sites show that highest vanadium contents (up to 1200 ppm) nearly always occur within reduction haloes (R.A. Hodgkinson, pers. comm., 1992). This implies that, in contrast to the other elements discussed, a mobile V fraction has migrated into, rather than out of, the haloes and has

been immobilized there. Vanadium can have an appreciably enhanced concentration in marine pore waters compared with seawater (Emerson and Huested, 1991), and does undergo valency changes at near zero E_h and near neutral pH values (Lewan, 1984; Breit and Wanty, 1991). A close relationship between V and Fe has been demonstrated in hydrothermal precipitates and sediments (Trefry and Metz, 1989). From comparison of the V and Fe profile shapes (Figs. 4–5), however, it appears that V is behaving differently from Fe within the haloes because the profile shapes are different and the maximum V values do not coincide with those for Fe.

On this interpretation, the haloes are hemipelagic sediments whose appearance has been altered as a consequence of metal migration following reduction. Support for this contention is seen in the isocon diagrams (Fig. 7), made by plotting the average elemental concentrations in the haloes vs. the average elemental concentrations in the underlying sediments (Grant, 1986). Although the geochemically inert elements lie close to the isocon equiline, the redox-sensitive elements Mn, Co, and Cu are clearly depleted in the haloes and are V enriched (Fig. 7). The apparent Ca, Sr, and Mg enrichment in the halo of Section 135-834A-2H-1 is a result of the greater carbonate content of the halo (Fig. 4).

Persistence of Reduction Haloes

The haloes have been ascribed to the local absence of Mn oxyhydroxide in the sediments. Deeply buried sediments are often anoxic, so that Mn oxides and hydroxides have been reduced, Mn^{2+} has diffused upward and little Mn persists in the anoxic deep sediments. This is clearly not the case in these cores, where high levels of solid-phase Mn are still found at depth (e.g., at 67 m depth in Section 135-837A-8H-2; Fig. 5). Recent accumulation rates of sediments in the Lau Basin are variable (Cronan et al., 1986), but Reich (1990) has estimated an average rate around 1.5 cm k.y.^{-1} over the past 900 k.y.; and Rothwell et al. (this volume) deduce a similar average hemipelagic rate over the last 3 m.y. at Sites 834 and 835. At low pelagic rates of sediment accumulation, most C_{org} remineralization occurs by oxic degradation, so that only refractory C_{org} persists at depths greater than several centimeters or a few decimeters (Rabouille and Gaillard, 1991). All available C_{org} analyses in Hole 837A cores are very low

(average of eight finite values in ten determinations: 0.12%, range 0.01%–0.2%; Parson, Hawkins, Allan, et al., 1992, p. 319). Pore-water data also show clearly that buried C_{org} remineralization is driving very little sulfate reduction, because SO_4^{2-} was observed to be close to the seawater value and NH_4^+ is at low levels, respectively, at all depths (Parson, Hawkins, Allan, et al., 1992, p. 320). Decreasing SO_4^{2-} and increasing NH_4^+ levels are found with increasing depth in sediments where sulfate reduction and sulfide production are active. It is inferred from these data, therefore, that the geochemical environment of the Lau Basin cores is post-oxic rather than sulfidic (Berner, 1981), although the critical parameters to demonstrate this unequivocally are not available. This implies that the persistence of Mn oxyhydroxides is a consequence of the low levels of refractory buried C_{org} . The Mn^{2+} levels observed in pore-water solution (Parson, Hawkins, Allan, et al., 1992, p. 320) are likely to be controlled by an equilibrium uptake onto $CaCO_3$ surfaces to form $(Mn,Ca)CO_3$ (Middleburg et al., 1987).

Implications for Visual Core Interpretation

The above mechanism of the formation of reduction haloes leads to some generalizations that may be useful in sedimentologic interpretations of fine-scale depositional history:

1. A halo is unlikely to form if turbidite emplacement is erosive, so that it removes the near-surface layer. This is generally the most fluid part of the sediment (i.e., it has the highest water content) and contains the highest levels of reactive C_{org} to drive the reduction process.
2. Conversely, the presence of a halo implies that emplacement of the overlying turbidite did not erode the pre-existing sediment surface to a marked extent.
3. The thickness of the halo under thick turbidites (meters in thickness) represents the profile of labile C_{org} of the buried surface. If the turbidite is thin (a few decimeters in thickness), then the halo development may have been terminated before completion by the breakthrough of bottom-water oxygen by downward diffusion. In such cases, a diagenetic enrichment of Mn oxyhydroxides can be formed in the lower reaches of the turbidite.

Figure 7. Isocon diagrams (Grant, 1986) for Sections 135-834A-2H-1 (left) and 135-837A-8H-2 (right). In this diagram, the average elemental concentration value in the halo section is plotted vs. the average elemental concentration value in the underlying sediments. Arbitrary factors have been selected to bring all elements on to the same scale as follows: 0.01 = Sr; 0.1 = Cu, Ni, V, and Y; 0.2 = Zn; 0.5 = Ca and Co; 2 = Na; 5 = Al, Mg, and Fe; 10 = Mn and K; 20 = Ti; and 40 = P.

4. It is the absence of Mn oxyhydroxides that causes the light color of haloes, rather than any variation in Fe content. It has been stated that the red/brown color of the Lau Basin carbonate sediments is caused by the presence of amorphous Fe and Mn oxides and oxyhydroxides (Moorby et al., 1986; Reich, 1990; Reich et al., 1990); the sections investigated here make it likely that Mn is the dominant control on brown coloration (Fig. 6).

The development of reduction haloes beneath turbidites is generally uncommon at all the backarc sites, with the exception of Sites 837 and 839, where 30%–40% of turbidite events show the development of reduction haloes. Sites 837 and 839 contain both the greatest number and thickest haloes (Figs. 8–9). Both these sites were drilled on basin floors, within 70 km of the axial rift zone of the East Lau Spreading Center, and show a similar sequence of thick, vitric silt and sand turbidites interbedded with hemipelagic clayey nannofossil oozes and mixed sediments.

Reduction haloes are rarely developed at Sites 834 and 835, with under 10% of turbidites showing haloes. Of all the Lau Basin backarc sites, reduction haloes are the least common at Site 835, where redeposited sediments comprise 66% of the sediment column above basement. These allochthonous sediments comprise thick, muddy, debris-flow deposits; coherent rafted blocks; and thick, mud turbidites derived from catastrophic failure around the basin margins (Rothwell et al., this volume). The basin flanks surrounding the basin in which Site 835 was drilled are exceptionally steep (up to 30°), and stratigraphic evidence is present for erosive emplacement of at least some of the sediment gravity-flow deposits (Rothwell et al., this volume). This may account for the rarity of reduction haloes at this site. Equal numbers of haloes occur at Sites 836 and 835, although the former sediment column above basement is only 13% of the thickness at Site 835.

Site 838 was drilled on the sediment covered, lower flank of a basement high. The allochthonous sediments here are generally much coarser grained than those drilled at Sites 837 and 839, and are dominated by coarse disorganized vitric gravels (probably deposited by cohesive debris flows) and coarse-grained, structureless volcanic sands (probably deposited by high concentration turbidity currents).

Figure 8. Histogram showing the number of turbidite events present at each Leg 135 backarc site with and without underlying haloes. Turbidites showing the development of a reduction halo are a minority case. Note that a turbidite event is defined as either a single turbidite interbedded in hemipelagic clayey nannofossil ooze or mixed sediment or as a discrete "package" of stacked turbidites interbedded with hemipelagic deposits.

Figure 9. Histogram showing the distribution of halo thickness at each Leg 135 backarc site. Note the occurrence of longer haloes at Sites 837 and 839 (see discussion in text).

The redeposited sediments drilled at Site 838 are generally the coarsest grained of those drilled at all the backarc sites. The paucity of reduction haloes at Site 838 may reflect the greater potential for erosion of underlying deposits provided by such coarse-grained sediment gravity flows on the relatively steep local slopes.

The largest concentrations of in-situ labile C_{org} necessary to fuel the formation of the reduction haloes are expected to be present in the uppermost few decimeters of the sediment (Grundmanis and Murray, 1982; Thomson et al., 1989); indeed, 26 out of the 29 haloes identified under 169 turbidite events at six backarc sites are <50 cm in length (Fig. 9). Three haloes are longer than this, two of which are shown in Figure 10, and these merit further consideration. In certain modern oxic sediments, detailed C_{org} profiles have been determined where the amount of labile C_{org} declines quasi-exponentially with depth down to 100 cm (Muller and Mangini, 1980). In slowly accumulated sediments, the depth over which labile C_{org} is consumed is a function of several parameters, including bottom-water O_2 concentration, the fluxes of C and total sediment, and the rate constant of labile C_{org} oxidation (Rabouille and Gaillard, 1991). Modern models visualize that labile C_{org} is composed of a series of components with successively slower remineralization kinetic constants (Westrich and Berner, 1984; Middleburg, 1989). It may be that the unusually long (70 and 88 cm) haloes observed in Sections 135-839A-5H-2 and -5H-4 (Fig. 10) are the result of turbidite emplacement during a period when hemipelagic sediment accumulation conditions were conducive to labile C_{org} persistence at depth. These long haloes have a gradation of color from top to bottom, varying from very pale (10YR 8/2) or pale orange (10YR 7/2) directly beneath the turbidite base, through grayish orange (10YR 7/4) to dark grayish orange (10YR 7/6), and finally to dark yellowish orange (10YR 6/6) at the bases of the haloes. Although the geochemistry of such long haloes has not been investigated, it seems possible from their color variations that they may have been formed at former surfaces where labile C_{org} profiles declined more slowly than usual with depth.

The haloes discussed here have been ascribed to the reductive effects of reactive surficial C_{org} buried by turbidites. It is probable that they are generically related to other reduction phenomena observed in predominantly oxic sediments (e.g., the reduction spheroids often observed in red beds; see review by Hoffman, 1990). Unlike the haloes here, the nature of the reducing agent in rocks often has to be inferred. For example, to explain a 0.5-m bleached section immediately underlying the Cretaceous/Tertiary boundary at one exposure,

Figure 10. Photograph showing split core Sections 135-839A-5H-1 through -5H-5. Note the very long reduction haloes present in Sections 135-839A-5H-2 and -5H-4. The reduction halo in Section 135-839A-5H-2 is 70 cm thick and varies from pale orange (10YR 7/2) directly beneath the overlying volcanic sand grading into grayish orange (10YR 7/4), to yellowish orange (10YR 7/6) to dark yellowish orange (10YR 6/6) down through the halo. The clayey nannofossil ooze below the halo is moderate yellowish brown (10YR 5/4) in color. The reduction halo in Section 135-839A-5H-4 is 88 cm thick and is yellowish gray (5Y 7/2) grading to very pale orange (10YR 8/2), to yellowish orange (10YR 7/6) to dark yellowish orange (10YR 6/6) down through the halo. The clayey nannofossil ooze below the halo is moderate yellowish brown (10YR 5/4) in color.

Lowrie et al. (1990) invoke "downwards infiltration of reducing waters resulting from the large quantity of organic matter produced by the extinctions at the K-T boundary." Advection or diffusion often also has to be invoked to supply sufficient reductant (electrons) to react with the large quantities of exotic redox-sensitive elements immobilized within reduction spheroids (Hoffman, 1990).

CONCLUSIONS

In the cores from six Leg 135 backarc sites, a bleached sediment color of variable length (<1 to 88 cm) was observed immediately under 29 of 168 turbidite events, but nowhere else in the same cores. By analogy with studies elsewhere on brown clays, these light-colored sediments are identified as reduction haloes, caused by the burial of labile C_{org} at the former sediment surface by turbidite emplacement. The oxyhydroxides of Mn and Fe are then utilized as electron acceptors to remineralize this C_{org} in the absence of oxygen, and Mn and Fe have profiles of a characteristic shape within the haloes. Manganese is consistently at low levels and appears responsible for the color changes, whereas Fe has lowest values immediately under the turbidite, increases through a maximum, and then declines. The elements Co, Ni, and Cu are also present at lower levels in the haloes, although their concentration depth profiles are not identical with each other or with those for Mn. In contrast, V appears to have migrated into the halo sections and to have been retained there. The two halo examples selected for investigation underlay long (>3 m thick) turbidites, and as a result no elemental relocation into the turbidites was observed. Haloes appear to be least common and to have the smallest thicknesses at sites where the redeposited sediments are either unusually coarse grained or are the result of catastrophic failure of steep basin margins. The absence of haloes, therefore, suggests that emplacement of the corresponding turbidites was erosive, and this is borne out by the nature of the turbidites and their geological settings.

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