

Copper and manganese in hemipelagic sediments at 21°N, East Pacific Rise: Diagenetic contrasts

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Abstract—Relatively rapidly-accumulating (>7 cm kyr⁻¹) and organic-rich ($\sim 1.5\%$ C_{org}) EPR sediments near 21°N are characterized by pronounced nitrate reduction in the upper decimetre and by an enrichment of Mn and increased Fe/Al ratio in surficial sediments. Joint consideration of solid-phase and pore water data indicates that the distributions of both Mn and Fe in the sediments are in disequilibrium with their respective pore water profiles: precipitation of upward-diffusing Mn and Fe is occurring at present below the enriched horizons, producing “perched” enrichments indicative of non-steady-state diagenesis. Consideration of a high resolution ¹⁴C age vs. depth curve and a decrease toward the interface (from 1.51 to 1.37 wt%) over the top 7 cm of the C_{org} profile suggests that the diagenetic disequilibrium evident for Mn and Fe may be due to a geologically recent decrease in productivity. Such a decrease would be manifest in the sediments by a downwardly-migrating oxidation front which would progressively erode the Mn and Fe pore water profiles, producing the existing decoupled surface enrichments.

In contrast to Mn, the distribution of Cu has apparently not been perturbed by non-steady-state phenomena. A first-order decrease with depth of the dissolved copper concentration is accompanied by a first-order increase in solid-phase Cu. Application of a diffusion-reaction model to these data predicts a sedimentation rate of ~ 8 cm kyr⁻¹ which agrees well with the ¹⁴C-determined rate of ~ 7.3 cm kyr⁻¹, implying that the pore water and solid-phase distributions are in diagenetic equilibrium. Available evidence suggests that the major host for non-detrital Cu in hemipelagic sediments is authigenic nontronite. Because this phase appears to form slowly, there may be a kinetic constraint on the amount of copper which can be incorporated authigenically in rapidly-accumulating hemipelagic deposits. Support for this hypothesis is given by the observed inverse proportionality between the sedimentation rate and the concentration of non-detrital Cu in surface sediments from at least seven widespread locations in the eastern Pacific. It is suggested that the variation observed in the salt- and CaCO₃-free Cu concentration in hemipelagic sediments is a consequence largely of the residence time of sediments at the surface, where high dissolved Cu concentrations prevail.

INTRODUCTION

IT HAS BEEN ASSUMED frequently in the past that early chemical diagenesis in marine sediments proceeds under steady-state conditions (e.g., JAHNKE *et al.*, 1982; GOLOWAY and BENDER, 1982). This assumption is usually reasonable for species such as nitrate which are not partitioned between solid and dissolved phases but are uniquely restricted to interstitial solution. Because diffusion over distances of a few decimetres is rapid enough to allow pore water profiles to readjust to perturbations on time scales of a few years, steady-state conditions in interstitial water can be relatively quickly established. However, the term steady-state, as used in this sense, does not mean that the pore water distribution of an element is necessarily in equilibrium with the solid phase. Disequilibrium between solid and solution is manifest by the inability of pore water diffusion models to predict adequately the solid-phase profiles of elements. Such conditions represent non-steady-state diagenesis, and have been recognized in a number of recent studies; it now appears that non-steady-state may be a diagenetic condition more widespread than previously realized. For example, FROELICH *et al.* (1979) and BURDIGE and GIESKES (1983) suggested that disagreement between modelled and real pore water and solid phase Mn profiles in eastern equatorial

Atlantic sediments indicated non-steady-state diagenesis. Similarly COLLEY *et al.* (1984), WILSON *et al.* (1985) and COLLEY and THOMSON (1985) described chemical disequilibria in northeast Atlantic pelagic clays which were induced by intermittent deposition of organic-rich turbidites derived from the northwest African margin, and BERGER *et al.* (1983) and THOMSON *et al.* (1984) showed that glacial-interglacial variations in oceanic fertility can produce non-steady-state distributions of diagenetically-mobile elements such as Mn in equatorial Pacific and equatorial Atlantic sediments, respectively.

In this paper we describe the nature of early diagenesis of manganese and copper in hemipelagic sediments collected at 21°N on the East Pacific Rise. Interstitial water and solid sediment data are used together with accelerator ¹⁴C dates, diffusion-reaction models and accumulation rate data to demonstrate that the observed distribution of copper at this location is consistent with the assumption of steady-state diagenesis, but that observed for manganese is not. The sediments near 21°N on the EPR are ideal for early diagenetic studies of this type for two reasons: first, the flux of organic matter is high at this site which underlies the productive southern reaches of the overlying California Current and second, the sedimentation rate of terrigenous detritus is relatively high which reflects the proximity of

continental source areas. These two factors together are responsible for relatively rapid consumption of oxidants and consequent redistribution of diagenetically labile phases.

SAMPLING AND METHODS

Box-core HUD 22 was raised from a depth of 2768 m at 20°53.65'N, 109°12.8'W during the C.S.S. Hudson-81 cruise (Fig. 1). The core was collected from the first sediment pond observed on the 11 kHz echo sounder record while steaming northwest at approximately right angles to the EPR crest. The ~800 m wide pond is located 13.8 km WNW of the black smoker field at 20°50.1'N, 109°05.7'W described by SPIESS *et al.* (1980). The 50 × 50 × 44 cm deep core was subsampled on deck by slowly inserting 7.5 cm I.D. butyrate core barrels into the box.

The core exhibited a colourful stratigraphy, consisting of three zones separated by relatively distinct contacts: ~8 cm of chocolate-brown clay containing many ovoid, often cream-coloured faecal pellets 0.2–0.5 mm long was underlain by a 2 cm-thick cream-coloured stratum which in turn was sharply transitional to olive-green foram-bearing clay at 10 cm depth. This lower unit became darker green with increasing depth; the number of benthic foraminifera, largely *Planulina* and *Uvigerina* spp., increased steadily toward the bottom of the core.

One of the subcores was extruded vertically at room temperature (26°C) directly into a nitrogen-filled plexiglass glovebox; interstitial waters were extracted by centrifuging core slices under N₂ at 4°C. Pore water samples thus obtained were pressure-filtered with N₂ through 0.4 µm Nuclepore membranes housed in Swinlock polycarbonate filter holders. Samples for subsequent nutrient analysis were immediately frozen and aliquots for determination of dissolved metals were acidified to pH 2 with Merck Ultrapur HCl and stored under refrigeration. Pore water extraction was completed within six hours of core collection. All plasticware used in the extraction, filtration and storage procedures was rigorously acid-washed prior to use. Sediment samples were stored frozen in the centrifuge bottles.

Nitrate and ammonia were subsequently determined in the laboratory using a Technicon autoanalyzer and dissolved Fe and Mn were measured in pore waters by direct injection graphite furnace AAS using a Perkin-Elmer 560 spectrophotometer coupled to an HGA 400 furnace programmer. Total dissolved copper was measured by anodic stripping voltammetry following UV photooxidation of the samples in stoppered quartz test tubes. Elemental concentrations in sediments were determined by automated X-ray fluorescence spectrom-

etry using a Philips PW 1400 spectrometer equipped with a Rh-target anode. Analytical details for both the XRF and ASV methods are described elsewhere (PEDERSEN, 1985).

Organic carbon was measured by gravimetric absorption of the CO₂ produced by combustion in a stream of O₂ in a Leco induction furnace. Carbonate carbon had been removed previously from weighed finely-ground sediment samples as described in PEDERSEN (1983).

Radiocarbon ages were determined at McMaster University by tandem Van de Graaf accelerator mass spectrometry on the organic carbon fraction. CO₂ derived from organic carbon by combustion of pre-acidified, carbonate-free bulk samples was reduced to C by iron catalyst graphitisation (VOGEL *et al.*, 1984) for introduction to the accelerator ion source. ¹⁴C/¹²C ratios were then measured as described by NELSON *et al.* (1986). The dates are reported assuming a δ¹³C of 15‰. The choice of this value is not critical to this study; each 1 per mil difference from 15‰ will produce an error of only eight radiocarbon years.

Estimates of precision (±1σ relative standard deviation) for the analytical data presented in this paper are as follows: C_{org}, 2%; NO₃⁻, 4%; NH₄⁺, 4%; dissolved Mn, Fe and Cu: 7%, 3% and better than 10%, respectively; and solid-phase Mn, Fe, Cu, Al, CaCO₃: 1%, 0.8%, 5%, 0.1% and ~1%, respectively.

RESULTS

Pore water and solid phase data are listed in Table 1 and plotted in Figs. 2 to 5. Dissolved nitrate decreases from 41 µmol L⁻¹ in the 0–2 cm depth interval to undetectable levels below 18 cm depth; the downward concavity of the profile indicates that denitrification commences at this site at shallow depths. Sampling resolution is insufficient to define a nitrate maximum produced by aerobic oxidation. The NO₃⁻ concentration in bottom water in the area is 40 µmol kg⁻¹ (JAHNKE *et al.*, 1982) which is analytically indistinguishable from the concentration measured in the upper 2 cm of HUD 22. The 0–2 cm interval therefore probably integrates nitrate production in the upper cm or so and nitrate depletion below this shallow depth. This suggestion is supported by comparison with pore water O₂ and NO₃⁻ data at Manop Site C where nitrate gradients are weak over the upper 20 cm (GOLOWAY and BENDER, 1982), even though oxygen is nearly entirely depleted below a depth of 1.5 cm (REIMERS *et al.*, 1984); the much steeper nitrate gradient shown in Fig. 1 therefore implies that O₂ reduction and nitrification are essentially confined to the upper 20 mm of core HUD 22, but this implication must be tempered by the important caveat discussed below. Dissolved manganese is undetectable (<0.02 µmol L⁻¹) in the upper 4 cm of the core (Fig. 1) and is first measurable (0.14 µmol L⁻¹) in the 4–6 cm interval where only ~25% of the NO₃⁻ inventory remains. The negative (concave upward) form of the Mn(II) profile between 5 and 11 cm depth indicates (KLINKHAMMER, 1980) that Mn is being oxidized in this zone. NO₃⁻ can theoretically oxidize Mn²⁺, although this reaction is barely thermodynamically favourable (FROELICH *et al.*, 1979). It is more probable that Mn²⁺ is being oxidized by traces of downward-diffusing O₂ which escape reduction in the upper 2 cm.

The sequence of overlapping electron-transfer reactions by which early diagenesis proceeds is well

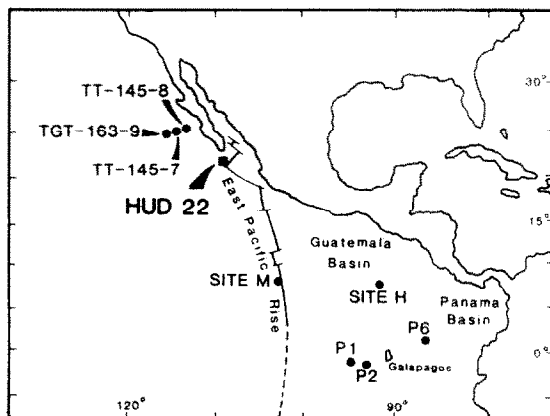


FIG. 1. Locations of eastern Pacific cores discussed in the text.

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