

# Precipitation and post-depositional mobility of cadmium in reducing sediments: implications for the Cd oceanic budget

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Reconstructions of past nutrient distribution and deep ocean circulation patterns are typically inferred from the  $\delta^{13}\text{C}$  and Cd composition of benthic foraminifera from deep sea sediments; the modern oceanic distribution of  $\delta^{13}\text{C}$  and Cd reflect the biological cycling of nutrients (e.g.  $\text{PO}_4$ ) as modified by deep ocean circulation. This correlation between Cd and  $\text{PO}_4$  is the basis for using Cd, as recorded in foraminiferal shells, for reconstructing changes in deepwater circulation patterns (Boyle, 1988). Because of the relatively long residence time of Cd and  $\text{PO}_4$  (100,000–200,000 years) glacial-interglacial changes in Cd can be interpreted as reflecting variations in nutrients distribution. However, Cd and  $\text{PO}_4$  are controlled by different diagenetic processes. The strong tendency of Cd to form highly insoluble sulphide phases in the presence of  $\text{H}_2\text{S}$  explains its substantial enrichment in sulphide-bearing sediments as already was noted by Goldschmidt (1958). In recent studies we have investigated the possibility that temporal changes in the areal extent of reducing sediments may affect the Cd oceanic budget thus leading to de-coupling of Cd from the nutrient cycle (Rosenthal *et al.*, 1993). The current work focuses on the precipitation of authigenic Cd in suboxic sediments and its mobility in response to post-depositional re-oxidation of reducing sediments. The implications of these processes for the global Cd budget and for paleoceanographic interpretation are discussed below.

## Uptake of Cd into reducing sediments

In the modern ocean, authigenic Cd precipitates primarily in continental margin and organic rich sediments where reducing conditions occur in close proximity to the sediment–water interface. Pore-water profiles from such environments indicate that Cd is diffusing downward and is precipitating near the redox boundary, within the interval between the depth of Fe-oxides precipitation and the onset of Fe-oxides remobilization

(Gobeil *et al.*, 1987; McCorkle and Klinkhammer, 1991; Lapp and Balzer, 1993). With the available sampling resolution it is difficult to determine, from pore-water data, whether Cd is scavenged onto Fe-oxyhydroxides within the oxic zone, as suggested by McCorkle and Klinkhammer (1991), or removed as CdS below the redox front. However, there is some evidence to support the latter process: 1) Sediment data show very low Cd levels in the zone of high Fe-oxides; 2) There is no discernible increase in pore-water Cd associated with the remobilization of Fe-oxides in the reducing zone; and 3) Strong enrichments of authigenic Cd are observed in anoxic, sulphide-bearing sediments, despite the absence of Fe-oxides.

Precipitation of CdS is predicted in seawater containing low to moderate amounts of  $\text{H}_2\text{S}$  (e.g. Davies-Colley *et al.*, 1985) and therefore has been called upon to explain the depletion of Cd in anoxic environments (Jacobs and Emerson, 1982; Gobeil *et al.*, 1987; Lapp and Balzer, 1993). Cadmium precipitation was also observed in suboxic sediments where no  $\text{H}_2\text{S}$  was detected. However, this does not preclude CdS precipitation. Solubility calculations suggest that in suboxic sediments dissolved sulphide is maintained at very low levels (below the detection limit of routine procedures i.e.  $< 1\ \mu\text{mol/kg}$ ) due to precipitation by Fe-sulphides in relatively shallow depths below the redox front. It is suggested that even at these low levels there is sufficient upward diffusive flux of sulphide to support CdS precipitation. This reaction is kinetically favored which explains the precipitation of CdS immediately below the redox front. Cadmium precipitation precedes the U removal in the diagenetic sequence. Using flux estimates from the pore-water and sediment data we suggest that the removal of Cd into reducing sediments balances all the riverine Cd inputs. In other words, the areally integrated removal of Cd into hemipelagic, and organic rich sediments constitutes the single largest sink in the modern oceanic budget of Cd.

### Post-depositional remobilization

The post-depositional mobility of Cd was investigated in the North Atlantic abyssal plains where pelagic sediments are interspersed with relatively organic-rich turbidites (Thomson *et al.*, 1993). Following emplacement of turbidite units an oxidation front has progressively migrated downwards into the suboxic turbidite, thus leading to redistribution of authigenic phases according to their affinity to different redox conditions. In these sediments Cd shows large peak at the redox boundary, which is substantially higher than the background Cd levels. Cadmium concentrations in the deeper, suboxic parts of the turbidite units are significantly higher than in the re-oxidized section, where the Cd content is similar to levels observed in pelagic sediments (0.1–0.2 ppm). Simple mass balance calculations suggest that the Cd enrichments in the peaks can be explained entirely by downward migration of remobilized Cd which was released by the oxidative erosion of the upper sections of the turbidites. Unlike uranium which shows broad peaks with relatively long tail below the redox front, Cd exhibits sharp and narrow peaks slightly before the increase in U.

Remobilization of Cd under oxic conditions is consistent with the suggestion that Cd precipitates as CdS under reducing conditions rather than scavenged onto Fe-oxides surfaces. There is no evidence of net release on Cd back into seawater following the re-oxidation of the turbidites, thus implying that precipitation of authigenic Cd in reducing sediments represents an irreversible sink.

### Glacial–interglacial variability

Down core records of authigenic Cd from sub-Antarctic sediments, where oxic conditions currently prevail, show enhanced accumulation of Cd and U during glacial intervals coinciding with relatively high % organic carbon. The records show strong coherence with other paleoclimatic records (e.g.  $\delta^{18}\text{O}$ ). These enrichments reflect higher glacial productivity in the sub-

Antarctic zone most likely due to northward displacement of the Antarctic Polar Front with the associated high siliceous productivity belt. It is suggested that higher biological productivity and higher organic carbon fluxes during glacial periods, led to more reducing conditions in sub-Antarctic sediments thus enhancing the precipitation of authigenic Cd and U. We suggest that the glacial increase in biological productivity might have doubled the areal extent of reducing sediments during glacial maxima (from 8 to 16%). A sensitivity analysis of the response of seawater Cd concentrations to doubling of its oceanic sink, suggests that if riverine inputs were constant, glacial-interglacial variations in the Cd oceanic inventory did not exceed 10–20% (but only 1–2% for U). This result is consistent with measurements of Cd/Ca in benthic foraminifera showing no long term changes in the Cd mean oceanic concentration (Boyle and Keigwin, 1985/6; Boyle, 1992). The oceanic Cd residence time is estimated here to be about 100,000 years.

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