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High Volumetric Resolution Reveals Inter-dependence of Metal Mobilisation in Sediments

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Mechanistic linkages between metals can be expected to operate at the scale of the governing process. For redox driven processes this scale depends on the rate of supply and decomposition of organic matter and can span cms or mms in sediments assumed to be horizontally uniform. When release of metals directly from individual units of decomposing organic material is considered the scale may be much smaller and there is unlikely to be horizontal uniformity. The new technique of DGT (diffusive gradients in thin-films) (1, 2) typically samples a 10 to 25 µl volume of sediment while traditional porewater measurements which horizontally average at 0.5 to 1 cm vertical resolution usually sample 10 to 50 ml of sediment. With this 1000 times differences in volumetric scale it is not surprising that DGT appears to reveal different processes to conventional measurement.

DGT measurements generally show pronounced structure that is not apparent with more conventional sampling techniques. The fine structure for Co and Mn is well matched and quite different from that of Fe. Deployment of DGT in situ in sediment traps has shown that, unlike Fe, Co and Mn are released rapidly and simultaneously from freshly recruited particles (3), suggesting that they are the immediate recipients of electrons supplied at the early stage of decomposition. The fine structure of Fe generally shows little relationship to other metals with the exception of As and possible Cr, consistent with known geochemical coupling. Ni and Co show some linkage, but evidence to date has failed to show consistent relationships in the fine structures of Zn, Cu and Pb.

These results demonstrate that sediments are very heterogeneous with respect to remobilisation of metals. Redox sensitive elements show particularly marked structure, suggesting that local perturbations of redox conditions, by for example, introduction through bioturbation of oxidants or fresh organic material, are responsible. However, each metal exhibits unique detailed structure and there are additionally sharp features of redox insensitive metals. While secondary linkage to a redox process cannot be excluded, this metal specific behaviour suggest that release of metal from, for example, decomposition of particulate organic carbon, may be driven by very specific mechanisms. The observed profiles are therefore likely to be transient on a time scale of days. Further systematic studies of this type and at this high resolution are needed to build an overall picture of mechanistic interdependencies.

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