The geochemistry of redox sensitive trace metals

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The characteristic enrichment/depletion of V, Mo, Cd, U and Re in sediments in response to different redox conditions highlight their potential as tracers of changes in palaeoproductivity and bottom water oxygen concentration. We have analysed these elements in surface sediments from the Northwest African margin, the U.S. Northwest coast and the Arabian Sea. The results of metal analysis for four samples from the top 15 cm of each core from the African margin and the U.S. coast are plotted in Fig. 1. The authigenic behaviour of each of these metals depends on the extent of the reducing conditions in the sediments which is determined by the organic carbon rain rate and the bottom water oxygen concentration. The cores off Africa (closed symbols) have a classic redox trend in which pore water oxygen goes to zero at depths >2 cm in the two deeper cores and <1 cm in the shallowest, most-near-shore station. In the more reducing cores, Mo and V follow the Mn depletion and there is enrichment of Re and U, but no large enrichments in Cd. On the U.S. Northwest continental margin (open symbols) the oxygen penetration depths are shallower (<1 cm). Molybdenum remains depleted following the Mn remobilization, whereas V is slightly enriched as it recycles with iron during diagenesis. Uranium, Re and Cd all show enrichment in these sediments, with the greatest enrichment in Re.

Schematic steady-state metal authigenic concentrations as a function of the redox state of the sediments from our observations and those of other workers (Nameroff, 1996; Shaw 1990) are summarized in Fig. 2. The horizontal axis indicates the primary electron acceptors that are present in the top 1 cm. (For example, vertical line #1 indicates oxygen is the only oxidant; line #2 indicates oxygen and manganese oxides; line #3 indicates oxygen, manganese and iron oxides are all present in the top cm.) The vertical axis is the authigenic fraction which is determined as the (Metal/Al) ratio in the sediment divided by the detrital (Metal/Al) ratio. The authigenic metal enrichment (>1) or depletion (<1) are plotted as log values to accommodate the large range in metal authigenesis. The lines represent values observed below the bioturbated layer in near-shore sediments. Surface Mn, Mo and V enrichments in surface sediments due to remobilization from depth are not included because they are buried only

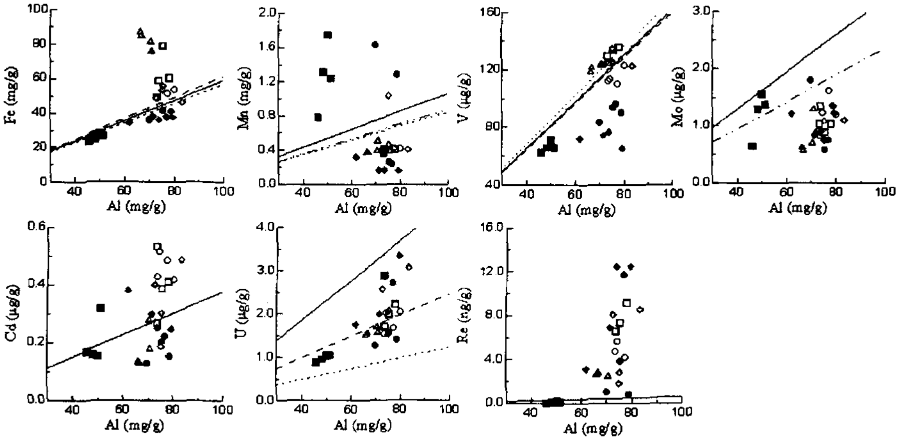

FIG. 1. Metal *vs.* Al in cores from the African margin (closed symbols; 1445 m ◆, 2981 m ●, 3804 m ■) and the N.W. U.S. coast (open symbols; 110 m ○, 620 m □, 1004 m ▽, 1994 m ◇).

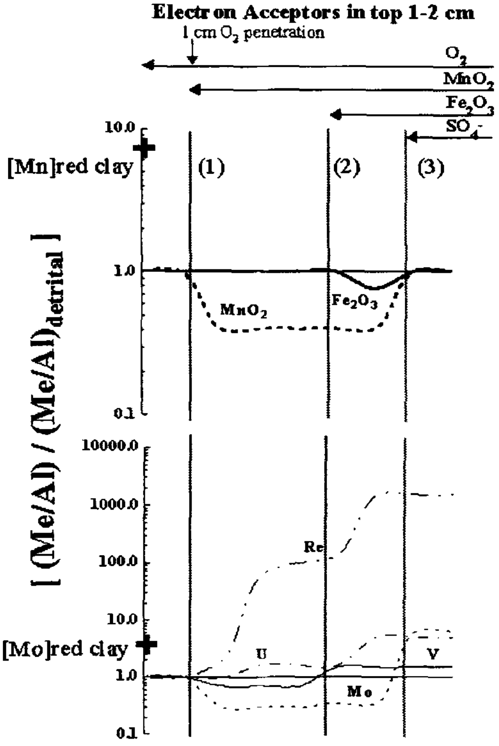

FIG. 2. Steady-state authigenic metal concentrations as a function of the redox state of the sediments.

under non-steady-state conditions. Enrichments of Mn and Mo in open-ocean, red clay sediments are indicated by + signs. We observe that when oxygen penetrates less than ~1 cm below the water-sediment interface but sulphate reduction is not present, Mo and V are remobilized to the overlying water with Mn reduction and remobilization. At about this redox level, authigenic enrichments of Re appear. As reducing conditions intensify to iron oxide reduction, Mo continues to be depleted while V becomes enriched. With the onset of sulphate reduction, Mo, V, U and Re accumulate authigenically with Re being by far the most sensitive to these conditions.

Using a simple diagenesis model (Emerson *et al.*, 1985) and global estimates of organic carbon rain rate and bottom water oxygen concentrations (Jahnke, 1996), we estimate the area of sediments in which pore water oxygen penetrates less than or equal to 1 cm to be 6% of the ocean floor. From the measured authigenic metal accumulation rates in our study areas, we predict that these sediments are a source to sea water for V, Mn and Mo. The V and Mn sources are greater than the dissolved river inputs by 4.5 and 2 times, respectively, whereas the Mo source is 15% of its dissolved river source. These sediments are a significant sink for Re (1.6 times its dissolved river source), Cd and U (50% and 25% of their dissolved river source, respectively). Remobilization of Mo and Mn from continental margin sediments support their higher concentration in deep sea, red clay sediments (+'s on Fig. 2), whereas the continental margin V source supports its hydrothermal sink. Rhenium enrichment in sediments is perhaps the purest indicator of local redox changes because of its low detrital concentration and lack of involvement in Mn or Fe cycling. On longer time scales, the accumulation of Mo in pelagic sediments, V in hydrothermal deposits and Re in continental margin sediments should be measures of the intensity of reducing conditions in the ocean, because of their dramatic internal cycling.

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