

Web Supplement 12.5.4

12.5.4 Diagenetic Overprinting of Fossil Oxidation Fronts

For chemicals that do not undergo diagenetic reactions, concentration profiles in the sediment can be used as records of changes in accumulation rate (Figure 12.6a). In some cases, similar information can be gleaned from the concentration profiles of reactive chemicals despite the altering effects of diagenesis. Since the sediments represent our primary source of information regarding past oceanic conditions, considerable effort has been focused on understanding how diagenesis can alter the sedimentary record.

Changes in primary production in the euphotic zone alter the POM flux to the sediments and, hence, the depth of the redox boundary. When production is low, the depth of the oxic zone increases. This leads to the formation of sediments with low organic contents. Increased production in the euphotic zone leads to an increased flux of sinking POM and, hence, increased remineralization rates at the seafloor. This causes the depth of the redox boundary to rise. The increased production also raises the sedimentation rate. This helps bury the organic matter fast enough to preserve much of its organic content, leading to the formation of a carbon-rich layer. (As explained in the next section, organic carbon remineralization rates tend to be slower in anaerobic sediments.)

Changes in the position of the redox boundary over time can also be recorded in the particulate iron and manganese profiles. This has been observed in the sediments of the Mediterranean Sea as illustrated in Figure 12.6. During periods of glaciation, organic-rich layers were deposited and the depth of O₂ penetration into the sediments was minimal. Under these conditions, the MnO₂ concentration maximum was near the top of the sediments. Once glaciation ended, the depth of O₂ penetration increased. The cause of this is unknown—perhaps productivity declined and/or the rate of supply of O₂ to the bottom waters increased as a result of changes in estuarine circulation in the Mediterranean.

As the sediment column grew, so did the MnO₂ enrichment, which was now positioned over the deeper redox boundary. Since that period, the depth of O₂ penetration has once again declined, leaving the MnO₂ layer stranded within the anoxic zone. The anoxic conditions have caused some of the MnO₂ to become reduced and solubilized,

supplying Mn^{2+} to form a shallower MnO_2 layer in sync with the present depth of the redox boundary. Some of the original MnO_2 layer has been retained as a diminished but still clearly evident concentration peak. Given sufficient time, this peak will eventually be obliterated by diagenetic overprinting. A similar record is seen in the particulate iron (III) concentration profiles, but at deeper depths due to the lower energy yield of iron respiration and faster reoxidation rates.

The redeposition of sediments is another mechanism by which redox conditions can change. For example, turbidity flows can reexpose buried organic matter to O_2 , thereby enhancing oxidation of organic compounds and reduced metals. In cases where organic-rich turbidites have lain exposed to oxic seawater for long periods, oxic diagenesis causes downcore redox changes that follow the zonation predicted by the free energy yields in Table 12.1. Pelagic sedimentation eventually covers the turbidite and cuts off the supply of O_2 , leaving a record of postdepositional migration associated with the former redox boundary.