

# Early Diagenesis of Mn in Continental Slope Sediments: Evidence for a Redox-Mediated Adsorbed Mn<sup>2+</sup> Trap

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The early diagenetic transformations of Mn are key processes which influence the biogeochemistry of marine sediments. Sediment layers highly enriched in Mn result from the formation of a redox-mediated trap; Mn oxides buried below the surface oxic layer undergo reductive dissolution to Mn<sup>2+</sup> in the interstitial waters, this Mn<sup>2+</sup> diffuses upwards under a concentration gradient and is re-precipitated as 'second generation', 'third generation' etc. oxides at the base of the oxic layer. Mineral surfaces can also provide an important sink for pore water Mn<sup>2+</sup> in the form of surface adsorption sites (Jenne, 1968). Here we present evidence for a sub-surface adsorbed Mn<sup>2+</sup> trap that is spatially distinct from the sedimentary redox-mediated Mn oxide trap.

## Methodology

Particulate Mn in sediments is speciated between a number of host associations. Solid state speciation data for total non-refractory Mn (i.e. non-lattice-held Mn) were obtained by applying a five stage sequential leaching scheme (Chester et al., 1988) to freeze dried sediments. Six cores were studied; two from the Gulf of Lions (L.-E. Lim, Pers. Comm.) and four from the Hebrides slope. The principal operationally-defined Mn host components associated with processes occurring in the sedimentary Mn trap are those of Stages 2 and 3. The reagents used to separate these phases are as follows:

Stage 2- sodium acetate (pH 5): Elements released in this stage are classified as being in '*carbonate*' and in '*surface associations*' with phases such as hydrous iron and manganese oxides.

Stage 3- sodium acetate + hydroxylammonium hydrochloride (pH 5): Elements released at this stage are classified as being mainly in '*easily reducible*' oxide associations.

## Results and discussion

For the investigation of any differences in the geochemical profiles of Stages 2 and 3 Mn, cores were selected on the basis that (i) they possessed a clearly defined Mn redox boundary, and (ii) the resolution was sufficient to detect differences in

sediment depth of individual peaks in the same core at the 1 cm level. An important characteristic of Mn diagenesis in sediments is the abrupt decrease in the concentrations of the Stage 3 (oxide-associated) Mn below the Mn redox boundary. This results from the stripping of Mn from oxides below the boundary, their upward migration through the interstitial waters, and their oxidative re-precipitation in the oxic layer above the boundary.

Results from the present study suggest that a recurrent feature of Mn diagenesis is that a peak in Stage 2 occurs at a position immediately below that of the main Stage 3 oxide Mn peak (e.g. Fig. 1). This feature was found in all six cores studied. The abrupt decrease in Stage 2 Mn was found to occur concomitantly with a decrease in Mn and Fe Stage 3 oxides, both of which undergo reductive dissolution in this region as a result of decreasing Eh. It is therefore likely that the Stage 2 Mn peak represents Mn<sup>2+</sup> adsorbed to the surfaces of Mn and Fe oxides. These oxides have a strong binding capacity for dissolved Mn<sup>2+</sup> (Jenne, 1968; Knocke et al., 1991), thus as the oxides undergo reductive dissolution, adsorbed Mn<sup>2+</sup> will be released into solution.

That the Stage 2 adsorbed Mn peak should occur immediately below the position of the Stage 3 Mn oxide peak may be explained by increasing concentrations of dissolved O<sub>2</sub> above the Stage 2 peak; as oxygen concentrations rise, the oxidation of Mn<sup>2+</sup> by dissolved O<sub>2</sub> is able to out-compete the adsorption of pore water Mn<sup>2+</sup> by mineral surfaces.

The Stage 2 Mn peak may thus represent a redox mediated Mn<sup>2+</sup> trap immediately below the Mn<sup>4+</sup> Stage 3 oxide peak, with redox cycling between dissolved Mn<sup>2+</sup> and solid MnO<sub>2</sub> in the upper peak driving additional Mn cycling between adsorbed Mn<sup>2+</sup> and dissolved Mn<sup>2+</sup> in the lower peak. From a comparison of Mn peak heights it is found that the Stage 2 peak is relatively small compared with the Stage 3 peak. It is concluded, therefore, that the amount of Mn<sup>2+</sup> stored in the Stage 2 (adsorbed) peak is likely to represent only a minor proportion of the total Mn present in the redox-mediated Mn trap.

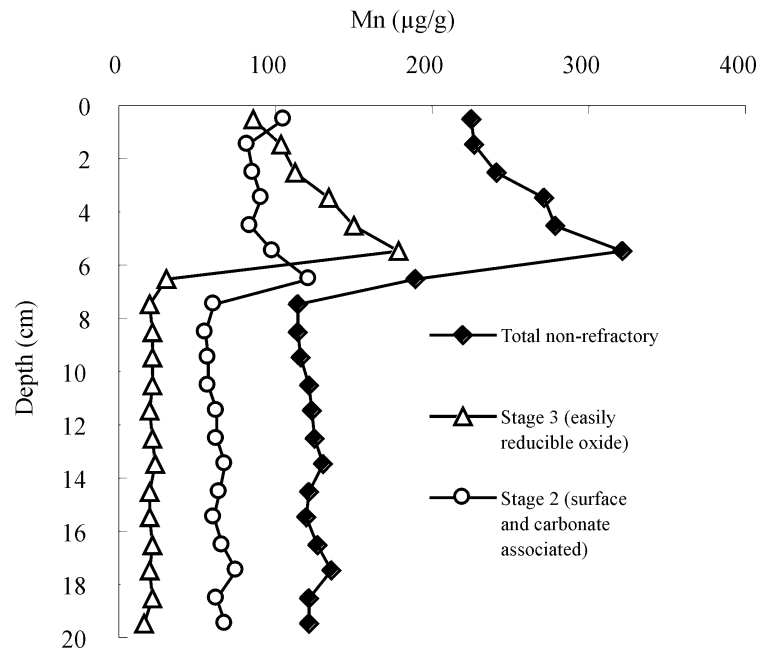


Fig. 1 Speciation profiles of Mn in the solid phase in a sediment core (1500D3C3) taken from the Hebrides slope.

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