High resolution profiles and fluxes of redox species in continental margin sediments: Implications for the cycles of nitrogen, iodide, manganese, and iron

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The preferential use of the electron acceptor that yields the highest amount of free energy in the bacterially mediated oxidation of organic matter constitutes a long-standing paradigm in biogeochemistry. In marine sediments, this leads to a well-established vertical sequence of redox reactions in which oxygen is reduced near the sediment-water interface, followed in turn by the reduction of nitrate and manganese oxide, iron oxide, sulphate, and finally carbon dioxide (e.g. Froelich et al., 1979). The early expressions of the paradigm were limited to these major redox elements, but thermodynamic calculations and experimental observations have shown that other redox elements (for example I, Se, Cr) can also be involved in organic carbon oxidation, either directly or by responding to changes in redox potential. Progress in understanding the zonation of redox reactions in sediments is closely tied to the ability to make high resolution measurements. Here we report new measurements of redox species in undisturbed sediment cores from 100m, 200 m and 325 m depth along a cross-channel section in the Laurentian Trough in the Gulf of St. Lawrence. The vertical distributions of O_2, $Mn(II)$, $Fe(II)$, $I(-I)$, and $HS(-I)$ were measured with millimeter resolution in the top several cm of the cores using a voltammetric Hg/Au amalgam microelectrode (Brendel and Luther, 1995). The distributions of NO_3^-, NH_4^+ and HPO_4^{2-} were measured colorimetrically, using porewater samples obtained by conventional slicing and centrifugation of replicate cores. Solid-phase Mn was extracted with HCl and measured by AA-spectrometry. Benthic fluxes of O_2, NO_3^- and NH_4^+ were measured by incubating cores at the in situ temperature.

The vertical distributions we measured were qualitatively similar at the three sites. In all cores, O_2 disappeared at about 4 mm depth, followed by the successive appearance of I(I-), Mn(II) and Fe(II). The appearance of Fe(II) was very abrupt and was accompanied by a broad peak in the voltammogram consistent with the presence of colloidal Fe(III). As in our previous studies with this microelectrode, there was a depth interval in which neither O_2 nor Mn(II) could be detected. The concentration of iodide increased sharply below the sediment surface and displayed a sharp subsurface maximum of about 5 μM at the very depth where Mn(II) was first detected. NO_3^- decreased rapidly across the sediment-water interface to levels below detection limits at 10 mm depth. Below this depth NO_3^- increased again and displayed a broad concentration maximum with concentrations as high as 15−40 μM. These data are consistent with the successive use of electron acceptors during organic carbon degradation according to free energy yield. However, a close examination of the data reveals new details about diagenetic processes.

Thus, a nitrate minimum located near the base of the oxic sediment layer supports a flux of nitrate from the water column into the sediment which agrees with the measured nitrate flux. This is consistent with classical anaerobic denitrification. However, a sharp ammonium gradient across the oxic surface layer is not reflected in a corresponding release of ammonia from the sediment, indicating there is an important ammonium sink within the oxic layer. A possible sink could be the coupled nitrification-denitrification within this layer; this would require the presence of
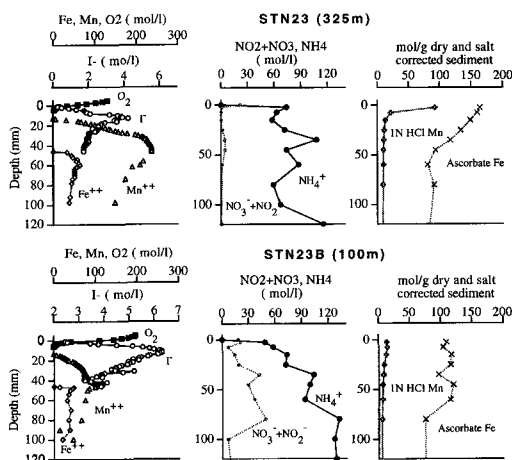
FIG. 1. Profiles of dissolved redox species and reactive particulate Mn and Fe(III) from two sediment cores collected along a cross-channel section in the Laurentian Trough. Left: Au/Hg microelectrode profiles; Middle: Nitrate+nitrite and ammonium; Right: particulate Mn extracted with 1N HCl and particulate Fe extracted with the ascorbate buffer (Kostka and Luther, 1994; Anschutz *et al.* 1998).

aerobic denitrifying bacteria. Alternatively, ammonia could be oxidized to dinitrogen by manganese dioxide, abundant in the surface layer, as proposed by Luther *et al.* (1997).

Below the nitrate minimum the nitrate concentration increases with depth and reaches maximum values as high as 40 µM at a depth that coincides with the depth of the Mn(II) maximum. We suggest that the anaerobic production of nitrate is via the oxidation of ammonia, abundant at this depth, with MnO_2. In theory, some aqueous Fe(III) species can also produce nitrate via NH_4^+ oxidation. The nitrate maximum implies that nitrate is transported upward into the denitrification zone as well deeper into the sediment. The absence of Fe(II) within the nitrate maximum and the abrupt appearance of Fe(II) below it suggests that Fe(II) is oxidized by nitrate in this zone.

As in previous studies with this microelectrode, there was no overlap between dissolved O_2 and Mn(II) suggesting that other oxidants than O_2 are involved in reoxidizing the upward diffusing Mn(II).

One candidate is nitrate which is being consumed within the sediment layer where neither O_2 nor Mn(II) could be detected. A second candidate, although quantitatively less important, is iodate. One iodate is reduced by six Mn^{2+} to give iodide and MnOOH. Iodate reduction with Mn^{2+} could become important if iodate is regenerated through a rapid redox cycle where iodide is re-oxidized by oxygen or nitrate in the top centimetre of the sediment. We observed a sharp increase of iodide across the sediment-water interface with a well defined maximum located near the depth of Mn(II) removal. The iodide concentration within this maximum was more than an order of magnitude higher than total iodine in seawater. The iodide peak is likely derived from iodate reduction and iodide containing organic matter. It is not clear what reactions contribute to the removal of iodide below the depth of the peak. Oxidation of I^- by subsurface nitrate can be a possible pathway.

A number of unresolved but intriguing questions remain: Which are the dominant reactions that remove the Mn(II) that diffuses upward from the Mn(II) maximum and which reactions remove the Mn(II) that diffuses downward? Which are the reactions that remove ammonium in the oxic surface layer? Which mechanism maintains the position and strength of the iodide peak, and which reaction removes the downward diffusing iodide? Which is the anaerobic process that produce nitrate, and by which process is this nitrate consumed? These questions are deserving of further research.

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