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Fine-scale *in situ* measurements of oxygen distribution in marine sediments

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Abstract

A new profiling bottom lander (Profiluren) mounted with microelectrodes can measure oxygen profiles through the undisturbed sediment-water interface with 25-50 μm spatial resolution. The high spatial resolution of the *in situ* profiles reveal the thickness of the diffusive boundary layer (DBL) and allow calculations of: 1) the diffusive oxygen flux through the DBL, 2) the limitation of mass transfer between sediment and water due to the DBL and, 3) the oxygen consumption in discrete layers of the mm thick aerobic zone of marine sediments. The lander is thus an excellent tool for *in situ* analysis of oxygen dynamics at the sediment-water interface. Here we demonstrate two *in situ* oxygen profiles from a Danish coastal sediment at 15 m water depth, and discuss the impact of high resolution oxygen measurements.

Introduction

The introduction of oxygen microelectrodes in microbial ecology by REVSBECH et al. (1980) has revealed the steep microgradients at the sediment-water inter- face, and the microelectrodes have proven to be very powerful tools for analysis of oxygen dynamics in sediments (REVSBECH and JØRGENSEN 1986). There are, however, some problems in investigations of oxygen uptake in sediment cores brought to the laboratory: A) The oxygen consumption is dependent upon the wa- ter flow above the sediment (BOYNTON et al. 1981), and the oxygen flux can vary by more than a factor of two within a natural interval of flow velocities (JØRGENSEN and DES MARAIS 1991). The choice of flow regime in the labora- tory will not necessarily reflect the true *in situ* situation. B) Even in minimally disturbed cores there can be loss or redistribution of surface material, which alters the oxygen profiles (REIMERS et al. 1986). C) When the sediment is brought to the water surface the pressure difference can cause changes in the carbonate equilibria, which again will influence the diagenetic processes (MUR- RAY et al. 1980). For these reasons REIMERS (1987) constructed a microprofiler capable of *in situ* measurements with microelectrodes. The profiler can be mounted in a free falling vehicle and is capable of oxygen measurements in the deep sea with a 1 mm spatial resolution. Based upon this design ARCHER et al. (1989) constructed another profiling instrument, which can operate in the deep sea inside a box corer with a 0.5 mm spatial resolution. Here we demonstrate

results from a new profiling lander also based upon the design of REIMERS (1987). The instrument can be deployed in coastal shallow water sediments with mm-scale oxygen penetration, due to a further improvement in the spatial resolution.

Material and methods

The measurements were carried out in a Danish coastal sediment (Århus Bay) at 15 m water depth. The profiler was lowered to the sea floor on a wire. On-line data acquisition allowed changes in the measuring procedure according to the results obtained. We used Clark-type oxygen microelectrodes with an internal guard cathode (REVSBECH 1989), an outside tip diameter of < 10 μm, a 90 %-response time of < 1 s and a velocity sensitivity of < 2 %. The electrode recordings were calibrated by Winkler titration of bottom water samples and the zero readings in the sediment below the aerobic zone. A rough estimate of the bottom water current was obtained by underwater video observations of suspended particles.

Results and discussion

Figure 1 shows *in situ* oxygen profiles from October (A) and November (B) 1989. In October the water column was stratified and the sediment oxygen consumption resulted in a low bottom water oxygen content (65 μM). Oxygen penetration was only 1 mm although the brown oxidized zone was several cm thick. In November after the autumn turnover of the water column the bottom water was oxygen saturated (290 μM) and oxygen penetrated 2.5 mm into the sediment.

DBL

The thickness of the DBL as defined by JØRGENSEN and REVSBECH (1985), was 250 μm (A) and 475 μm (B). The DBL thickness decreases strongly with increasing water flow velocity (GUNDERSEN and JØRGENSEN 1990), which is in accordance with the rough estimates made from video flow observations of 12 cm/s (A) and 5 cm/s (B). The limitation of mass transport between water and sediment exerted by the DBL can be calculated from the DBL thickness and the relation between the diffusion coefficient (D) of oxygen and the solute of interest (BOUDREAU and GUINASSO 1982). The oxygen consumption in (A) was limited approximately 20 % by the DBL.

Sediment-water interface

The sediment-water interface relative to the oxygen profile was determined as the break in the oxygen concentration gradient due to impeded diffusive conditions in the sediment compared to the water (SWEERTS et al. 1989). The significant increase in the gradient is 40 % and 70 % respectively, and the break can easily be seen by placing a ruler on the figure. The ratio between the gradient above and below the sediment surface expresses the ratio between the diffusion coefficient in water (D_w) and the diffusion coefficient in the sediment (D_s) times the porosity. Microscale heterogeneity, however, causes variability and the mean value of several ratios is therefore required for more accurate calculations. This technique of defining the sediment-water interface is very precise compared to video observation (ARCHER, EMERSON and SMITH 1989) and use of resistivity data (ARCHER, EMERSON and REIMERS 1989), but unfortunately
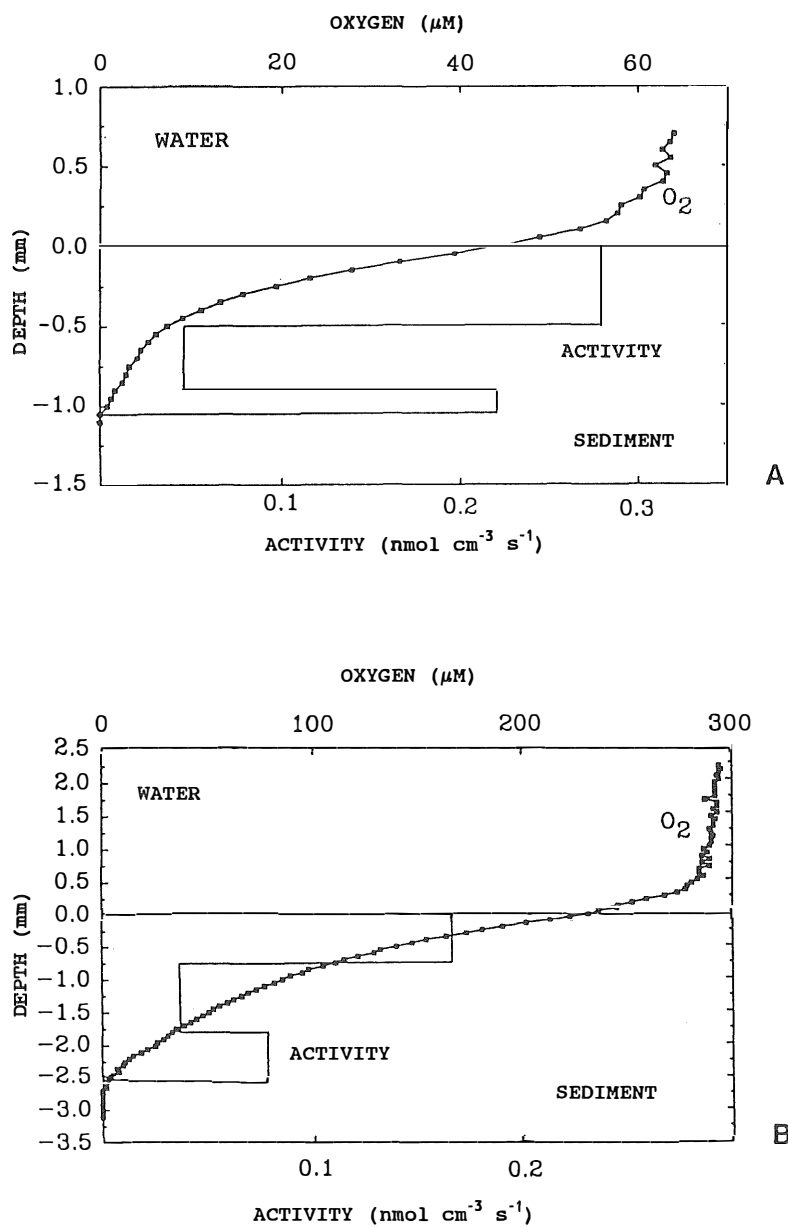
Fig. 1. *In situ* oxygen profiles from a coastal Danish sediment, (A) in October and (B) in November 1989. Notice the different scales on both axes. The sediment surface is indicated by a line at depth 0 mm. The concentration measurements are .temporally separated by 5 s. Activity (oxygen consumption rates per sediment volume) as calculated by the best fit of parabolic functions are symbolized by boxes.

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only 35-50 % of the oxygen profiles exhibit a significant change in the gradient probably due to the presence of fluffy material on the sediment surface (GUN-DERSEN and JØRGENSEN 1990).

Diffusive oxygen uptake

When the oxygen gradient in the DBL is determined at high spatial resolution, the diffusive oxygen flux across the sediment-water interface can be calculated from $J_{water} = D_W (dC/dz)_{water}$ (CRANK 1975). This determination is simpler than a flux calculation just below the sediment surface where the oxygen may be easier to measure but where determination of D_S and porosity at high spatial resolution are required (REIMERS et al. 1986). The one-dimensional diffusive flux of oxygen into the sediment was 14.9 (A) and 19.4 (B) mmol m^{-2} day^{-1}.

Depth distribution of oxygen consumption

On the assumption of uniform D_s and porosity in the mm thick aerobic zone, the oxygen consumption in discrete layers will be reflected by the second derivative of the oxygen profile (CRANK 1975). The distribution of activity can thus be modelled by fitting parabolic functions to the oxygen concentration profile (NIELSEN et al. 1990). The specific activity calculated from the best fit of parabolic functions is indicated in the figure, and exhibits the same pattern in A and B: The highest oxygen consumption is in the upper part of the aerobic zone where the availability and quality of organic substrates must be highest. It is likely that this elevated activity coincides with the very thin biofilm, which is observed at the very top of the sediment. Below this zone the lower activity must be due to a poorer quality or quantity of substrates, whereas the bottom of the aerobic zone exhibits an increased activity which probably is due to upward diffusion of reduced organic and inorganic solutes from the anaerobic mineralization processes below.

Acknowledgements

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