Early diagenetic processes in northwestern Black Sea sediments

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CHAPTER 7

Summary

Transport between the sea floor and the overlying water is essential for benthic pelagic coupling in marine systems (Graf, 1992). Not only organic matter, but also other solid phase components such as iron- and manganese-oxides that are crucial for many early diagenetic processes reach the sea floor through deposition. Additionally, dissolved nutrients and gasses are exchanged between the sediment and water column through diffusive-type of transport. This thesis deals with the response of early diagenetic processes in Black Sea sediments to changes in sedimentation and nutrient composition of the water overlying the sea floor.

Sediment respiration, which is directly linked to the flux of degradable organic matter to the sea floor, is the key factor for many early diagenetic processes in the sediment. In chapter 2 we have developed a conceptual model for sediment respiration versus water depth that takes into account different transport modes of organic matter to the sediment operating in shallow and deep-water columns. In shallow water, turbulent mixing dominates, while in deep water, rapid sinking is the major deposition pathway. Fitting of this model to a comprehensive dataset of sediment community oxygen consumption (SCOC) measurements from a variety of marine systems (ranging from shallow estuaries and coastal seas to deep-sea sediments up to 6,000 m depth) from all over the world resulted in relation 2.4. SCOC in this model is a measure for the flux of degradable organic matter to the seafloor. According to this model, 86 % of the organic matter production in the water column at Z=0 is subject to turbulent mixing, deposition-resuspension cycles and has a low net settling velocity. The remaining 14 % reaches the sediment by rapid particle settling. This settling transport is by far the major transport mechanism of organic carbon to deep-sea sediments and can be regarded as the “new” production, resulting in an f–ratio of 0.14, which corresponds to previous reported f–ratios for deep-sea environments (Eppley and Peterson, 1979; Wollast, 1998).

Although on a global scale water depth seems to be the dominant factor determining sediment respiration rates, other factors such as primary production in the water column and the quality of the sedimenting material account for much of the variation in benthic respiration rates at a local scale. In the northwestern continental shelf of the Black Sea, for example, sedimentation processes are largely influenced by the river Danube. In chapter 3, we have distinguished three areas on the northwestern shelf based on the spatial distribution of abiotic sediment characteristics and the macrobenthos community: (1) The area just in front of the Danube Delta where large amounts of nutrients and suspended solids are discharged. High sedimentation rates of relatively fine-grained sediments and high benthic mineralization rates characterized
this area. The macrobenthos community was dominated by deposit feeders. (2) The northern part of the continental shelf, where an anticyclonic gyre is located. The majority of the Danube discharge is transported to this region. This area is characterized by low sedimentation rates. However, the deposited material contained a larger fraction of labile organic matter than the delta area, resulting in high benthic mineralization rates. Suspension feeders dominated the macrobenthos community. (3) The southern part of the continental shelf was characterized by low sedimentation rates and low rates of benthic mineralization. In this area suspension feeders dominated the macrobenthos community. SCOC rates ranged between 2 and 52 mmol $O_2$ m$^{-2}$ d$^{-1}$ (average 21 mmol $O_2$ m$^{-2}$ d$^{-1}$) decreasing with water depth. Macrobenthos accounted on average for 20% of the total benthic oxygen consumption. In the northern part of the continental shelf and in the coastal stations, microorganisms, and micro- and meio-benthos dominated benthic community respiration, while macrobenthos became relatively more important in terms of oxygen consumption in the southern part of the continental shelf.

In order to study the response of early diagenetic processes in the northwestern Black Sea sediments to changes in the boundary conditions, a numerical model has been developed, which is presented in chapter 4. Low oxygen concentrations in the bottom water and high carbon deposition rates, which are characteristic features of the northwestern Black Sea, resulted in a dominance of anoxic mineralization processes including manganese, iron and sulfate reduction. The model includes six solid phase (two carbon fractions with different reactivity, iron- and manganese oxides, iron monosulfide and pyrite) and eight solute variables (oxygen, nitrate, ammonium, manganese, iron, sulfate, hydrogen sulfide and methane). The cycling of iron and sulfur is explicitly incorporated in the model because these elements play an important role in the mineralization of organic matter on the continental shelf. The model is capable to perform both steady state and dynamic simulations and because of its simplicity and calculation speed it can easily be coupled to biogeochemical models for water-column processes. The output of the model is composed of depth profiles of the state variables and their biogeochemical reaction rates and fluxes of the solute substances across the sediment-water interface. The model has been applied to solid-phase and pore-water data from station 9 (May 1997) near the Danube Delta. A steady state simulation reasonably reproduced the main features, but not the distribution of iron and the concentrations of oxygen and total organic carbon in the first two cm. A dynamic simulation revealed that a pulse flux of organic matter, resulting from the spring bloom, could be responsible for the deviation from steady state in the near surface distribution of total organic carbon and oxygen.

With the use of the model, the effect of variable carbon loading on organic matter degradation pathways has been investigated. There is a gradual increase in the relative importance of anoxic mineralization pathways as carbon loadings increase, but the transitions from manganese-based respiration to iron-based respiration and from iron-based respiration to sulfate reduction are rather abrupt. The first jump is due to the positive feedback between manganese reduction coupled to ferrous iron oxidation and iron oxide reduction. The second swap is due to the formation of iron sulfides. This will consume part of the reduced iron, which is consequently not available for re-oxidation to iron oxide and iron-reducing bacteria then become iron oxide limited. The cycling efficiency of iron changes abruptly and a larger part of the iron will be fixed as iron sulfides.

The model confirmed that anaerobic mineralization processes such as iron- and sulfate reduction were relatively important in the sediments of the northwestern
Black Sea. At station 9 (May 1997), for example, sulfate reduction alone accounted for almost 50 % of the total benthic carbon mineralization. The dissolved sulfide that is formed during this sulfate reduction quickly reacts with the reactive iron that is present in the sediments to form iron sulfides such as FeS and pyrite. Through this mechanism, reactive iron acts as a buffer to prevent free sulfide accumulation in the sediment. As a result of the formation of iron sulfides, the cycling patterns of iron and sulfur are intensively coupled. In chapter 5, the cycling of sulfur and iron was analyzed in the sediments of the northwestern Black Sea by means of depth profiles of various sulfur (pyrite; acid volatile sulfides (AVS); \( S_0 \); \( H_2S \), sulfate) and iron (dissolved and dithionite-extractable iron, pyrite and AVS) species and the sulfur isotope ratios of sedimentary pyrite. Sulfur and iron cycling in surface sediments of the northwestern part of the Black Sea is largely influenced by (1) organic matter supply to the sediment, (2) availability of reactive iron compounds and (3) oxygen concentrations in the near-bottom waters. Biologically active sediments just in front of the river deltas were characterized by high AVS contents and a fast depletion of pore water sulfate with depth, most likely due to high sulfate reduction rates (SRR). The \( \delta^{34}S \) values of pyrite in these sediments were relatively high (-8 \(^\circ\) to -21 \(^\circ\) vs. V–CDT). On the central shelf, where benthic mineralization rates are lower, re-oxidation processes may become more important resulting in pyrite extremely depleted in \( ^{34}S \) (-39 \(^\circ\) to -46 \(^\circ\) vs. V–CDT). A high variability in \( \delta^{34}S \) values of pyrite in sediments from the shelf-edge (-6 \(^\circ\) to -46 \(^\circ\) vs. V–CDT) reflects characteristic fluctuations in the oxygen concentrations of near-bottom waters. During oxic conditions, re-oxidation processes became important, resulting in low AVS concentrations and light \( \delta^{34}S \) values. Anoxic conditions of the bottom waters overlying shelf-edge sediments are reflected in enhanced AVS contents and higher sulfur isotope values. The sulfur and iron contents, and the pyrite isotopic composition (-37 \(^\circ\) to -39 \(^\circ\) vs. V–CDT) of sediments in the permanently anoxic deep-sea (1494 m water depth) reflect the formation of pyrite in the upper part of the sulfidic water column and the anoxic surface sediment. It is demonstrated that pyrite, extremely enriched in \( ^{32}S \), can be found in the Black Sea surface sediments which are positioned both above and below the chemocline, in spite of different biogeochemical and microbial controlling factors.

A remarkable feature of the euxinic Black Sea is that iron sulfides are formed in the anoxic water column and sink to the deep-sea floor where they are buried in the sediment (e.g. Goldhaber and Kaplan, 1974). Consequently, the deep-sea is a sink for sulfur and reactive iron from the system. The flux of iron sulfides from the water column is reflected in enhanced concentrations of highly reactive iron and a high degree of pyritization (0.57 – 0.80) for the deep-water sediments of the Black Sea (Chapter 6). The iron enrichment of deep-water sediments is balanced by a loss of highly reactive iron from the oxic continental shelf. Calculations from a numerical diagenetic model and reported in situ flux measurements indicate that the dissolved iron flux out of the shelf sediments is more than sufficient to balance for the excess sink of reactive iron in deep-sea sediments. This iron mobilization mechanism likely operates in most shelf areas, but its net effect becomes only apparent when reactive iron is trapped in sulfidic water bodies as iron sulfides or when iron is incompletely oxidized in low oxygen zones of the ocean.

Due to a lack of historical data on sediment respiration, we were not able to relate benthic mineralization rates on the northwestern Black Sea shelf to eutrophication effects. However, gradients in organic loading induced by the Danube discharges allowed us to investigate effects of this predicted increase in organic
loading due to eutrophication. SCOC measurements were in the same range as other (eutrophicated) continental shelf systems and did not reveal an extremely eutrophicated situation in the Black Sea in summer 1995 and spring 1997. This does not mean that the Black Sea has not suffered from enhanced levels of eutrophication in a previous period (between 1960 and 1990). It could be that the level of eutrophication has decreased during the last couple of years. Recently, some positive signs of ecosystem recovery in the Black Sea were observed. Due to the economic collapse of the Eastern and Central-European countries in the early nineties, phosphorus and nitrogen loads have decreased (Cociasu and Popa, 2000). Consequently, a diminution of algal blooms and total phytoplankton abundance was observed on the shelf (Bodeanu et al., 2000). Some planktonic and benthic species that were considered to be extinct or very rare have become very common again in the Black Sea. Moreover, the abundance of undesirable jellyfish has leveled out and the number of anchovy eggs and larvae has increased (Final report EROS–21 project, January 1999).

The recent history has shown that the ecosystem of the Black Sea continental shelf is very vulnerable to human perturbations. This is mainly caused by the large number of people that live in the catchment areas of the rivers discharging in the shallow continental shelf. In 1992, about 81 million people lived in the drainage basin of the Danube compared to 41 million for the drainage basin of the Rhine (Mee, 1992). Much of the pollutants and nutrients that are produced by this population reach the waters of the continental shelf where they can enhance the primary production. High benthic mineralization rates that result from mass deposition of organic material at the sea floor after a phytoplankton bloom could easily result in anoxic conditions of the near-bottom water. Especially during summer, when mixing processes in the water column are restricted due to temperature stratification.