BIOGEOCHEMICAL MODELING OF SEDIMENTS FROM THE SANTA BARBARA BASIN (CALIFORNIA)

S. Madani, F. J. R. Meysman & J. J. Middelburg

The MEDIA (Modelling Early Diagenesis) environment is a flexible and extensible software system that provides problem-solving assistance for simulating 1D reactive transport in surface sediments. MEDIA allows multiple diagenetic models to be built by extending a template with new model components from a toolbox of available objects (elements, species, parameters, reactions). As a test, a diagenetic model was constructed to analyze an extensive sediment dataset from the Santa Barbara Basin off California. Porewater and solid phase concentration profiles were generated and compared to the available data. Concentration depth profiles were reproduced with great accuracy. The different pathways of organic matter mineralization were modeled, and the coupling among the biogeochemical cycles of C, O, N, S, Mn and Fe was investigated. This paper focuses on the coupled cycles of sulfur and iron. It illustrates the prominent role of sulfur in organic matter degradation in an anoxic environment.

Introduction

The Santa Barbara Basin (SBB) is a semi-enclosed basin of 340 to 800 m depth in the California Borderland. REMERS et al. (1996) published an extensive porewater and solid phase geochemistry data set of the deep basin sites from box and kasten cores. Here we construct a diagenetic model in the MEDIA environment adequately identifying and quantifying the dominant biogeochemical processes in the SBB.

Diagenetic modelling environment

The MEDIA software environment was developed to simulate the coupling of geochemical, physical and biological processes in surface sediments. The MEDIA software allows user-tailored models to be built from a set of basic building blocks and provides an efficient numerical solution for these models. A detailed review of the transport and reaction components is given in MeyesMAN et al. (in press).

Concentration depth profiles

Fig. 1 compares the steady-state resulting output of the model with the data profiles. The steady-state model profiles of both porewater constituents and solid-phase constituents closely fit the observations, indicating that the model explains a substantial part of the geochemical complexity in the SBB.

OM mineralization pathways

The model estimates the total mineralization rate (i.e., the combined rate of all three fractions integrated over depth) at 145 mmol C cm⁻² y⁻¹. The rates attributed to the different mineralization pathways are shown in Table 1. Sulfate reduction is by far the dominant pathway, and Fig. 2b compares the Sulfate Reduction Rate (SRR) obtained from S³² incubations, with the modeled SRR. A good fit to the observations is obtained, except for the first two centimeters. This is the zone where the labile organic matter is processed, resulting in a sharp peak in the SRR. Possibly due to insufficient resolution, this peak is not observed in the SRR data.


Sulfur and iron cycling

Fig. 3 shows that the main source of sulfur in the sediment comes from the water column through influx of SO₄²⁻. A third of this incoming SO₄²⁻ flux is transferred to deeper lying sediment below 140 cm. As can be seen from the SO₄²⁻ porewater profile (Fig. 1), strong sulfate consumption takes place just below our modeled sediment stratum, presumably due to the oxidation of a significant flux of methane diffusing.
upwards [1]. The remaining two thirds of the incoming \( \text{SO}_4^{2-} \) flux is used for sulfate reduction, mostly through direct mineralization of \( \text{C}_{\text{org}} \). Nevertheless, some sulfate is used to oxidize \( \text{H}_2 \) [2], a highly reactive intermediate in the \( \text{C}_{\text{org}} \) mineralization process, although resulting here from pyrite formation. Sulfate reduction produces \( \text{HS}^- \), of which equal amounts are engaged in FeS formation on the one hand [3] and the acid-base equilibrium with \( \text{H}_2\text{S} \) on the other [4]. The latter combines with FeS to produce pyrite [5]. Within the modeled stratum, all the FeS formed is converted into pyrite, resulting in a significant burial of sulfur. Looking at the sulfide fluxes to and from the sediment, some is coming from deeper layers (presumably produced by methane oxidation through sulfate), whereas three times that amount is transferred across the sediment-water interface. The latter flux of sulfide into the water column then produces the suboxic to anoxic conditions observed in the lower water column of the SBB.

Black arrows represent geochemical reactions that take place in surface sediments. Green arrows show the fluxes across the water-sediment interface and the surface sediment-deep sediment interface. The unit of the figures is \( \mu \text{mol C cm}^{-2} \text{yr}^{-1} \).

Due to the importance of sulfate reduction, we took a closer look at the cycling of sulfur within the modeled stratum. Because iron is a key player in the sulfur cycle due to precipitation of FeS and FeS\(_2\), we also looked at the Fe cycle. Table 2 lists the most important reactions involved in these two cycles.

Fig. 3. Main sources of sulfur in the sediment

Fig. 4. The iron cycle in the sediment.

Fig. 4 shows that the main supply of iron in the sediment comes from the water column through the deposition of solid FeOOH. There is also a recycling of FeOOH through the oxidation of particles containing iron (\( X_{\text{Fe}} \)) [6]. This iron oxide is reduced mainly via the mineralization of \( \text{C}_{\text{org}} \), and only a negligible fraction combines with hydrogen and hydrogen sulfide. The ferrous iron (\( \text{Fe}^{2+} \)) produced is engaged partly in FeS formation and the subsequent burial of pyrite on the one hand [3]. On the other hand, \( \text{Fe}^{2+} \) partly diffuses to the overlying water column, where it contributes to the anoxia of the overlying water through scavenging of molecular oxygen. Consequently, there is only a minor recycling pathway of \( \text{Fe}^{2+} \) to FeOOH within the sediment (via the adsorption of \( \text{Fe}^{2+} \) to the matrix and the subsequent oxidation of this \( X_{\text{Fe}} \)). Most of the \( \text{Fe}^{2+} \) recycling is displaced to the overlying water.

Coupling between S and Fe

Fig. 5 shows the coupling of the Fe and S cycles. In addition to the transformations within the modeled sediment stratum, we also tentatively depicted the cycling within the overlying bottom water as well as the presumed transformations in the reactive zone just below the modeled sediment layer. In the case of iron, 10% enters the BBL as pyrite (FeS\(_2\)), whereas the other 90% arrives as iron (hydr)oxides (FeOOH). In the end, all iron is buried as pyrite. In the case of sulfur, all enters the BBL as sulfate, and roughly 80% is buried as pyrite. Surprisingly, about 20% of the sulfur is buried in reduced form other than pyrite (elemental and organic S).

Table 2. Summary of the reactions described above.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SO}_4^{2-} + \text{CH}_4 \rightarrow \text{CO}_2 + \text{H}_2\text{S} )</td>
<td>[1]</td>
</tr>
<tr>
<td>( \text{SO}_4^{2-} + 4.5 \text{H}_2 \rightarrow \text{H}_2\text{S} + 4 \text{H}_2\text{O} )</td>
<td>[8]</td>
</tr>
<tr>
<td>( \text{HS}^- + \text{Fe}^{2+} \rightarrow \text{FeS} + \text{H}^+ )</td>
<td>[9]</td>
</tr>
<tr>
<td>( \text{HS}^- + \text{H}^+ \rightarrow \text{H}_2\text{S} )</td>
<td>[10]</td>
</tr>
<tr>
<td>( \text{FeS} + \text{H}_2\text{S} \rightarrow \text{FeS}_2 + 2 \text{H}^+ )</td>
<td>[11]</td>
</tr>
<tr>
<td>( X_{\text{H}} + \text{Fe} \rightarrow X_{\text{Fe}} + \text{H}^+ )</td>
<td>[12]</td>
</tr>
</tbody>
</table>

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References


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