Anaerobic degradation of organic matter controlled by productivity variation in a restricted Late Triassic basin

I. Vető a,*, M. Hetényi b, M. Hámor-Vidó a, H. Hufnagel c, J. Haas d

a Geological Institute of Hungary, Stefánia út 14, 1143 Budapest, Hungary
b József Attila University, 6701 Szeged, PO Box 651, Hungary
c Bundesanstalt für Geologie und Rohstoffe, Stilleweg 2, D-30655 Hannover, Germany
d Academic Research Group, Department of Geology, Eötvös Loránd University, Műzeum krt. 4/A, 1088 Budapest, Hungary

Abstract

The organic-rich late Triassic Kőssen Formation (Hungary) was deposited in a shallow basin, situated between a carbonate platform and the continent. A large number (107) of samples of a 240 m thick, steeply dipping core section of the Kőssen Fm., built up of mostly non-bioturbated sediments have been analysed by Rock-Eval pyrolysis. Organic petrographic studies, sulphur and iron speciation (total sulphur, HCl-soluble sulphate sulphur, pyrite iron and HCl-soluble iron) and CO2 measurements have been carried out on smaller sample sets. According to Rock-Eval pyrolysis and organic petrography the immature organic matter (OM) is of dominantly marine origin throughout the section. Unicellular planktonic algae are remains of the most important organic constituents but microbial-algal mat material is also of importance. The carbonate and TOC contents and HI values display much scatter and upward decreasing trends. Type II-S OM is common in the lower third of the section and it occurs in its middle interval, too. The marked downward decrease of \( T_{\text{max}} \) values is explained by the downward increase of the OM sulphur content. The original organic carbon content (TOC_{or}) was calculated. The degree of OM preservation, expressed in term of TOC/TOC_{or}, varies between 0.36 to 0.89 and shows an upward decreasing trend, interrupted by high values around the middle of the section. This strengthening of the degradation during the black shale event was the result of the parallel decreasing rate of sedimentation and OM deposition. The high TOC/TOC_{or} values found around the middle of the section are mostly the result of a temporary acceleration of OM deposition. Sulphur richness of the OM shows no positive correlation with the degree of organic preservation. Sulphur partitioning between pyrite and OM was controlled by the ratio of reactive iron to OM. Average rates of planktonic productivity (\( C_{\text{prod}} \)) vary between 6–9 and 60–88 t C_{org}/m²/Ma. The rough covariance of the degree of preservation and \( C_{\text{prod}} \) suggests that variations in planktonic productivity exerted a strong control on preservation in the suboxic, low to medium productivity Kőssen Formation. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Late Triassic; Type II-S OM; Bacterial sulphate reduction; Degree of OM preservation; Productivity assessment

1. Introduction

Shallow depressions, developed in the onshore marginal belt of the huge late Triassic carbonate platform of the Alps–Apennines domain, were the site of deposition of thick (up to 2 km) black shale sequences (Fig. 1) which sourced most of the oil fields of the area (Matta-veli and Novelli, 1990; Stefani and Burchell, 1993; Clayton and Koncz, 1994). Bulk characteristics of some of these black shales have recently been published (Brukner-Wein and Vető, 1986; Brosse et al., 1988, 1990; Köster et al., 1988; Hetényi, 1989) and the presence of sulphur-rich kerogens has been reported by Brukner-Wein and Vető (1986) and Köster et al. (1988). However, a geochemical assessment of production and preservation
of organic matter (OM) in the Late Triassic back-platform basins has not yet been reported.

In this paper, we present organic geochemical and petrographical data obtained on core samples collected from an immature section of the Kössen Formation (Kössen Fm.), a latest Norian-Rhaetian black shale sequence of Western Hungary, penetrated by the well Rezi 1 (for location see Fig. 1). On the basis of these data and those obtained earlier by Brukner-Wein and Vető (1986) and Hetényi (1989) on the same well section, the original organic carbon (TOCor) contents and the degrees of organic carbon preservation (TOC/TOCor) are calculated, the factors governing OM preservation (especially natural sulphurization) are discussed and an evaluation of productivity changes during deposition of the Kössen Fm. is attempted.

2. Geological setting

In the western part of the Transdanubian Range Unit, black shales (Kössen Fm.) were deposited under restricted basin conditions during the latest Norian to Early–Middle Rhaetian interval (Haas, 1993). The depositional basin of the Kössen Fm. began to form at the end of the Middle Norian as a result of extensional tectonics which led to disintegration of the previously existing large carbonate platform. In the early stage of the evolution of the basin, platy dolomites (Rezi Dolomite Formation) were formed. According to conodont studies (Budai and Kovács, 1986) this formation represents the uppermost part of the Alaunian and the lower part of the Sevatian substages. Then a climate-induced intensification of terrigenous influx led to deposition of clayey limestones and shales of the Kössen Fm., starting in the late Sevatian (latest Norian). As a consequence, in the inner part of the 100–150 m deep basin, limestones, argillaceous marls, marls, and siltstones settled under stagnant, oxygen-depleted conditions. The gentle slope between the basin and the platform was populated by a rich epibenthic bivalve fauna, whereas the upper slope and the platform margin were inhabited by a shallow subtidal biota. Redeposited remnants of the aforementioned organisms were accumulated at the toe of the
Sedimentological analyses revealed that sea-level changes significantly controlled the features of the succession. In the studied area, the lower part of the Kössen Fm. consists mostly of non-bioturbated, commonly laminated sediments, interlayered with slump beds, rich in lithoclasts. This lower part, interpreted as a toe-of-slope facies is overlain by a laminitic deeper basin facies. At the maximum of the transgression, the shaly basin facies extended over onto the upper slope and even some parts of the platform. This was followed by a regression in the highstand interval when the “Dachstein platform”, a widely extended carbonate platform complex that existed in late Carnian to Hettangian interval (Haas and Budai, 1995), re-occupied a large part of the former basin. This long-term cycle was superimposed by high-frequency 4th and 5th order transgression–regression cycles which also influenced the sedimentological and geochemical characteristics of the sequences (Haas, 1993).

The Rezi 1 well penetrated a 240 m thick, steeply dipping section of the Kössen Fm., underlain by the Rezi Dolomite, much less rich in OM and sulphur (S). The truncated surface of the section is covered by late Neogene silty layers. Its uppermost 15 m (between 24.8 to 39.9 m) are characterised by yellow spots, considered as the results of weathering. The sediments of the Kössen Fm. display a gradual but well pronounced upward decrease of carbonate content (Fig. 2). On the basis of qualitative XRD study of 11 samples (M. Tóth, pers comm.) calcite appears as the main carbonate mineral. The strong predominance of HCl-soluble CaO over HCl-soluble MgO (unpublished results) supports the above finding. Aragonite, quartz and pyrite are ubiquitous and dolomite-ankerite is present in all but one sample. Clay minerals consist mainly of kaolinite and illite-smectite. The section probably represents the transgressive part of the third order cycle mentioned above. The transgression increased the distance between the central part of the basin and the platform and likely resulted in a decrease in the platform-derived carbonate input. The upward decrease of carbonate content, displayed by the studied section (Fig. 2) at least partly reflects this reduction of carbonate transport. On the basis of the chronostratigraphic chart of Gradstein et al. (1994) and sequence stratigraphic data of Haq et al. (1987), the studied section was deposited during an 1.5 Ma time interval, covering the late Sevatan (about 0.5 Ma) and the early Rhaetian (about 1.0 Ma). The corresponding sea-level rise, measured on the short term eustatic curve, displayed in Fig. 5 of Haq et al. (1987), was about 25 m.

3. Experimental methods

TOC content, hydrogen index (HI) and $T_{\text{max}}$ were determined with a Delsi Oil Show Analyser. The total sulphur (S) was weighed as BaSO$_4$ and the HCl-soluble sulphate bound sulphur (SSO$_4$) was weighed either as BaSO$_4$ (Brukner-Wein and Veto´´, 1986) or by ICP technique (this work); the pyrite-bound sulphur was calculated from the iron content of the pyrite, isolated by H$_2$SO$_4$–HF treatment (the iron to sulphur atomic ratio of pyrite was considered to equal 1:2). The organically bound sulphur (S$_{\text{org}}$) was calculated from the difference between total sulphur and the sum of SSO$_4$ and pyrite-bound sulphur (S$_{\text{py}}$). The calculation of S$_{\text{org}}$ is influenced by both the analytical errors of the sulphur and iron speciation studies and the possible deviation of pyrite composition from that corresponding to FeS$_2$. But the few published data shows no significant deviation: the average S/Fe weight ratio for 18 sedimentary pyrites is 1.144 (Table 2 in Kohn et al., 1998) while the theoretical value is 1.147. The non-pyritised reactive iron (Fe$_{\text{HCl}}$) content was leached by 1 N cold HCl during 24 h as suggested by Leventhal and Taylor (1990) and measured by ICP technique. CO$_2$ liberated by HCl was volumetrically measured. Organic petrographic observations were carried out on polished sections of crushed bulk rocks with reflected light microscopy in oil immersion. Both normal and fluorescence light (UV and blue excitation, 420–490 nm; barrier filter 515 nm) were used.

4. Results

Rock-Eval pyrolysis and organic petrography reveal that the OM is of predominantly marine origin. The
whole sequence contains very small amounts of vitrinite particles derived from terrigenous OM and minor amounts of non-fluorescing vitrinite-like material, intercalated in the fluorescing algal matter. Comparable particulate organic matter was described by Buchardt and Lewan (1990) who assumed a multicellular algal seaweed origin and by Stasiuk (1993). The amounts of inertinite in the OM is usually low, on average 2%.

The lower interval between 270 and 190 m is built up of calcareous marls and to a lesser extent of limestones. In this interval, TOC, S contents and HI values, except for one slump bed sample, range between 1.20 and 10.34%, 0.94 and 2.45% and 254 and 833 mg HC/g TOC (but see the two exceptionally high HI values, over 900 mg HC/g TOC), respectively (Fig. 3, Table 1). Petrographically, the bulk of the OM consists of unicellular algae. The main forms are the Calcispherae, small globular planktonic algae, 5–10 μm in size, concentrated in laminae. The yellow fluorescing liptinitic cell wall often surrounds the calcified interior of the Calcisphera and in some cases the small globules are also filled by similarly fluorescing OM. Besides these algae laminated alginite is the next most common constituent. Laminated alginite, bright yellow under fluorescence light excitation or brownish if it is more degraded, can originate both from algal and microbial mats. Colonies of tubular algae are common in the 236 m sample. The amounts of pyrite-bound iron (Fe_{py}) and Fe_{HCl} range between 0.38 and 1.34% and 0.17 and 0.31%, respectively (Table 2). The TOC/S_{org} ratio, except for three values below 9.4 shows the presence of Type II kerogen (Table 3, Fig. 4). The few negative S_{org} values, calculated for samples from the 140–100 m depth interval, even if they obviously are analytical artefacts, suggest that the corresponding kerogens are not rich in sulphur.

In the middle interval (between 190 and 70 m, built up of calcareous marls, marls and siltstones) TOC, S contents and HI values, except for those of one slump bed sample, range between 0.67 and 14.60%, 0.08 and 3.51% and 103 and 794 mg HC/g TOC, respectively, (Fig. 3, Table 1). The OM is dominated by laminated alginite and/or rests of Calcisphera (Fig. 5), but their ratio shows extreme variations although laminated alginite is more frequent here than in the lower interval. Rests of tubular algae are present only in one sample (151.5 m), and in this organic-rich sample 20% of the OM consists of tubular algae. Fish scales are also detected in this sample. Except for this sample, vitrinite is practically absent between 170 and 139.2 m. The inertinite content increases significantly upwards from 2 to 10% between 190.8 and 95.2 m. The continental input is indicated also by the presence of sporinite. No organic petrographic observations were carried out above 95.2 m. The amounts of Fe_{py} and Fe_{HCl} range between 0.17 and 1.63% and 0.25 and 0.76%, respectively (Table 2). The TOC/S_{org} ratio, except for three values below 9.4 shows the presence of Type II kerogen (Table 3, Fig. 4). The few negative S_{org} values, calculated for samples from the 140–100 m depth interval, even if they obviously are analytical artefacts, suggest that the corresponding kerogens are not rich in sulphur.

Siltstones of the upper interval (above 70 m) display low TOC and HI values but the sulphur content does not discriminate with the middle and the upper intervals (Fig 3, Table 2). Relatively higher contribution of land-derived OM only partly explains the low HI values, which can be probably attributed to some extent to the very strong degradation of the marine OM and/or to matrix effect. The uppermost metres probably experienced some alteration due to weathering (see Geological setting) and for this reason they are beyond the scope of this study.

$T_{\text{max}}$ values show a substantial upward increase (Fig. 4): they range between 395 and 415°C at the base of the formation while a 420 to 435°C range is observed at the top of the middle interval. The upward increase of $T_{\text{max}}$ is obviously not related to an upward increase in maturity. This maturity parameter is known to be also affected by the chemical composition of immature OM and this effect is especially pronounced up to the oil window. Type II-S kerogens are more thermally labile than their low-sulphur type II counterparts because the weak carbon–sulphur bonds are broken before stronger carbon–carbon bonds (Tissot et al., 1987; Baskin and Peters, 1992; Radke et al., 1997). For this reason the beginning of the oil window corresponds to lower $T_{\text{max}}$ value for type II-S kerogen (420°C) than for type II kerogen (435°C) (Bordenave et al., 1993). $T_{\text{max}}$ ranges observed for the middle and lower intervals therefore reflect the occurrence of immature type II and II-S kerogens, respectively. The few Ro values, measured on
Table 1
Geochemical characteristics of the Kössen Formation section, well Rezi 1<sup>a,c</sup>

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>TOC (%)</th>
<th>sulphur (%)</th>
<th>TOC&lt;sub&gt;cor&lt;/sub&gt; (%)</th>
<th>TOC/TOC&lt;sub&gt;cor&lt;/sub&gt;</th>
<th>HI (mg HC/g TOC)</th>
<th>T&lt;sub&gt;max&lt;/sub&gt; (°C)</th>
<th>CO&lt;sub&gt;2&lt;/sub&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>43.6</td>
<td>0.90</td>
<td>1.23</td>
<td>2.13</td>
<td>0.42</td>
<td>n.d.</td>
<td>42</td>
<td>426</td>
</tr>
<tr>
<td>44.0</td>
<td>0.84</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>n.d.</td>
<td>37</td>
<td>424</td>
</tr>
<tr>
<td>49.1</td>
<td>0.78</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>0.38</td>
<td>52</td>
<td>423</td>
</tr>
<tr>
<td>51.8</td>
<td>0.78</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>3.15</td>
<td>2.32</td>
<td>340</td>
</tr>
<tr>
<td>52.0</td>
<td>0.65</td>
<td>1.18</td>
<td>1.83</td>
<td>0.36</td>
<td>n.d.</td>
<td>n.d.</td>
<td>2.9</td>
</tr>
<tr>
<td>54.0</td>
<td>0.67</td>
<td>0.08</td>
<td>0.75</td>
<td>0.89</td>
<td>279</td>
<td>432</td>
<td>n.d.</td>
</tr>
<tr>
<td>54.7</td>
<td>1.90</td>
<td>0.42</td>
<td>2.32</td>
<td>0.82</td>
<td>233</td>
<td>437</td>
<td>340</td>
</tr>
<tr>
<td>55.3</td>
<td>1.50</td>
<td>1.53</td>
<td>3.03</td>
<td>0.50</td>
<td>163</td>
<td>425</td>
<td>340</td>
</tr>
<tr>
<td>57.4</td>
<td>1.84</td>
<td>1.42</td>
<td>3.26</td>
<td>0.56</td>
<td>n.d.</td>
<td>n.d.</td>
<td>14.5</td>
</tr>
<tr>
<td>57.3</td>
<td>1.06</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>138</td>
<td>425</td>
<td>n.d.</td>
</tr>
<tr>
<td>58.2</td>
<td>1.38</td>
<td>0.67</td>
<td>2.05</td>
<td>0.67</td>
<td>n.d.</td>
<td>410</td>
<td>n.d.</td>
</tr>
<tr>
<td>59.2</td>
<td>1.56</td>
<td>0.87</td>
<td>3.56</td>
<td>0.76</td>
<td>417</td>
<td>190</td>
<td>n.d.</td>
</tr>
<tr>
<td>59.7</td>
<td>2.03</td>
<td>0.86</td>
<td>2.89</td>
<td>0.70</td>
<td>421</td>
<td>503</td>
<td>n.d.</td>
</tr>
<tr>
<td>60.5</td>
<td>1.88</td>
<td>0.85</td>
<td>2.73</td>
<td>0.69</td>
<td>254</td>
<td>420</td>
<td>15.6</td>
</tr>
<tr>
<td>61.2</td>
<td>4.76</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>607</td>
<td>426</td>
<td>n.d.</td>
</tr>
<tr>
<td>61.7</td>
<td>2.36</td>
<td>0.86</td>
<td>3.22</td>
<td>0.73</td>
<td>n.d.</td>
<td>638</td>
<td>418</td>
</tr>
<tr>
<td>62.8</td>
<td>3.46</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>540</td>
<td>420</td>
<td>n.d.</td>
</tr>
<tr>
<td>63.4</td>
<td>3.40</td>
<td>1.02</td>
<td>4.42</td>
<td>0.77</td>
<td>794</td>
<td>420</td>
<td>22.5</td>
</tr>
<tr>
<td>63.8</td>
<td>3.75</td>
<td>1.01</td>
<td>4.76</td>
<td>0.79</td>
<td>466</td>
<td>421</td>
<td>8.6</td>
</tr>
<tr>
<td>64.2</td>
<td>2.00</td>
<td>1.09</td>
<td>3.09</td>
<td>0.65</td>
<td>345</td>
<td>425</td>
<td>15.0</td>
</tr>
<tr>
<td>64.6</td>
<td>5.01</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>503</td>
<td>417</td>
<td>n.d.</td>
</tr>
<tr>
<td>65.2</td>
<td>3.10</td>
<td>0.71</td>
<td>3.81</td>
<td>0.81</td>
<td>638</td>
<td>418</td>
<td>28.4</td>
</tr>
<tr>
<td>64.3</td>
<td>2.50</td>
<td>0.69</td>
<td>3.19</td>
<td>0.78</td>
<td>510</td>
<td>426</td>
<td>31.4</td>
</tr>
<tr>
<td>64.5</td>
<td>3.19</td>
<td>1.03</td>
<td>4.22</td>
<td>0.76</td>
<td>n.d.</td>
<td>417</td>
<td>n.d.</td>
</tr>
<tr>
<td>64.7</td>
<td>3.13</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>494</td>
<td>420</td>
<td>n.d.</td>
</tr>
<tr>
<td>64.9</td>
<td>14.10</td>
<td>3.51</td>
<td>17.61</td>
<td>0.80</td>
<td>n.d.</td>
<td>552</td>
<td>417</td>
</tr>
<tr>
<td>64.9</td>
<td>3.20</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>552</td>
<td>422</td>
<td>424</td>
</tr>
<tr>
<td>65.0</td>
<td>1.94</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>503</td>
<td>417</td>
<td>n.d.</td>
</tr>
<tr>
<td>65.0</td>
<td>11.10</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>769</td>
<td>413</td>
<td>9.4</td>
</tr>
<tr>
<td>65.6</td>
<td>5.98</td>
<td>2.28</td>
<td>8.26</td>
<td>0.72</td>
<td>n.d.</td>
<td>517</td>
<td>423</td>
</tr>
<tr>
<td>65.8</td>
<td>7.30</td>
<td>2.17</td>
<td>9.47</td>
<td>0.77</td>
<td>639</td>
<td>411</td>
<td>8.3</td>
</tr>
<tr>
<td>65.6</td>
<td>6.08</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>517</td>
<td>423</td>
<td>n.d.</td>
</tr>
<tr>
<td>65.5</td>
<td>3.40</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>390</td>
<td>417</td>
<td>n.d.</td>
</tr>
<tr>
<td>65.6</td>
<td>2.03</td>
<td>1.45</td>
<td>3.48</td>
<td>0.58</td>
<td>n.d.</td>
<td>417</td>
<td>n.d.</td>
</tr>
<tr>
<td>65.4</td>
<td>4.04</td>
<td>2.08</td>
<td>6.12</td>
<td>0.66</td>
<td>n.d.</td>
<td>417</td>
<td>n.d.</td>
</tr>
<tr>
<td>65.2</td>
<td>5.53</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>558</td>
<td>417</td>
<td>n.d.</td>
</tr>
<tr>
<td>65.2</td>
<td>0.33</td>
<td>0.16</td>
<td>n.c.</td>
<td>n.c.</td>
<td>n.d.</td>
<td>417</td>
<td>n.d.</td>
</tr>
<tr>
<td>66.0</td>
<td>14.60</td>
<td>2.89</td>
<td>17.46</td>
<td>0.84</td>
<td>780</td>
<td>403</td>
<td>17.8</td>
</tr>
<tr>
<td>67.0</td>
<td>6.10</td>
<td>1.63</td>
<td>7.73</td>
<td>0.79</td>
<td>720</td>
<td>410</td>
<td>21.2</td>
</tr>
<tr>
<td>67.1</td>
<td>3.03</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>468</td>
<td>421</td>
<td>n.d.</td>
</tr>
<tr>
<td>67.4</td>
<td>1.20</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>172</td>
<td>415</td>
<td>30.5</td>
</tr>
<tr>
<td>67.5</td>
<td>1.66</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>257</td>
<td>426</td>
<td>n.d.</td>
</tr>
<tr>
<td>67.6</td>
<td>2.60</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>438</td>
<td>415</td>
<td>18.6</td>
</tr>
<tr>
<td>67.5</td>
<td>2.21</td>
<td>1.57</td>
<td>3.78</td>
<td>0.58</td>
<td>n.d.</td>
<td>n.d.</td>
<td>11.4</td>
</tr>
<tr>
<td>67.5</td>
<td>2.25</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>271</td>
<td>415</td>
<td>n.d.</td>
</tr>
<tr>
<td>67.8</td>
<td>2.30</td>
<td>0.84</td>
<td>3.14</td>
<td>0.73</td>
<td>520</td>
<td>407</td>
<td>28.0</td>
</tr>
<tr>
<td>67.9</td>
<td>3.55</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>403</td>
<td>423</td>
<td>n.d.</td>
</tr>
<tr>
<td>68.5</td>
<td>3.19</td>
<td>1.70</td>
<td>4.89</td>
<td>0.65</td>
<td>n.d.</td>
<td>n.d.</td>
<td>11.3</td>
</tr>
<tr>
<td>68.1</td>
<td>2.66</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>400</td>
<td>418</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

(Table continued overpage)
Table 1 (continued)

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>TOC (%)</th>
<th>sulphur (%)</th>
<th>TOC_{o,ob} (%)</th>
<th>TOC/TOC_{o,ob}</th>
<th>HI (mg HC/g TOC)</th>
<th>( T_{max} ) (°C)</th>
<th>( \text{CO}_2 ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>185.9</td>
<td>1.60</td>
<td>0.84</td>
<td>2.44</td>
<td>0.66</td>
<td>270</td>
<td>419</td>
<td>21.0</td>
</tr>
<tr>
<td>187.5</td>
<td>2.76</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>458</td>
<td>420</td>
<td>n.d.</td>
</tr>
<tr>
<td>190.5</td>
<td>1.62</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>254</td>
<td>422</td>
<td>n.d.</td>
</tr>
<tr>
<td>190.8</td>
<td>2.60</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>383</td>
<td>414</td>
<td>17.1</td>
</tr>
<tr>
<td>192.5</td>
<td>2.15</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>433</td>
<td>413</td>
<td>n.d.</td>
</tr>
<tr>
<td>196.3b</td>
<td>0.07</td>
<td>0.15</td>
<td>n.c.</td>
<td>n.c.</td>
<td></td>
<td></td>
<td>42.5</td>
</tr>
<tr>
<td>200.5</td>
<td>5.30</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>762</td>
<td>403</td>
<td>27.5</td>
</tr>
<tr>
<td>202.7</td>
<td>2.69</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>737</td>
<td>419</td>
<td>n.d.</td>
</tr>
<tr>
<td>203.0</td>
<td>4.60</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>781</td>
<td>400</td>
<td>28.7</td>
</tr>
<tr>
<td>205.6</td>
<td>3.71</td>
<td>1.94</td>
<td>5.65</td>
<td>0.66</td>
<td>n.d.</td>
<td></td>
<td>n.d.</td>
</tr>
<tr>
<td>207.5</td>
<td>4.60</td>
<td>1.67</td>
<td>6.27</td>
<td>0.73</td>
<td>820</td>
<td>402</td>
<td>30.5</td>
</tr>
<tr>
<td>211.9</td>
<td>3.73</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>570</td>
<td>404</td>
<td>n.d.</td>
</tr>
<tr>
<td>212.0</td>
<td>3.99</td>
<td>1.68</td>
<td>5.67</td>
<td>0.70</td>
<td>n.d.</td>
<td></td>
<td>n.d.</td>
</tr>
<tr>
<td>212.5</td>
<td>4.20</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>691</td>
<td>395</td>
<td>27.1</td>
</tr>
<tr>
<td>212.8</td>
<td>2.49</td>
<td>0.95</td>
<td>3.44</td>
<td>0.72</td>
<td>n.d.</td>
<td></td>
<td>35.0</td>
</tr>
<tr>
<td>213.2</td>
<td>7.00</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>794</td>
<td>402</td>
<td>38.5</td>
</tr>
<tr>
<td>213.8</td>
<td>10.34</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>788</td>
<td>415</td>
<td>n.d.</td>
</tr>
<tr>
<td>214.9</td>
<td>4.90</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>790</td>
<td>405</td>
<td>37.4</td>
</tr>
<tr>
<td>215.9</td>
<td>4.43</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>833</td>
<td>414</td>
<td>n.d.</td>
</tr>
<tr>
<td>216.6</td>
<td>8.65</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>604</td>
<td>414</td>
<td>n.d.</td>
</tr>
<tr>
<td>217.4</td>
<td>6.05</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>968</td>
<td>436</td>
<td>n.d.</td>
</tr>
<tr>
<td>218.0</td>
<td>4.02</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>653</td>
<td>414</td>
<td>n.d.</td>
</tr>
<tr>
<td>220.9</td>
<td>4.12</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>469</td>
<td>423</td>
<td>n.d.</td>
</tr>
<tr>
<td>223.8</td>
<td>2.72</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>420</td>
<td>420</td>
<td>n.d.</td>
</tr>
<tr>
<td>224.5</td>
<td>6.20</td>
<td>2.23</td>
<td>8.43</td>
<td>0.74</td>
<td>797</td>
<td>402</td>
<td>24.1</td>
</tr>
<tr>
<td>225.8</td>
<td>8.57</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>326</td>
<td>412</td>
<td>n.d.</td>
</tr>
<tr>
<td>227.4</td>
<td>5.59</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>740</td>
<td>410</td>
<td>n.d.</td>
</tr>
<tr>
<td>229.5</td>
<td>4.01</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>715</td>
<td>407</td>
<td>n.d.</td>
</tr>
<tr>
<td>230.5</td>
<td>5.76</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>672</td>
<td>413</td>
<td>n.d.</td>
</tr>
<tr>
<td>234.5</td>
<td>2.73</td>
<td>1.30</td>
<td>4.03</td>
<td>0.68</td>
<td>n.d.</td>
<td></td>
<td>29.2</td>
</tr>
<tr>
<td>234.7</td>
<td>8.60</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>676</td>
<td>411</td>
<td>n.d.</td>
</tr>
<tr>
<td>235.7</td>
<td>2.72</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>535</td>
<td>401</td>
<td>n.d.</td>
</tr>
<tr>
<td>236.0</td>
<td>5.10</td>
<td>2.45</td>
<td>7.55</td>
<td>0.68</td>
<td>694</td>
<td>391</td>
<td>22.9</td>
</tr>
<tr>
<td>238.0</td>
<td>2.20</td>
<td>0.94</td>
<td>3.14</td>
<td>0.70</td>
<td>491</td>
<td>393</td>
<td>n.d.</td>
</tr>
<tr>
<td>238.1</td>
<td>2.60</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>592</td>
<td>391</td>
<td>31.0</td>
</tr>
<tr>
<td>240.4</td>
<td>2.90</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>479</td>
<td>401</td>
<td>n.d.</td>
</tr>
<tr>
<td>240.6</td>
<td>2.50</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>550</td>
<td>398</td>
<td>36.0</td>
</tr>
<tr>
<td>241.0</td>
<td>6.80</td>
<td>2.08</td>
<td>8.88</td>
<td>0.77</td>
<td>750</td>
<td>393</td>
<td>25.2</td>
</tr>
<tr>
<td>241.4</td>
<td>6.49</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>608</td>
<td>400</td>
<td>n.d.</td>
</tr>
<tr>
<td>242.0</td>
<td>6.58</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>568</td>
<td>403</td>
<td>n.d.</td>
</tr>
<tr>
<td>250.0</td>
<td>2.97</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>464</td>
<td>414</td>
<td>n.d.</td>
</tr>
<tr>
<td>251.6</td>
<td>4.02</td>
<td>1.26</td>
<td>5.28</td>
<td>0.76</td>
<td>999</td>
<td>407</td>
<td>31.6</td>
</tr>
<tr>
<td>253.6</td>
<td>3.60</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>670</td>
<td>407</td>
<td>n.d.</td>
</tr>
<tr>
<td>255.3</td>
<td>1.40</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>401</td>
<td>388</td>
<td>n.d.</td>
</tr>
<tr>
<td>256.0</td>
<td>1.34</td>
<td>1.52</td>
<td>2.86</td>
<td>0.47</td>
<td>n.d.</td>
<td></td>
<td>26.7</td>
</tr>
<tr>
<td>258.8</td>
<td>2.30</td>
<td>1.03</td>
<td>3.33</td>
<td>0.69</td>
<td>547</td>
<td>393</td>
<td>29.7</td>
</tr>
<tr>
<td>264.0</td>
<td>1.60</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>587</td>
<td>404</td>
<td>n.d.</td>
</tr>
<tr>
<td>266.3</td>
<td>2.60</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>762</td>
<td>436</td>
<td>n.d.</td>
</tr>
<tr>
<td>268.0</td>
<td>1.20</td>
<td>n.d.</td>
<td>n.c.</td>
<td>n.c.</td>
<td>385</td>
<td>393</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

**Number of data**

BW-V 27 27 4 4 27
H 44 0 44 44 0
This work 36 19 36 36 36
Total 107 46 84 84 63

---

*a* n.d., not determined n.c. not calculated; \( \text{CO}_2 \), amount of \( \text{CO}_2 \) released upon acid treatment.

*b* Slump bed.

vitrinite particles, range between 0.27 to 0.39% and thus support the low maturity of the samples.

Pyrite is present in framboids and as replacements of shell fragments. The bright yellow fluorescing laminated alginite is remarkably free of pyrite. This observation makes probable that the bacterially-generated H₂S met very few reactive iron in these bright yellow laminae and the incorporation of sulphur into the organic matter was the main mechanism of sulphur incorporation in the laminae. It can be noted that in their study on the Kimmeridgian shales of Dorset, UK, Lallier-Vergès et al. (1993) found that the sites of organic sulphur enrichment are the elongated amorphous organic particles, bright yellow under UV excitation, that they termed “algal bodies”.

5. Discussion

5.1. Bottom water oxygen content

Terms used here to characterise the degree of oxygen depletion in bottom waters are from the paper of Tyson and Pearson (1991). On the basis of the common occurrence of lamination, the bulk of the formation is considered as deposited under at least suboxic conditions. On the other hand, the presence of remains of tubular algae and the occurrence of benthic foraminifera *Eoguttulina* make improbable a constantly sulphidic bottom water. The relatively thin intervals with clasts and slumping probably represent short periods of better oxygenation.

5.2. Degree of preservation of organic matter

The ratio of the TOC to the organic carbon content of the sediment just at the time of deposition (TOC/TOC₀) quantitatively expresses the degree of organic carbon preservation characterising the sediment [some of the abbreviations used here have been introduced by (Vető et al., 1995)] but does not take into account the degradation of OM that occurred in the water column. In most of the non-bioturbated marine sediments containing immature OM the greatest part of the early diagenetic loss of organic carbon is related to bacterial sulphate reduction [however, see the case of the Mn-rich Toarcian black shales, (Vető et al., 1997, Ebli et al., 1998)]. Hence the amount of organic carbon oxidised by sulphate reducing bacteria (TOCₛᵣₑᵣ) depends on the reduced sulphur (Sₑᵣᵣₑ) content and in non-bioturbated, moderately organic rich, clayey sediments it can be calculated as follows:

### Table 2
Iron speciation

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Fe&lt;sub&gt;HC1&lt;/sub&gt; (%)</th>
<th>Fe&lt;sub&gt;py&lt;/sub&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>82.4</td>
<td>0.44</td>
<td>0.17</td>
</tr>
<tr>
<td>85.3</td>
<td>0.66</td>
<td>0.52</td>
</tr>
<tr>
<td>95.2</td>
<td>0.60</td>
<td>0.77</td>
</tr>
<tr>
<td>105.2</td>
<td>0.73</td>
<td>0.66</td>
</tr>
<tr>
<td>113.5</td>
<td>0.76</td>
<td>1.10</td>
</tr>
<tr>
<td>139.2</td>
<td>0.36</td>
<td>0.53</td>
</tr>
<tr>
<td>144.3</td>
<td>0.39</td>
<td>0.65</td>
</tr>
<tr>
<td>148.6</td>
<td>n.d.</td>
<td>1.42</td>
</tr>
<tr>
<td>150.6</td>
<td>n.d.</td>
<td>1.63</td>
</tr>
<tr>
<td>151.5</td>
<td>0.40</td>
<td>1.40</td>
</tr>
<tr>
<td>156.6</td>
<td>n.d.</td>
<td>1.48</td>
</tr>
<tr>
<td>168.0</td>
<td>0.25</td>
<td>0.83</td>
</tr>
<tr>
<td>170.0</td>
<td>0.37</td>
<td>0.88</td>
</tr>
<tr>
<td>176.5</td>
<td>n.d.</td>
<td>0.82</td>
</tr>
<tr>
<td>178.8</td>
<td>0.72</td>
<td>0.80</td>
</tr>
<tr>
<td>180.5</td>
<td>n.d.</td>
<td>1.13</td>
</tr>
<tr>
<td>185.9</td>
<td>0.63</td>
<td>0.80</td>
</tr>
<tr>
<td>205.6</td>
<td>n.d.</td>
<td>1.07</td>
</tr>
<tr>
<td>207.5</td>
<td>0.17</td>
<td>0.79</td>
</tr>
<tr>
<td>212.0</td>
<td>n.d.</td>
<td>0.75</td>
</tr>
<tr>
<td>212.8</td>
<td>n.d.</td>
<td>0.38</td>
</tr>
<tr>
<td>224.5</td>
<td>0.31</td>
<td>0.79</td>
</tr>
<tr>
<td>234.5</td>
<td>n.d.</td>
<td>0.64</td>
</tr>
<tr>
<td>236.0</td>
<td>0.22</td>
<td>1.34</td>
</tr>
<tr>
<td>241.0</td>
<td>0.28</td>
<td>0.83</td>
</tr>
<tr>
<td>251.6</td>
<td>n.d.</td>
<td>0.51</td>
</tr>
</tbody>
</table>

* n.d., not determined; data from Brukner-Wein and Vető (1986) and this work.

### Table 3
Sulphur speciation, TOC/S<sub>org</sub> and sulphur partition ratios

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>S&lt;sub&gt;py&lt;/sub&gt; (%)</th>
<th>S&lt;sub&gt;SO₄&lt;/sub&gt; (%)</th>
<th>S&lt;sub&gt;org&lt;/sub&gt; (%)</th>
<th>TOC/S&lt;sub&gt;org&lt;/sub&gt;</th>
<th>S&lt;sub&gt;py&lt;/sub&gt;/S&lt;sub&gt;org&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>85.3</td>
<td>1.20</td>
<td>0.14</td>
<td>0.19</td>
<td>7.9</td>
<td>6.3</td>
</tr>
<tr>
<td>105.2</td>
<td>0.88</td>
<td>0.14</td>
<td>−0.15</td>
<td>n.c.</td>
<td>n.c.</td>
</tr>
<tr>
<td>113.5</td>
<td>0.76</td>
<td>0.15</td>
<td>−0.06</td>
<td>n.c.</td>
<td>n.c.</td>
</tr>
<tr>
<td>139.2</td>
<td>0.61</td>
<td>0.17</td>
<td>−0.07</td>
<td>n.c.</td>
<td>n.c.</td>
</tr>
<tr>
<td>148.6</td>
<td>1.63</td>
<td>0.17</td>
<td>1.71</td>
<td>8.3</td>
<td>1.0</td>
</tr>
<tr>
<td>150.6</td>
<td>1.87</td>
<td>0.15</td>
<td>0.26</td>
<td>23.0</td>
<td>7.2</td>
</tr>
<tr>
<td>151.5</td>
<td>1.61</td>
<td>0.23</td>
<td>0.33</td>
<td>22.1</td>
<td>4.9</td>
</tr>
<tr>
<td>156.6</td>
<td>1.70</td>
<td>0.23</td>
<td>0.15</td>
<td>26.9</td>
<td>11.3</td>
</tr>
<tr>
<td>168.0</td>
<td>0.95</td>
<td>0.22</td>
<td>1.69</td>
<td>8.6</td>
<td>0.6</td>
</tr>
<tr>
<td>170.0</td>
<td>1.01</td>
<td>0.22</td>
<td>0.40</td>
<td>15.3</td>
<td>2.5</td>
</tr>
<tr>
<td>176.5</td>
<td>0.94</td>
<td>0.43</td>
<td>0.20</td>
<td>11.1</td>
<td>4.7</td>
</tr>
<tr>
<td>180.5</td>
<td>1.30</td>
<td>0.16</td>
<td>0.24</td>
<td>13.3</td>
<td>5.4</td>
</tr>
<tr>
<td>205.6</td>
<td>1.23</td>
<td>0.34</td>
<td>0.37</td>
<td>10.0</td>
<td>3.3</td>
</tr>
<tr>
<td>207.5</td>
<td>0.91</td>
<td>0.16</td>
<td>0.60</td>
<td>7.7</td>
<td>1.5</td>
</tr>
<tr>
<td>212.0</td>
<td>0.86</td>
<td>0.27</td>
<td>0.55</td>
<td>7.3</td>
<td>1.6</td>
</tr>
<tr>
<td>212.8</td>
<td>0.44</td>
<td>0.08</td>
<td>0.43</td>
<td>5.8</td>
<td>1.0</td>
</tr>
<tr>
<td>224.5</td>
<td>0.91</td>
<td>0.37</td>
<td>0.95</td>
<td>6.5</td>
<td>1.0</td>
</tr>
<tr>
<td>234.5</td>
<td>0.73</td>
<td>0.16</td>
<td>0.41</td>
<td>6.7</td>
<td>1.8</td>
</tr>
<tr>
<td>236.0</td>
<td>1.54</td>
<td>0.26</td>
<td>0.65</td>
<td>7.9</td>
<td>2.4</td>
</tr>
<tr>
<td>241.0</td>
<td>0.95</td>
<td>0.34</td>
<td>0.79</td>
<td>8.6</td>
<td>1.2</td>
</tr>
<tr>
<td>251.6</td>
<td>0.58</td>
<td>0.17</td>
<td>0.51</td>
<td>7.9</td>
<td>1.1</td>
</tr>
</tbody>
</table>

* n.c., not calculated; data from Brukner-Wein and Vető (1986) and this work.
where the constants take into consideration (i) the atomic weights of carbon and sulphur and the stoichiometry of bacterial sulphate reduction and (ii) the assumption that about 25% of the H2S generated by this reaction escapes the sediment (Vető et al., 1995), respectively. On the basis of Eq. (1)

\[ \text{TOC}_{sr} = S_{\text{red}} \times 0.75 \times 1.33 = S_{\text{red}} \]  

(1)

\[ \text{TOC}_{or} = \text{TOC} + S_{\text{red}} \]  

(2)

and

\[ \frac{\text{TOC}_{or}}{\text{TOC}} = \frac{\text{TOC}}{(\text{TOC} + S_{\text{red}})} \]  

(3)

Here it is worth to noting that the above ratio is close to the reciprocal of the sulfate reduction index (SRI), expressing the ratio of the original organic carbon and the residual organic carbon contents and defined by Lallier-Vergès et al. (1993) as follows:

\[ \text{SRI} = \frac{\text{TOC}}{(\text{TOC} + S/1.33)/\text{TOC}} \]

One cannot exclude that only a part of the measured SSO4 was originally in sulphatic form in the sediment, probably in the carbonate crystall lattice (see Strauss, 1997). Pyrite-bound sulphur, oxidised to a minor extent during the long storage of the samples (the well Rezi 1 has been drilled in 1982) may also have contributed to the measured SSO4. In view of the minor amounts of SSO4 and the virtual absence of elemental sulphur (all but one of the 27 samples studied by Brukner-Wein and Vető (1986) did not contain elemental sulphur), the total S content is considered to roughly correspond to the Sred content. Thus the TOC and S data listed in Table 1 allowed us to calculate TOC_{or} and TOC / TOC_{or} values for a large number of samples (Fig. 6 and Table 1). The depth variation of the TOC_{or} is very similar to that of the TOC (Fig 3). Except for a low value at the bottom

Fig. 4. Plots of TOC/S_{org} ratio and Tmax vs depth. The vertical dashed line corresponds to the limit of Type II and Type IIS organic matter, proposed by Orr (1986).

Fig. 5. Photomicrograph of a Kössen Fm. sample, well Rezi 1, 168.00 m. Blue light excitation with oil immersion; a, laminated alginite; c, Calcsphaera; m, mineral matter; p, pyrite.
of the section, the TOC / TOCor ratio is above 0.60 and follows an upward mildly decreasing trend in the lower interval, then it shows a high scatter in the middle interval, especially between 100 and 70 m. It is worthy to note that one of the two surprisingly high values found here corresponds to the carbonate-rich sample taken from 82.7 m. The few values in the upper interval are relatively low (0.36 to 0.42).

5.3. Factors affecting the degree of organic matter preservation

In organic-rich, non-bioturbated marine sediments the aerobic loss of $C_{\text{org}}$ is insignificant and the amount of sulphate, originally present in the pore-water is sufficient for the oxidation of only a minor portion of the reactive OM (Zaback and Pratt, 1992; Zaback et al., 1993). In such facies the bulk of the sulphate needed for OM oxidation is supplied by downward diffusion from bottom water. The driving force of the diffusion is the sulphate concentration gradient, which increases when the rate of sedimentation decreases, all other conditions being the same. It is easy to understand that the rates of OM deposition and of sedimentation exert a strong control on OM oxidation/sulphate reduction processes. While the first determines the need for sulphate supply the second limits its rate, in other words the magnitude of the diffusive sulphate flux. When both the rates of OM deposition and of sedimentation are sufficiently low the downward diffusion can import enough sulphate for the oxidation of the bulk of the OM, resulting in a low degree of OM preservation. On the contrary, when both rates of deposition of reactive OM and of sedimentation are sufficiently high, the diffusive flux supplies sulphate for the oxidation of only a relatively small part of the sedimentary OM, resulting in a high degree of OM preservation (e.g. Pedersen and Calvert, 1990).

A part of the H$_2$S produced by sulphate-reducers is retained in the sediment by reaction with reactive iron and by incorporation into OM. When sulphur incorporation into OM reaches a certain limit it makes the later refractory towards a further oxidation by sulphate reducing-bacteria and results in a better preservation. This process is termed natural sulphurization (Adam et al., 1993; Tribovillard et al., 1994). Preservation of both lipids (e.g. Sinninghe Damste and de Leeuw, 1990; Boussafir et al., 1995) and carbohydrates (e.g. Kaam-Peters et al., 1997) are reported to be enhanced by this way. However there are some doubts about the possibility for assessing the quantitative importance of this process to the overall preservation of OM (Brüchert, 1998). Beside natural sulphurization, the selective preservation of cell wall material, (Largeau et al., 1984; Tegelaar et al., 1989) and adsorption onto mineral surfaces (Keil et al., 1994) are considered as mechanisms enhancing OM preservation.

In the following we will discuss the variations of the rates of sedimentation of the whole sediment, the non-carbonate mineral matter and the OM and their influences on OM preservation during accumulation of the Kössen Fm.

The upward decrease of the carbonate content (Fig. 2) can reflect two fundamentally different scenarios: either the rate of sedimentation of non-carbonate mineral matter ($SR_{\text{noncarb}}$) increased and that of the carbonate ($SR_{\text{carb}}$) remained constant, hence the sedimentation accelerated with time, or the $SR_{\text{noncarb}}$ remained constant while the deposition of the carbonate slowed down, in other words the sedimentation rate decreased with time. Obviously, transitions between these two “pure” scenarios can be considered. The increase in the sedimentation rate with time should have lead to a decrease of sulphate concentration gradient which in turn would have resulted in a lowering of the diffusive sulphate supply and an upward increase of TOC/TOCor. Since TOC/TOCor displays a decreasing upward trend we have to conclude that the sedimentation rate (and the $SR_{\text{carb}}$) decreased with time. The decrease with time of the platform derived carbonate input (see Geological setting) also supports the general slowing down of the sedimentation during the black shale event. Thus the conditions were closer to the second scenario (e.g. slowing down of carbonate deposition and constancy of $SR_{\text{noncarb}}$).

In the following the $SR_{\text{noncarb}}$ will be considered as constant what is obviously a simplification. The ratio of the whole sediment matter to the amount of the non-carbonate mineral matter (NC), which corresponds to the ratio of the sedimentation rate to $SR_{\text{noncarb}}$, has been calculated for the samples free of slumping and analysed for TOC and CO$_2$ and S contents, as follows:

$$\text{Whole sediment/NC} = \frac{100}{(100 - (\text{CO}_2 \times 2.27) - (\text{TOC}_{\text{or}} \times 1.40))}$$  (4)
where CO₂ and TOC_{or} are expressed in percents. The denominator is considered to be the amount of the non-carbonate mineral matter, expressed in percentage. In view of the strong predominance of calcite among the carbonate minerals CO₂ is considered to be exclusively bond to CaCO₃. The factor used to convert organic carbon to OM in immature Type II-S samples (1.40) was calculated on the basis of the elemental composition of the immature sulphur-rich kerogen isolated from an Upper Cretaceous oil shale of Jordania (Sinninghe Damsté et al., 1998). This value is close to the conversion factor of immature Type II kerogen (1.34) given by Tissot and Welte (1984). It is worthy to note that the same 1.34 value has been calculated from the elemental composition of 10 sulphur-rich, early mature Monterey kerogen samples, reported by Orr (1986). In the above calculations the effects of diagenesis (e.g. S content, contribution of CO₂ derived from OM oxidation to the carbonates) have not been taken into account. The ratio of the original amount of OM (OM_{or}) to that of the NC which corresponds to the ratio of the rate of sedimentation of OM (SR_{OM}) to SR_{noncarb} was estimated in a similar way:

\[
\frac{OM_{or}}{NC} = \frac{(TOC_{or} \times 1.40)/(100 - (CO₂ \times 2.27)) - (TOC_{or} \times 1.40)}{}
\]

(5)

Fig. 7 shows the variations of the whole sediment / non-carbonate mineral matter and original OM/non-carbonate mineral matter ratios which are proportional to those of the sedimentation rate and SR_{OM}, respectively. Since the assumption of the constancy of SR_{noncarb} is obviously a simplification the patterns on Fig. 7 display only the qualitative variations of the rate of sedimentation and SR_{OM}. With all of these caveats in mind, Fig. 7 shows the decrease of sedimentation rate and of SR_{OM} with time and a temporary rebound of the latter at around the middle of the black shale event, corresponding roughly to the 170–145 m depth interval. The simultaneous decreases of sedimentation rate and SR_{OM} with time mean an increase of sulphate concentration gradient and a decrease in need of sulphate supply (see above) thus they should have result in a lower degree of OM preservation. The general upward decrease of the TOC/TOC_{or} ratio supports this assumption. It is worthy to note that (i) the temporary acceleration of OM deposition in the middle of the black shale event is well reflected by the corresponding high TOC/TOC_{or} ratios (Fig. 6) and (ii) the temporary acceleration of the sedimentation, indicated by the high value of 100/NC ratio at 82.7 m corresponds to a high TOC/TOC_{or} ratio and a high carbonate content (Table 1).

Up to now we did not take into consideration the conditions of natural sulphurization in the Kössen Fm. The partition of sulphur between pyrite and OM is thought to primarily depend on the ratio of reactive iron to OM, present at the beginning of bacterial sulphate reduction (Neruchev et al., 1974; Powell et al., 1975). Fig. 8 displays the variation of the sulphur partition ratio (S_{py}/S_{org}) in function of the (Fe_{py} + Fe_{HCl})/TOC_{or} ratio for seven samples of the section studied. All these samples are relatively rich in OM (TOC ranges between 4.60 and 14.60%). S_{org} and Fe_{HCl} values of the other samples are lacking or non-reliable, hence these samples are not displayed on Fig. 8. Seven samples of the Kössen Fm. from well Z1 drilled in the area (Brukner-Wein and Vető, 1986), have been also plotted on Fig. 8. The
Spy/Sorg ratio quite regularly increases with increasing 
\((\text{Fe}_{\text{py}} + \text{Fe}_{\text{HCl}})/\text{TOCor}\) ratio until it reaches a value of
about 2.5. The location of the two samples characterised
by higher Spy/Sorg ratios is somewhat dubious; the ana-
lytical errors and uncertainties of the sulphur and iron
speciation studies, leading to an underestimation of the
amount of Sorg (see the negative values in Table 3) can
result in irrealistically high Spy/Sorg ratios. On the basis
of the correlation observed between \((\text{Fe}_{\text{py}} + \text{Fe}_{\text{HCl}})/\text{TOCor}\)
and Spy/Sorg ratios, it seems likely that in the
relatively organic-rich parts of the Kössen Fm., in good
agreement with the literature, sulphur partition between
pyrite and OM was strongly influenced by the reactive
iron to OM ratio.

Fig. 9 displays the variation TOC/TOCor versus of
TOC/Sorg ratio. All but one of the samples containing
Type II-S kerogen are characterised by TOC/TOCor
ratio over 0.65 but six out of the seven samples with
Type II kerogen also show similarly good organic pre-
servation. The lack of a negative correlation between
TOC/TOCor and TOC/Sorg ratios does not permit to
assume that in the Kössen Fm. the improvement of OM
preservation would have been the result of the intensifi-
cation of natural sulphurization.

5.4. Assessment of planktonic productivity

The assessment of the magnitude of OM production
will be done in two steps. First the rate of organic car-
don deposition \((C_{\text{dep}})\) will be estimated then, taking into
account the degradation experienced by the organic
particles during their fall through the water column, an
estimation of OM production will be attempted.

The rate of organic carbon deposition \((C_{\text{dep}})\) can be
assessed as follows:

\[
C_{\text{dep}} = \text{TOC}_{\text{cor}} \times \text{sedimentation rate} \times \rho
\]

where \(\rho\) is the density of the dry sediment.

Since TOC_{\text{cor}} varies considerably along the section,
average TOC_{\text{cor}} values were calculated for the lower (L)
and upper (U) intervals and for three parts of the middle
interval \((M_1, M_2, M_3)\) (Table 4) which are characterised
by distinctly different TOC_{\text{cor}} values (see Fig. 6). Due to
steep dipping the stratigraphic thickness of the section
between 270 and 40 m is about 161 m. The correspond-
ing thicknesses of the L, M1, M2, M3 and U intervals are
listed in Table 4.

The simplifying assumption of the constancy of
\(\text{SR}_{\text{noncarb}}\) permits to calculate the average rates of sedi-
mentation for the depth intervals. In the first step the
following equation has to be resolved for \(\text{SR}_{\text{noncarb}}\)

\[
T = (Z_L \times \text{NC}_L + Z_{M1} \times \text{NC}_{M1} + Z_{M2} \times \text{NC}_{M2} + Z_{M3} \times \text{NC}_{M3} + Z_U \times \text{NC}_U)/(\text{SR}_{\text{noncarb}} \times 100)
\]

where \(T\) is the time elapsed during the build-up of the sec-
tion studied and \(Z_L, Z_{M1}, Z_{M2}, Z_{M3}, Z_U\) and \(\text{NC}_L, \text{NC}_{M1}, \text{NC}_{M2}, \text{NC}_{M3}, \text{NC}_U\) are the stratigraphic thicknesses and
average non-carbonate mineral matter contents of the L,
\(M_1, M_2, M_3\) and U intervals, respectively. Replacing \(T\)
with 1.5 Ma (see Geological setting) and stratigraphic
thicknesses and average non-carbonate mineral matter
contents with the corresponding \(Z\) and NC values
(Table 4), 53 m/Ma has been obtained for \(\text{SR}_{\text{noncarb}}\).

Since \(\rho\) data are not available for the section studied,
a 2.16 t/m³ value, extrapolated from the data reported
by Dudko and Ódor (1980) for the Mesozoic shales of
the Transdanubian Range Unit, is used as average \(\rho\).
Replacing \(\rho\) with 2.16 t/m³ and average sedimentation
rate and average TOC_{\text{cor}} with the values listed in Table 4,
\(C_{\text{dep}}\) values have been calculated from Eq. (6) for the L,
\(M_1, M_2, M_3\) and U intervals (Table 4). The higher is the
amount of OM the lower should the density of the
sediment hence the \(C_{\text{dep}}\) values calculated for the \(M_1\)
and \(M_3\) and even more the L and the M2 intervals are
probably somewhat overestimated. Nevertheless during
deposition of the organic-rich L and M2 intervals \(C_{\text{dep}}\)
was markedly higher than during that of the other
intervals of the section.

Remains of tubular algae obviously represent OM
newly produced on sediment surface but their contribu-
tion to the OM, less than 10% in the case of the lower
interval and sporadic in the case of the middle interval,
can be neglected during assessment of \(C_{\text{prod}}\). The high
amount of lamalginite reflects either the transformation
of an important portion of the deposited algal OM by
benthic heterotrophic bacteria or a considerable pro-
duction of new OM on the bottom. In the first case the
organic productivity equals the planktonic productivity
\((C_{\text{prod}})\). Therefore, the formula developed by Suess
Table 4
Rates of deposition of organic carbon and planktonic productivity for five intervals of the Kössen Formation section of well Rezi 1 and data used for calculations

<table>
<thead>
<tr>
<th>Interval</th>
<th>Depth range (m–m)</th>
<th>Real thickness (m)</th>
<th>Rate of sedimentation (m/Ma)</th>
<th>Average Nc (%)</th>
<th>Average TOC/TOCor (%)</th>
<th>C&lt;sub&gt;dep&lt;/sub&gt; (/ Corg/m²/Ma)</th>
<th>C&lt;sub&gt;prod&lt;/sub&gt; (/ Corg/m²/Ma)</th>
<th>Average TOC/TOCor</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>70–40</td>
<td>21.0</td>
<td>58</td>
<td>91</td>
<td>1.91</td>
<td>2.4</td>
<td>6–9</td>
<td>0.39</td>
</tr>
<tr>
<td>M&lt;sub&gt;3&lt;/sub&gt;</td>
<td>145–70</td>
<td>52.5</td>
<td>116</td>
<td>53</td>
<td>2.89</td>
<td>7.2</td>
<td>19–27</td>
<td>0.70</td>
</tr>
<tr>
<td>M&lt;sub&gt;2&lt;/sub&gt;</td>
<td>170–145</td>
<td>17.5</td>
<td>109</td>
<td>52</td>
<td>9.29</td>
<td>21.9</td>
<td>57–83</td>
<td>0.74</td>
</tr>
<tr>
<td>M&lt;sub&gt;1&lt;/sub&gt;</td>
<td>190–170</td>
<td>14.0</td>
<td>107</td>
<td>54</td>
<td>3.56</td>
<td>8.2</td>
<td>21–31</td>
<td>0.66</td>
</tr>
<tr>
<td>L</td>
<td>270–190</td>
<td>56.0</td>
<td>193</td>
<td>29</td>
<td>5.58</td>
<td>23.3</td>
<td>60–88</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Replacing C<sub>flux</sub> with the C<sub>dep</sub> values for the L, M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub> and U intervals and z with 100 m and 150 m, the corresponding ranges of average C<sub>prod</sub> have been obtained (Table 4). The effect of the sea-level rise, taking place during deposition of the section studied has not been considered in the above calculations. The upper limits of C<sub>prod</sub> values calculated for the L and M<sub>2</sub> intervals are close to the lowest ones characterising the present-day upwelling systems. The M<sub>1</sub> and M<sub>3</sub> intervals and the U interval were deposited under medium and low productivity conditions, respectively. Due to the uncertainties of the calculation and the problems arising from the use of the Suess formula, developed for present-day oceans for an ancient sea, these results are only semi-quantitative. If lamalginite represents remains of autotrophic bacteria then C<sub>prod</sub> ranges, characterizing the M<sub>1</sub>, M<sub>2</sub> and M<sub>3</sub> intervals, where lamalginite is abundant are somewhat overestimated but the trends in productivity changes remain similar.

Table 4 shows that the L and M<sub>2</sub> intervals, deposited under relatively high productivity conditions are characterized by the highest average TOC/TOCor values. Thus in the non-bioturbated sediments deposited from the suboxic (and anoxic?), medium to low productivity Kössen basin the increase of the planktonic (and benthic?) organic production led to an improvement of OM preservation. It is worthy to note that samples of the medium productivity M<sub>3</sub> interval, having TOC/TOCor values above 0.80 and analysed for CO<sub>2</sub> content, correspond to carbonate-rich samples (Table 1). In these cases the fast deposition of carbonates and the resulting high rate of sedimentation and not the high C<sub>prod</sub> were the main factors for the improvement of preservation.

Recently, studying the relationship between productivity and organic preservation in two short-term (about 30 Ka) depositional cycles of the Kimmeridge series from the Cleveland Basin, UK, Lallier-Vergès et al. (1997) have found that with increasing productivity SRI (close to the reciprocal of the TOC/TOCor ratio) first decreased from 1.2–1.4 to 1.1–1.2 then increased again to 1.2–1.4. We can speculate that productivity that prevailed during deposition of the L and M<sub>2</sub> intervals of the Kössen Fm. section was similar to that characterizing the Kimmeridge black shale samples of Lallier-Vergès et al. (1997), showing the lowest SRI values (1.1–1.2), in other words characterized by the highest preservation.

6. Conclusions

The studied section of the Kössen Fm. was deposited beneath at least suboxic waters. The bulk of the immature OM is of marine, planktonic origin. According to organic petrographic observations benthic algae significantly contributed to the OM content in the lower interval of the section.

T<sub>max</sub> values show a substantial downward decrease. This phenomenon, not related to maturity changes, is probably caused by the downward increasing sulphur richness of the OM.

Based on TOC and reduced sulphur contents, it appears that 36 to 89% of the organic carbon present in the sediments at the time of their deposition has been preserved. The variations of the degree of OM preservation were primarily determined by those of the rates of sedimentation and of OM deposition; their simultaneous slowing down with time resulted in a strengthening of the degradation of the OM. There is no positive correlation between sulphur richness of the OM and its degree of preservation; thus in the case of the Kössen Fm. one cannot assume that the intensification of the natural sulphurization led to an improvement of OM preservation. The partition of the reduced sulphur between pyrite and OM was primarily determined by the reactive iron to OM ratio.

The studied part of the Kössen Fm. was deposited under low- to medium productivity waters; the estimated range of C<sub>prod</sub> varies between 6–9 and 60–88 t organic carbon/m²/Ma. Due to the uncertainties of the
calculation the absolute values have to be considered with some caution. Variations of planktonic productivity exerted a strong control on preservation of sedimentary OM; intervals characterized by the highest preservation roughly correspond to times for which the highest productivities have been assessed.

Acknowledgements

The authors wish to thank the Hungarian Scientific Foundation (OTKA grants No. T 22223 and T 15999) for funding this work. The manuscript benefitted from helpful comments and criticism of Elisabeth Lallier-Vergès and François Baudin. The thorough corrections of Matthew McCarthy greatly improved the English.

References


