New geochemical data on fossil wood from the Albian of the Dolomites (Southern Alps, Italy)

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Abstract: Information is provided about organic-matter bearing sediments and fossil drift-wood from the Puez area (Col de Puez, Southern Alps) near Wolkenstein (S. Tyrol, Italy). The locality is located on the Trento Plateau which represents a submarine high during the Lower Cretaceous. Its terpenoid hydrocarbon composition indicates that the wood fragment derived from a conifer belonging to the family Podocarpaceae or Araucariaceae. Intense degradation of OM argues for lengthier drifting. Long-term drifting is also indicated by the infestation of the bivalve Teredo (“ship-worm”). The finding of a fossil tree trunk sheds some light on the early Lower Cretaceous tectonic history of the Trento Plateau and the Dolomites.

Key words: Drift-wood, Albian, Early Cretaceous, Dolomites, Italy.

Introduction

The geology of the Dolomites and adjacent areas has recently been summarized in detail by Lukeneder & Aspmair (2006), and Lukeneder (2008, 2010, 2011). According to recent investigations by Muttoni et al. (2005), the Lombardian Basin — and thus the adjacent Trento Plateau to the east — were located at approximately 35°N to 25°N in the Early Jurassic, at 10°N in the Middle-Late Jurassic (lowest latitude in the Kimmeridgian), at approximately 20°N in the Valanginian-Hauterivian time and back to almost 30°N in the Early Cretaceous (Aptian).

The complex Mediterranean paleogeography of Jurassic and Cretaceous domains (Fourcade et al. 1993) is characterized by microplates within the Tethyan oceanic corridor between the African and European landmasses (Dercourt et al. 1993; Cecca 1998; Zharkov et al. 1998; Stampfli & Mosar 1999; Scotese 2001; Stampfli et al. 2002). The region of the Southern Alps, including the investigated area (i.e. Puez area), was situated on the northern border to the Penninic Ocean (=Alpine Tethys) during the Jurassic and Early Cretaceous. This area represents a passive continental margin of the Apulian Plate (Jud 1994) of the South Alpine-Apennine chain that emerged during the deformation of the passive continental margin of the Adriatic (Jud 1994; Bosellini et al. 2003; Castellarin et al. 2006). For a more detailed geology of the Puez area see Lukeneder (2010, 2011, 2012; Fig. 1).

Geographical and geological setting

Geography

The outcrop is situated on the Puez-Odle-Gardenaccia Plateau in the Dolomites, 30 km northeast of Bozen, 6 km northeast of Wolkenstein (Selva in Val. Gardena, =Sölva), in the Department Trentino-Alto Adige (maps Trentino — Alto Adige; South Tyrol, Italy; Tappeiner 2003). The locality is situated in the heart of the natural park Puez-Odle within the UNESCO world heritage area of the Dolomites (Lukeneder 2010, 2011, 2012; Fig. 1).

Geological setting

The Puez area is situated on the northernmost part of the Trento Plateau within the Dolomites, formed on a Cretaceous submarine plateau, the Puez-Gardenaccia Plateau. The Dolomites (Permian to Cretaceous) are an internal part of the Southern Alps, representing a Northern Italian mountain chain that emerged during the deformation of the passive continental margin of the Adriatic (Jud 1994; Bosellini et al. 2003; Castellarin et al. 2006). For a more detailed geology of the Puez area see Lukeneder (2010, 2011, 2012).

The Albian Puez-Marl Member (approximately 60 m, Early Albian—Early Cenomanian) encompasses the marl-rich upper part of the Puez Formation (for a discussion see Lukeneder & Aspmair 2006; Lukeneder 2008, 2010, 2012). The analysed tree trunk derives from the mid part of this member, section Puz/P2 (bed P2/160; Figs. 1–2).

Biostratigraphical data (Lukeneder 2010; pers. comm. I. Soták) indicate Hedbergella ssp. and Rotalipora ssp. (up to the Thalmanninella globotruncanoides Biozone) along with calcareous nanofossils such as Eiffellithus ssp. (up to latest Albian CC9 Zone) and hint at an Early Albian to Late Albian
age (perhaps up to the Albian/Cenomanian boundary) for the Puez-Marl Member. The drift wood bed P2/160 shows Mid Albian age.

Material and methods

Drifted wood is not known from the Lower Cretaceous of the Southern Alpine region so far. The tree trunk (approximately 15×20 cm) derives from the mid part of the section Puez/P2 (log P2/160; Figs. 1–2). The specimen is covered by a yellowish layer consisting of limonite (Fig. 2). The still attached surrounding sediment comprised radiolarians and foraminifera. The trunk is well preserved and each wood fibre and cell is visible in detail. The specimen shows a trunk with the branching of a limb.

Beds were sampled for biostratigraphical (macro- and microfossils), and geochemical (CaCO₃) data. Calcium carbonate contents (CaCO₃; wt. % bulk rock, total carbonate) were determined using the carbonate bomb technique. All the chemical analyses were carried out in the laboratories of the Department of Applied Geosciences and Geophysics, Montanuniversität Leoben. Samples are stored at the Natural History Museum of Vienna (NHMW), in the collection of the Department of Geology and Palaeontology with inventory number from NHMW 2010/0095/0001. Microfossil analysis includes preliminary studies of foraminifera by Ján Soták.

Organic geochemistry

For organic geochemical analyses, representative portions of selected samples were extracted for approximately 1 h using dichloromethane in a Dionex ASE 200 accelerated solvent extractor at 75 °C and 50 bar. After evaporation of the solvent to 0.5 ml total solution in a Zymark TurboVap 500 closed cell concentrator, asphaltenes were precipitated from a hexane-dichloromethane solution (80:1) and separated by centrifugation. The fractions of the hexane-soluble organic matter were separated into NSO compounds, saturated hydrocarbons, and aromatic hydrocarbons by medium-pressure liquid chromatography using a Köhnen-Willsch MPLC instrument (Radke et al. 1980).

The saturated and aromatic hydrocarbon fractions were analysed on a gas chromatograph equipped with a 30-m DB-1
Results and discussion

Molecular composition of hydrocarbons

n-Alkanes, isoprenoids

The n-alkane patterns of most samples are dominated by short-chain n-alkanes (>n-C_{15-19}). The short-chain n-alkanes (<C_{20}), which are predominantly found in algae and microorganisms (Cranwell 1977), are detected in high relative amounts (>30 % of the total n-alkane concentrations) in the sediment samples (Table 2; Fig. 5). The predominance of n-alkanes with even carbon numbers (e.g. n-C_{14}, n-C_{16}, n-C_{18}) indicates reducing conditions during early diagenesis of the sediments (Welte & Waples 1973). In contrast, long-chain n-alkanes (>n-C_{23}) are characterized by a slight odd over even predominance, as indicated by values of the Carbon Preference Index (CPI) between 1.2 and 1.4 (Table 2; Fig. 3). The CPI was calculated from the concentrations of individual n-alkanes using the formula of Bray & Evans (1961). Long-chain (C_{27}-C_{33}) n-alkanes are interpreted to be derived from vascular plants, where they occur as the main components of plant waxes (Eglinton & Hamilton 1967). Clearly, land plant organic matter had experienced aerobic degradation before its deposition in the sedimentary environment.

The fossil wood sample is characterized by the complete absence of short-chain n-alkanes and no odd over even predominance in the long-chain homologues (Table 2; Fig. 3). The CPI close to 1.0 and the presence of a hump in the high-molecular range argues for intense biodegradation of the fossil wood.

According to Didyk et al. (1978), pristane/phytane ratios between 1.0 and 3.0 indicate dysaerobic conditions during early diagenesis. This is in contrast to the reducing environment indicated by the even carbon number predominance of short-chain n-alkanes. However, pristane/phytane ratios are also known to be affected by maturation (Tissot & Welte 1984) and by differences in the precursors for acyclic isoprenoids (i.e. bacterial origin; Volkman & Maxwell 1986; ten Haven et al. 1987). In the present case, the influence of different ranks on pristane/phytane ratios can be ruled out.

Table 1: Bulk organic geochemical data of sediment samples and fossil wood.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TOC (wt. %)</th>
<th>EOM (mg/g TOC)</th>
<th>Saturated HC (wt. %, EOM)</th>
<th>Aromatic HC (wt. %, EOM)</th>
<th>NSO (wt. %, EOM)</th>
<th>Asphaltenes (wt. %, EOM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1/18</td>
<td>0.20</td>
<td>21.8</td>
<td>20</td>
<td>11</td>
<td>36</td>
<td>13</td>
</tr>
<tr>
<td>P1/1a</td>
<td>0.25</td>
<td>23.1</td>
<td>21</td>
<td>2</td>
<td>63</td>
<td>14</td>
</tr>
<tr>
<td>P1/98</td>
<td>0.20</td>
<td>31.6</td>
<td>16</td>
<td>6</td>
<td>64</td>
<td>14</td>
</tr>
<tr>
<td>P2/35</td>
<td>0.39</td>
<td>10.7</td>
<td>13</td>
<td>4</td>
<td>66</td>
<td>17</td>
</tr>
<tr>
<td>P2/96</td>
<td>0.48</td>
<td>14.0</td>
<td>16</td>
<td>4</td>
<td>71</td>
<td>9</td>
</tr>
<tr>
<td>P2/104</td>
<td>0.31</td>
<td>19.8</td>
<td>10</td>
<td>2</td>
<td>67</td>
<td>21</td>
</tr>
<tr>
<td>P2/138</td>
<td>0.49</td>
<td>11.2</td>
<td>15</td>
<td>5</td>
<td>76</td>
<td>4</td>
</tr>
<tr>
<td>P2/208</td>
<td>0.38</td>
<td>19.5</td>
<td>15</td>
<td>3</td>
<td>78</td>
<td>5</td>
</tr>
<tr>
<td>P2/247</td>
<td>0.74</td>
<td>6.1</td>
<td>12</td>
<td>2</td>
<td>81</td>
<td>5</td>
</tr>
<tr>
<td>P2/268a</td>
<td>0.69</td>
<td>8.4</td>
<td>15</td>
<td>3</td>
<td>77</td>
<td>5</td>
</tr>
<tr>
<td>P3/1a</td>
<td>0.25</td>
<td>17.2</td>
<td>18</td>
<td>2</td>
<td>73</td>
<td>7</td>
</tr>
<tr>
<td>P3/19</td>
<td>0.22</td>
<td>33.8</td>
<td>13</td>
<td>5</td>
<td>77</td>
<td>6</td>
</tr>
<tr>
<td>P2/160 FW</td>
<td>14.25</td>
<td>65.7</td>
<td>51</td>
<td>2</td>
<td>28</td>
<td>19</td>
</tr>
</tbody>
</table>

TOC = Total organic carbon, EOM = Extractable organic matter, HC = Hydrocarbons, NSO = NSO compounds.
In contrast, a proportion of pristane may be derived from tocopherols (Goossens et al. 1984), or may simply reflect the contribution of land plants to organic matter accumulation (Tissot & Welte 1984). No acyclic isoprenoids of low-molecular weight are present in the saturated hydrocarbon fraction of the fossil wood sample, most probably due to intense biodegradation.

**Steroids**

In all sediment samples, the 5α C27 and C29 steranes, dominating over the corresponding 5β steranes, are present in concentrations sufficient for peak integration (Table 2; Fig. 3). The C28 pseudohomologues occur in lower relative concentrations. The presence of 5β steranes is in agreement with the immature character of the samples.

Algae are the predominant primary producers of C27 sterols, while C29 sterols are more typically associated with land plants (Volkman 1986). Nonetheless, numerous results from recent biomarker studies add to the growing list of microalgae that contain high proportions of 24-ethylcholesterol (Volkman et al. 1999). The occurrence of C27 and C29 steranes in the sediments is consistent with a mixed origin of organic matter from phytoplankton and land plants. In the EOM from the fossil wood, no steranes were detected.

**Hopanoids**

Hopanes are constituents of the non-aromatic cyclic triterpenoids in most

### Table 2: Concentration and concentration ratios of compounds and compound groups identified in the hydrocarbon fractions of the Puez samples.

<table>
<thead>
<tr>
<th>n-Alkanes (µg/g TOC)</th>
<th>n-C25-Al/ n-Alkanes</th>
<th>n-C27-Al/ n-Alkanes</th>
<th>CPI</th>
<th>Pristane/ Phytane</th>
<th>C27 Steranes (µg/g TOC)</th>
<th>C28 Steranes (µg/g TOC)</th>
<th>C29 Steranes (µg/g TOC)</th>
<th>Hopanes (µg/g TOC)</th>
<th>Sesquiterpenoids (Arom.) (µg/g TOC)</th>
<th>Diterpenoids (Arom.) (µg/g TOC)</th>
<th>PAH (µg/g TOC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>0.27</td>
<td>0.32</td>
<td>1.29</td>
<td>1.09</td>
<td>1.4</td>
<td>1.1</td>
<td>1.7</td>
<td>25.2</td>
<td>17.3</td>
<td>18.3</td>
<td>13.4</td>
</tr>
<tr>
<td>282</td>
<td>0.44</td>
<td>0.24</td>
<td>1.30</td>
<td>0.96</td>
<td>8.9</td>
<td>7.5</td>
<td>9.4</td>
<td>56.7</td>
<td>13.2</td>
<td>14.0</td>
<td>10.2</td>
</tr>
<tr>
<td>124</td>
<td>0.44</td>
<td>0.24</td>
<td>1.28</td>
<td>1.02</td>
<td>1.8</td>
<td>1.5</td>
<td>2.1</td>
<td>23.1</td>
<td>45.4</td>
<td>46.1</td>
<td>49.7</td>
</tr>
<tr>
<td>51</td>
<td>0.45</td>
<td>0.17</td>
<td>1.18</td>
<td>0.91</td>
<td>0.6</td>
<td>0.5</td>
<td>0.7</td>
<td>8.3</td>
<td>32.9</td>
<td>2.5</td>
<td>4.8</td>
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<tr>
<td>108</td>
<td>0.43</td>
<td>0.20</td>
<td>1.36</td>
<td>0.84</td>
<td>4.8</td>
<td>3.0</td>
<td>6.1</td>
<td>30.8</td>
<td>34.1</td>
<td>2.3</td>
<td>8.3</td>
</tr>
<tr>
<td>55</td>
<td>0.52</td>
<td>0.16</td>
<td>1.43</td>
<td>1.10</td>
<td>1.0</td>
<td>0.8</td>
<td>1.4</td>
<td>7.3</td>
<td>34.3</td>
<td>2.4</td>
<td>11.9</td>
</tr>
<tr>
<td>64</td>
<td>0.52</td>
<td>0.13</td>
<td>1.18</td>
<td>1.11</td>
<td>1.3</td>
<td>1.2</td>
<td>1.6</td>
<td>7.7</td>
<td>20.5</td>
<td>1.5</td>
<td>7.3</td>
</tr>
<tr>
<td>66</td>
<td>0.51</td>
<td>0.15</td>
<td>1.41</td>
<td>1.15</td>
<td>2.8</td>
<td>2.3</td>
<td>3.3</td>
<td>19.8</td>
<td>24.9</td>
<td>3.7</td>
<td>13.4</td>
</tr>
<tr>
<td>42</td>
<td>0.47</td>
<td>0.14</td>
<td>1.23</td>
<td>1.05</td>
<td>0.6</td>
<td>0.5</td>
<td>0.7</td>
<td>4.7</td>
<td>8.7</td>
<td>2.3</td>
<td>6.5</td>
</tr>
<tr>
<td>40</td>
<td>0.50</td>
<td>0.12</td>
<td>1.32</td>
<td>0.93</td>
<td>0.4</td>
<td>0.4</td>
<td>0.5</td>
<td>3.1</td>
<td>10.3</td>
<td>2.5</td>
<td>5.2</td>
</tr>
<tr>
<td>62</td>
<td>0.38</td>
<td>0.23</td>
<td>1.42</td>
<td>0.73</td>
<td>1.1</td>
<td>1.0</td>
<td>1.6</td>
<td>9.3</td>
<td>9.3</td>
<td>2.2</td>
<td>4.9</td>
</tr>
<tr>
<td>117</td>
<td>0.50</td>
<td>0.13</td>
<td>1.34</td>
<td>1.38</td>
<td>1.5</td>
<td>1.2</td>
<td>1.8</td>
<td>17.2</td>
<td>34.9</td>
<td>6.9</td>
<td>13.3</td>
</tr>
</tbody>
</table>

CPI = Carbon preference index, PAH = Polycyclic aromatic hydrocarbons.

**Fig. 3.** Gas chromatograms (total ion current) of saturated hydrocarbon fractions of two sediment samples (a, b), and the fossil wood (c). n-Alkanes are labelled according to carbon number. Std. = standard (deuterated n-tetracosane).

In contrast, a proportion of pristane may be derived from tocopherols (Goossens et al. 1984), or may simply reflect the contribution of land plants to organic matter accumulation (Tissot & Welte 1984). No acyclic isoprenoids of low-molecular weight are present in the saturated hydrocarbon fraction of the fossil wood sample, most probably due to intense biodegradation.

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**Hopanoids**

Hopanes are constituents of the non-aromatic cyclic triterpenoids in most
samples (Fig. 3; Table 2). The samples show similar patterns, characterized by the occurrence of 17α, 21β(H)-type hopanes from C_{27} to C_{30}, with C_{28} hopanes absent. The 17β, 21α(H) hopanes from C_{29} to C_{31} are present in very low amounts. The predominant hopanoid is either the αβ-C_{29} hopane or the αβ-C_{30} hopane. The most probable biological precursors of the hopanes are bac teri o hopanopolyols (Ourisson et al. 1979; Rohmer et al. 1992). These compounds have been identified in aerobic bacteria and fungi, as well as in crypto-games (e.g. ferns, moss) and, most recently, sulphate-reducing bacteria (Blumenberg et al. 2006).

The ratio of the 22S/(22S+22R) isomers of the 17α, 21β(H) C_{31} hopanes of most samples is in the range of 0.51 to 0.55, close to the equilibrium value of ca. 0.6 (Mackenzie et al. 1982). These values argue for a thermal maturity equivalent to vitrinite reflectance values around 0.5 % R_t (Mackenzie & Maxwell 1981), slightly higher than the value of 0.4 % R_t measured within the fossil wood sample.

Sesquiterpenoids and diterpenoids

In all samples, sesquiterpenoid tetrahydro cadalane predominates in the aromatic hydrocarbon fractions (Fig. 4; Table 2). Further constituents of the aromatic sesquiterpenoids are calamenene, curcumene and cadalene (Simoneit & Mazurek 1982). The aromatic diterpenoids present in the samples consist of compounds of the abietane-type (e.g. simonellite, retene; Philip 1985) (Fig. 4; Table 2).

The sesqui- and diterpenoids are most probably derived from precursor molecules abundant in resins of conifers belonging to the families Podocarpaceae, Araucariaceae, and Cupressaceae (Noble et al. 1985; Otto & Wilde 2001). Araucariaceae and Podocarpaceae evolved during the Early Triassic and are therefore considered as the most probable precursor plants for the sesqui- and diterpenoids found in the EOM of the samples (Stewart 1983). In the fossil wood, only aromatic sesquiterpenoids were identified.

Polycyclic aromatic hydrocarbons

The polycyclic aromatic hydrocarbon (PAH) phenanthrene was detected in all samples (Fig. 4; Table 2). Phenanthrene and its methylated analogues derive from a variety of non-specific precursor compounds such as steroids and triterpenoids (Tissot & Welte 1984). Polycyclic aromatic hydrocarbons (PAHs) with 4–5 rings ranging from fluoranthene to benz-(ghi)-pyrene are present in the samples (Fig. 4). In recent sediments, combustion products of fossil fuels represent the main source of these PAHs (Laflamme & Hites 1978). PAHs in ancient sediments may result from wildfires (Killops & Killops 1993), or may be formed during microbially mediated diagenetic processes (Alexander et al. 1992). Some compounds (i.e. perylene) may derive from polyaromatic precursors synthesized by living organisms such as fungi (Tissot & Welte 1984).

The PAHs present in the samples and the absence of their methylated analogues argue for the origin of these compounds from charcoal and/or an input of PAHs attributed to recurring forest or swamp fires. However, as outcrop samples are being investigated here, an anthropogenic source (i.e. combustion products of fossil fuels) cannot be excluded. Furthermore, perylene is the dominating compound in most samples. For this PAH, a variety of biological sources have been considered.
Conclusions

Drift-wood is reported for the first time from the Lower Cretaceous of the Southern Alpine region. According to its terpenoid hydrocarbon composition, the wood fragment derived from a conifer belonging to the family Podocarpaceae or Araucariaceae. The age of the drift-wood is assigned to the Mid-Albian on the basis of the foraminifera fauna. The wood derives from surrounding islands formed during the beginning of the Albian Trento Plateau. Long-term drifting is indicated by the infestation of the bivalve *Teredo* (“shipworm”) and by the intense degradation of the organic matter (OM). Other boring organisms, probably worms, are indicated by fecal pellets, confirming the long term drifting hypothesis.

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