Evidence for methanogenesis on slope sites during the late Paleocene and early Eocene: carbonate concretions from the Dukla Nappe, Outer Carpathians, Poland

by

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ABSTRACT

Evidence for methanogenesis on slope sites during the late Paleocene and early Eocene: carbonate concretions from the Dukla Nappe, Outer Carpathians, Poland

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The late Paleocene to early Eocene was a prolonged period of global warming punctuated by abrupt intervals of rapid temperature rise. These hyperthermal events, especially including the Paleocene-Eocene thermal maximum, are characterized by negative carbon isotope excursions (CIEs), which signify massive input of $^{13}$C-depleted carbon. A widely-discussed mechanism to explain such carbon injection is destabilization and degassing of methane hydrates in marine sediment. Although large amounts of methane hydrate deposits should have existed during the late Paleocene and early Eocene, evidence has been limited. This study documents late Paleocene and early Eocene siderite-dominated carbonate concretions hosted in turbidites of the Dukla Nappe, Outer Carpathians, Poland. These concretions have $\delta^{13}$C ranges attributable to formation in methanogenic environments. Furthermore, grain-to-grain relationships and preserved sedimentary fabrics indicate authigenic formation prior to compaction. Given that they were deposited in sufficient water depth to host stable hydrates despite elevated ocean temperatures, these concretions provide supporting evidence of active methanogenesis and the accumulation of methane hydrates during the late Paleocene and early Eocene.
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up to their examples.
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>ii</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>iv</td>
</tr>
<tr>
<td>Dedication</td>
<td>v</td>
</tr>
<tr>
<td>Table of Contents</td>
<td>vi</td>
</tr>
<tr>
<td>List of Figures</td>
<td>vii</td>
</tr>
<tr>
<td>List of Tables</td>
<td>ix</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2. Methanogenesis and Authigenic Minerals on Continental Slopes</td>
<td>7</td>
</tr>
<tr>
<td>3. Sites and Samples</td>
<td>9</td>
</tr>
<tr>
<td>3.1. Geologic Setting</td>
<td>9</td>
</tr>
<tr>
<td>3.2. Field Collection</td>
<td>12</td>
</tr>
<tr>
<td>4. Analytical Methods</td>
<td>13</td>
</tr>
<tr>
<td>4.1. Sample Preparation</td>
<td>13</td>
</tr>
<tr>
<td>4.2. Isotopic Analysis</td>
<td>13</td>
</tr>
<tr>
<td>4.3. Gas Chromatography Analysis</td>
<td>15</td>
</tr>
<tr>
<td>4.4. X-Ray Diffraction Analysis</td>
<td>15</td>
</tr>
<tr>
<td>4.5. Carbonate Bomb Analysis</td>
<td>16</td>
</tr>
<tr>
<td>4.6. Carbonate Dissolution Analysis</td>
<td>17</td>
</tr>
<tr>
<td>4.7. Thin Section Analysis</td>
<td>19</td>
</tr>
<tr>
<td>4.8. SEM &amp; EDAX Analysis</td>
<td>19</td>
</tr>
<tr>
<td>5. Results</td>
<td>20</td>
</tr>
<tr>
<td>5.1. Isotope Results</td>
<td>20</td>
</tr>
<tr>
<td>5.2. Gas Chromatography Results</td>
<td>20</td>
</tr>
<tr>
<td>5.3. XRD and Carbonate % Results</td>
<td>20</td>
</tr>
<tr>
<td>5.4. Thin Section Results</td>
<td>28</td>
</tr>
<tr>
<td>5.5. SEM &amp; EDAX Results</td>
<td>32</td>
</tr>
<tr>
<td>6. Discussion</td>
<td>40</td>
</tr>
<tr>
<td>7. Conclusions</td>
<td>51</td>
</tr>
<tr>
<td>References</td>
<td>53</td>
</tr>
<tr>
<td>Appendix I: Supplemental Figures</td>
<td>62</td>
</tr>
</tbody>
</table>
# List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.</td>
<td>Deep-sea benthic $\delta^{13}$C and $\delta^{18}$O curves from 45 to 65 Ma</td>
<td>2</td>
</tr>
<tr>
<td>Figure 2.</td>
<td>TOC, DIC, other select redox reagents &amp; products, and phases with depth</td>
<td>4</td>
</tr>
<tr>
<td>Figure 3.</td>
<td>Concentration and $\delta^{13}$C composition of methane and $\Sigma CO_2$ with depth</td>
<td>6</td>
</tr>
<tr>
<td>Figure 4.</td>
<td>Map of the Outer Carpathian Nappes with early Eocene cross-sectional model</td>
<td>10</td>
</tr>
<tr>
<td>Figure 5.</td>
<td>Isotopic and mineral compositions of the Moczarne section, Dukla Nappe</td>
<td>21</td>
</tr>
<tr>
<td>Figure 6.</td>
<td>Isotopic and mineral compositions of the Szypowaty section, Dukla Nappe</td>
<td>22</td>
</tr>
<tr>
<td>Figure 7.</td>
<td>Isotopic and mineral compositions of the Stradomka section, Silesian Nappe</td>
<td>23</td>
</tr>
<tr>
<td>Figure 8.</td>
<td>Gas chromatography scans of samples from the Moczarne section, Dukla Nappe</td>
<td></td>
</tr>
<tr>
<td>Figure 9.</td>
<td>XRD peaks typical of commonly-identified minerals</td>
<td>27</td>
</tr>
<tr>
<td>Figure 10.</td>
<td>Mica clast deformed during compaction (thin section)</td>
<td>29</td>
</tr>
<tr>
<td>Figure 11.</td>
<td>Fossil chamber in-filled with siderite and amorphous silica (thin section)</td>
<td>30</td>
</tr>
<tr>
<td>Figure 12.</td>
<td>Preserved sedimentary structures in a siderite nodule (thin section)</td>
<td>31</td>
</tr>
<tr>
<td>Figure 13.</td>
<td>Siderite crystals concentrated on linear feature (thin section)</td>
<td>33</td>
</tr>
<tr>
<td>Figure 14.</td>
<td>Siderite crystals in mud matrix (thin section)</td>
<td>34</td>
</tr>
<tr>
<td>Figure 15.</td>
<td>Low-magnesian calcite-filled foram chamber (thin section)</td>
<td>35</td>
</tr>
<tr>
<td>Figure 16.</td>
<td>Recrystallized and partially replaced fossil fragments (thin section)</td>
<td>36</td>
</tr>
<tr>
<td>Figure 17.</td>
<td>Siderite involvement in bending &amp; fracturing of mica sheet (SEM)</td>
<td>37</td>
</tr>
<tr>
<td>Figure 18.</td>
<td>Siderite filling a fossil chamber (SEM)</td>
<td>38</td>
</tr>
<tr>
<td>Figure 19.</td>
<td>Sequentially precipitated carbonates (SEM &amp; EDAX)</td>
<td>39</td>
</tr>
<tr>
<td>Figure 20.</td>
<td>Pyrite occurrence and siderite rimming of detrital grains (SEM)</td>
<td>41</td>
</tr>
<tr>
<td>Figure 21.</td>
<td>Siderite crystal distribution (SEM)</td>
<td>42</td>
</tr>
<tr>
<td>Figure 22.</td>
<td>Siderite crystal distribution and pyrite occurrence (SEM)</td>
<td>43</td>
</tr>
<tr>
<td>Figure 23.</td>
<td>Fossil chamber in-filled with siderite and silica (SEM &amp; EDAX)</td>
<td>44</td>
</tr>
<tr>
<td>Figure 24.</td>
<td>Vein-filled fracture (SEM)</td>
<td>45</td>
</tr>
<tr>
<td>Figure 25.</td>
<td>Histograms of inorganic $\delta^{13}$C in this study vs. other literature</td>
<td>46</td>
</tr>
<tr>
<td>Figure AI-1.</td>
<td>Location of sample MO 3, Majdan Beds</td>
<td>62</td>
</tr>
<tr>
<td>Figure AI-2.</td>
<td>Location of sample MO 5, Majdan Beds</td>
<td>63</td>
</tr>
<tr>
<td>Figure AI-3.</td>
<td>Location of sample MO 7A, Hieroglyphic Beds</td>
<td>63</td>
</tr>
<tr>
<td>Figure AI-4.</td>
<td>Location of samples SP 9 and SP 9A, Majdan Beds</td>
<td>64</td>
</tr>
<tr>
<td>Figure AI-5.</td>
<td>Locatoin of sample SP 17A, Hieroglyphic Beds</td>
<td>64</td>
</tr>
<tr>
<td>Figure AI-6.</td>
<td>Location of sample S 5, Upper Istebna Shales</td>
<td>65</td>
</tr>
</tbody>
</table>
| Figure AI-7. Location of samples S 14 and S 15, Upper Istebna Shales | .65  
| Figure AI-8. Location of sample S 29, Variegated Shales | .66  
| Figure AI-9. Sequentially precipitated carbonates (SP 17A, SEM & EDAX) | .67  
<p>| Figure AI-10. Sequentially precipitated carbonates (SP 17A, SEM &amp; EDAX) | .68  |</p>
<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Locations of outcrops sampled</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>Siderite dissolution techniques from literature</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>Isotopic and compositional data for the Moczarne section, Dukla Nappe</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>Isotopic and compositional data for the Szypowaty section, Dukla Nappe</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>Isotopic and compositional data for the Stradomka section, Silesian Nappe</td>
<td>26</td>
</tr>
<tr>
<td>6</td>
<td>Known inorganic $\delta^{13}$C ranges of siderite associated with methanogenesis</td>
<td>49</td>
</tr>
</tbody>
</table>
1. Introduction

The late Paleocene to early Eocene, from approximately 60 to 50 Ma, was characterized by a 5-15°C increase in high-latitude surface and world-wide deep-water temperatures that culminated in the warmest period of the Cenozoic: the Early Eocene Climatic Optimum (EECO). Superimposed on this long-term warming trend were several short-term (<20,000 yr) events termed “hyperthermals,” the most notable being the Paleocene-Eocene Thermal Maximum or PETM (see Figure 1; Thomas et al., 2000; Zachos et al., 2001). These are characterized by prominent, global negative carbon isotope excursions (CIEs) and decreased carbonate content in deep marine deposits (Lourens et al., 2005; Zachos et al., 2005). Both phenomena signify massive and rapid input of $^{13}$C-depleted carbon into the ocean and atmosphere. For the PETM, the total amount of carbon injected likely exceeded 2000 gigatonnes (Gt) (Dickens et al., 1997).

Destabilization of methane hydrate along continental slopes provides the most plausible cause for such tremendous carbon input (Dickens et al., 1995, Zachos et al., 2001). Methane hydrate is a solid wherein a methane molecule is surrounded by a crystalline lattice of water molecules known as a clathrate structure. Methane found in this solid form typically exhibits especially negative isotopic compositions of -60‰ or lighter derived from microbial methanogenesis (Kvenvolden, 1993). Methane clathrates occur in modern deep-water and polar settings within ~2000 m of the sediment surface (Kvenvolden, 1995) and comprise a massive carbon reservoir of ~ 3x10^{12} metric tons (Buffet and Archer, 2004). Methane clathrates exist within a narrow stability window favored by low temperature and high pressure, and relatively small changes in either can trigger voluminous clathrate dissociation (Dickens, 2000; Archer, 2007). These characteristics make them a carbon reservoir capable of driving global negative $\delta^{13}$C excursions such as those seen across the hyperthermal events (Dickens et al., 1995; Dickens, 2000; Zachos et al., 2001; Dupuis et al., 2003; Lourens et al., 2005). During the PETM, deep ocean temperatures rose 4-5° (Tripati and Elderfield, 2005). This may have released >2000 Gt of carbon from
Figure 1: Stable oxygen and carbon isotope curves for the early Cenozoic based on deep-sea DSDP and ODP sites. Select hyperthermal events are labeled. Oxygen isotopes correlate inversely to temperature. EECO = early Eocene climatic optimum; PETM = Paleocene-Eocene Thermal Maximum; ETM2 = Eocene Thermal Maximum 2 (a.k.a., ELMO = Eocene layer of mysterious origin). Adapted from Zachos et al., 2001, and Zachos et al., 2008.
methane hydrates (Dickens et al., 1995, Dickens et al., 1997; Zachos et al., 2005). Initial seafloor warming could have resulted from a change in deep ocean circulation possibly triggered by volcanism in the north Atlantic (Rea et al., 1990; Eldholm and Thomas, 1993; Svensen et al., 2004; Storey et al., 2007).

Thermal dissociation of gas hydrate, though widely acknowledged as an explanation for the CIEs, comes with several conceptional problems (Dickens, 2003; Pagani et al., 2006). Among these is whether a sufficiently large mass of gas hydrate existed during the late Paleocene and early Eocene. Deep ocean waters were at least 5°C warmer than present-day during the early Paleogene (Zachos et al., 2001). The potential volume of sediment hosting methane hydrate was therefore smaller than at present day (Dickens, 2001). However, methane production was probably much greater.

In the modern marine environment, most methane (> 80%), including that in methane hydrates, is of biogenic origin (Booth et al., 1996). More specifically, methanogens consume organic carbon after a cascade of other biomediated redox reactions, including oxic respiration and sulfate reduction, have occurred in the upper few meters of sediment (see Figure 2; Stumm and Morgan, 1996; Kehew, 2000; Appelo and Postma, 2005). Conditions during the early Paleogene likely accelerated the input of organic carbon to seafloor sediments and increased the fraction passing on to methanogenesis. Mean surface temperatures were 6 to 9°C warmer than at present (Budyko, 1999) and atmospheric pCO₂ was likely >1100 ppmv (Pearson and Palmer, 2000; Lowenstein and Demicco, 2006), both of which would have increased meteoric precipitation, weathering, and nutrient supply to the oceans (Crouch et al., 2003; Bowen et al., 2004; Zachos et al., 2008). Oxygen and sulfate concentrations in the ocean were almost certainly lower than modern levels (Thomas, 1990; Horita et al., 2002), so that more of the organic material deposited in sediments would have remained available for methanogenesis. Furthermore, increased deep ocean temperatures would have accelerated methanogenesis in sediments (Zeikus and Winfrey, 1976). For theoretical reasons, methanogenesis, methane, and gas hydrates should have
Figure 2: Reduction in total organic carbon (TOC), increase in dissolved inorganic carbon (DIC; i.e., carbonate alkalinity or $\Sigma$CO$_2$), other select redox reagent and product concentrations with depth, typical redox zones, and characteristic precipitates of redox zones. Increasing concentrations are produced primarily from organic decomposition or as byproducts of metabolism. Decreasing concentrations result from consumption during the continued oxidation of organic material and/or by the precipitation of solid phases. Adapted from Appelo and Postma, 2005, with redox classifications and phases from Berner, 1981, except in the case of dolomite which is discussed by Vasconcelos et al., 1995, and Mazzullo et al., 1999.
been abundant in continental margin deposits during the late Paleocene to early Eocene. The ephemeral nature of methane makes direct evaluation of its past presence in seafloor sediments impossible. However, certain biomediated redox reactions, including methanogenesis, produce carbonate alkalinity in the form of dissolved inorganic carbon (DIC), which can drive the formation of carbonate minerals. Of particular interest to seafloor methane cycling is the formation of carbonate concretions, particularly siderite, with distinctive isotopic ranges (see Figures 2 and 3; Berner, 1981; Coleman, 1993; Appelo and Postma, 2005). To date, there has been limited documentation of early Paleogene methane-related carbonates. In part, this reflects the fact that scientific drilling programs have generally avoided rapidly accumulating sequences of Paleogene age. Authigenic siderite concretions have been reported from Upper Paleocene to Lower Eocene sediment deposited in deep continental slope settings and now exposed in the Outer Carpathians of Eastern Europe (e.g., Narębski, 1956; Ślączka, 1958; Ślączka, 1971; Bąk, 2004; Dziubińska & Narębski, 2004). However, these concretions have not been considered within the context of methane cycling.

This study examines late Paleocene and early Eocene marine sediment sections now exposed in the Polish Outer Carpathian Mountains. The outcrops sampled are significant to the understanding of early Paleogene methane cycling because they represent an active continental margin environment where methane would likely occur today. They were emplaced at moderate to high sedimentation rates (~125 m/Myr) (Bąk, 2004; Bąk and Bąk, 2005) at a paleolatitude of approximately 45° N (Lawver et al., 1999). The sections sampled were also deposited in lower bathyal to abyssal settings below the calcite compensation depth (i.e., >2000 mbsl) (Bąk, 2004). This is well below the minimum depth for the formation of gas hydrate during the Paleogene (Dickens, 2001). Carbonate concretions from this study have δ13C compositions that are indicative of active methanogenesis, grain-to-grain relationships and preserved sedimentary fabrics indicative of in-situ formation, and therefore indicate the probable syndepositional accumulation.
Figure 3: Changes in CH$_4$, $\Sigma$CO$_2$ (i.e., DIC or carbonate alkalinity), and SO$_4^{2-}$ concentrations and CH$_4$ and $\Sigma$CO$_2$ isotopic compositions with depth. Depth scale is in arbitrary units. The most common isotopic range of carbonates precipitated at the sulfidic-methanic interface is highlighted in red on the $\Sigma$CO$_2$ curve. Adapted from Raiswell, 1988; originally after Reeburgh, 1980; chemical zones from Berner, 1981. Note that the SO$_4^{2-}$ curve from Raiswell, 1988 differs from that of Appelo and Postma, 2005 (see Figure 2).
of methane hydrates in their host sediments.

2. Methanogenesis and Authigenic Minerals on Continental Slopes

Organic carbon deposited on the seafloor undergoes a series of microbially-mediated redox reactions involving successive electron acceptors during burial. Reactions giving the greatest energy generally are utilized first, with the redox potential being buffered as each higher-potential reagent is consumed. The result is a stepped reaction series where dissolved O$_2$, dissolved nitrates, solid Mn-oxides, solid Fe-oxides and hydroxides, and dissolved sulfates are used sequentially, and these are followed by methanogenesis (see Figures 2 and 3). The non-organic reagents can be consumed rapidly upon burial, often being exhausted within the first few meters of sediment in areas with high sediment deposition and organic input (Stumm and Morgan, 1996; Kehew, 2000; Appelo and Postma, 2005). Methanogenesis can proceed using a variety of substrates including methylated amines, methanol, ethanol, carbon monoxide, benzoate, formate, etc. (Whiticar et al., 1986). However, the majority of methanogenic activity occurs via two metabolic pathways: acetate fermentation and CO$_2$ reduction. In acetate fermentation, organic matter is used as both an e\textsuperscript{-}-acceptor and e\textsuperscript{+}-donor, producing methane and CO$_2$. The process of CO$_2$ reduction consumes CO$_2$ as an e\textsuperscript{-}-acceptor and produces methane (Balch et al., 1979; Whiticar et al., 1986; Stumm & Morgan, 1996). Methane typically does not accumulate in sediments until sulfate concentrations are < 1.0 mM (Whiticar et al., 1986). This is a combined effect of the higher redox potential of sulfate reduction and the anaerobic oxidation of methane that occurs in the presence of sulfate. The ability of methane and CO$_2$ to be derived from each other through CO$_2$ reduction, methanotrophy, and a myriad of other reactions results in a process of methane cycling which is especially active and dynamic near the sulfate/methane interface (SMI) (Raiswell, 1988; Dickens et al., 2003; Hensen et al., 2003).

The rate and volume of methane production by methanogenesis is controlled by
the temperature of sediments and the abundance of organic matter. The temperature of sediments is a function of ocean temperature, the local geothermal gradient, and time. Below ~50°C, warming of sediments accelerates methanogenic activity (Zeikus and Winfrey, 1976). The volume of methane that can ultimately be produced is a function of the amount of organic material available for methanogenesis. This in turn depends on the initial volume of organic material deposited in sediments and the concentrations of higher-potential redox reagents (e.g., O₂, nitrates, and sulfate) which, when lower, consume less of the available organic matter (Stumm and Morgan, 1996). Along these same lines, faster depositional rates help preserve more organic material by preventing prolonged exposure to reagent-bearing seawater at the sediment surface. Certain environments, especially continental slopes, have optimal conditions of organic supply and depositional rates to help maximize methane production (D’hondt et al., 2002).

The ephemeral nature of methane complicates attempts at direct evaluation of its presence in seafloor sediments, especially those of significant age. However, certain biomediated redox reactions including methanogenesis produce carbonate alkalinity in the form of dissolved inorganic carbon (DIC), the oversaturation of which drives the formation of calcite, dolomite, siderite, and other carbonate concretions (see Figure 2; Berner, 1981; Raiswell, 1988; Coleman, 1993; Appelo and Postma, 2005). Other byproducts such as Fe²⁺-Fe³⁺ silicate minerals (e.g., glauconite), pyrite, and vivianite are also produced (Berner, 1981). These various phases can undergo progressive alteration as they move through different chemical zones.

The carbon isotopic composition of carbonates formed in anoxic sediments is largely inherited from the DIC (i.e., ΣCO₂) from which they precipitate (Raiswell and Fisher, 2000). Some DIC from seawater (δ¹³C ≈ 0‰) infiltrates sediments or is entrapped during deposition, but the majority of DIC is produced by microbial metabolism. Aerobic oxidation and the anaerobic reduction of nitrate, manganese, ferric iron, and sulfate all produce CO₂ with negative δ¹³C ranges close to that of the organic substrate being metabolized
(δ\(^{13}\)C ≈ -20 to -30%o) (Coleman, 1993). Methanogenesis, however, produces highly \(^{13}\)C-depleted methane (δ\(^{13}\)C ≈ -60%o) (Kvenvolden, 1993) and CO\(_2\) that is \(^{13}\)C-enriched compared to the original organic substrate (δ\(^{13}\)C\(_{\text{mean}}\) = -7.9%o; δ\(^{13}\)C\(_{\text{max}}\) ≈ +15%o) (Raiswell and Fisher, 2000). With methanotrophy occurring in the zone of anaerobic methane oxidation, isotopic compositions can be further complicated by the conversion of highly depleted methane into CO\(_2\). Nonetheless, the overall isotopic evolution of DIC follows general trends during burial: δ\(^{13}\)C\(_{\text{DIC}}\) decreases with depth toward the sulfate-methane interface and then increases into the methanic zone (see Figure 3). Since carbonate alkalinity comes close to its highest levels near the sulfate-methane interface and in the methanic zone, this is often where methane-related carbonate concretions begin to precipitate in earnest. As previously mentioned, concretion δ\(^{13}\)C values mimic those of the DIC from which they are derived (Raiswell and Fisher, 2000).

3. Sites and Samples

3.1. Geologic Setting

The Carpathian Mountains of Eastern Europe are an eastern extension of the Alps, having a related tectonic history. The Outer Carpathian Nappes (see Figure 4) are a band of overthrust sheets that border the Inner Carpathians to the northeast. Due to their depositional setting during the Paleogene, concretionary carbonates periodically formed which are of interest to this study.

Prior to accretionary thrusting in the middle Cenozoic, the nappes were a collection of foreland basins formed by crustal warping which began in the Late Jurassic (Cieszkowski, 2004). The innermost basins were deeply recessed within the continent (Winkler and Ślączka, 1992). The basins filled and subsided between the Late Jurassic and early Miocene with occasional short-lived periods of uplift. In the early Miocene, the basins were detached from the basement, folded, and overthrust over 100 km southward onto the
Figure 4: *Above:* Map showing select nappes of the Outer Carpathians and sites in this study (S = Stradomka section, MO = Moczarne section, SP = Szypowaty section; see Table 1). PKB = Pieniny Klippen Belt. Adapted from Oszczypko, 2006; originally after Kovač et al., 1998. *Below:* Cross-sectional model for the Carpathians in the early Eocene. Model is not to scale, and the A-A’ transect is not intended as literal. Adapted from Oszczypko, 2006; originally from Oszczypko, 1999.

Table 1: Locations of sampled outcrops.
Northern European Platform (Cieszkowski, 2004; Cieszkowski and Golonka, 2006). Of primary interest to this study are the Dukla Nappe and Silesian Nappe.

During the early Paleogene, the Dukla and Silesian basin sediments which would later be preserved in nappes were predominantly being deposited in deep marine slope environments with water depths exceeding 2000 mbsl (Bąk, 2004). Depositional rates were high to moderate at approximately 125 m/Myr (Bąk, 2004; Oszczypko, 2006). The mainly terrigenous sediments were sourced by the Silesian Ridge (Golonka et al., 2000) including an extension thereof referred to as the Bukowiec Ridge (Oszczypko, 2006; Ślączka, 2005; Ślączka and Golonka, 2006). Subsidence rates in these basins remained fairly consistent throughout the Paleogene with a slight decrease occurring from the Paleocene to the Eocene (Oszczypko, 2006).

The main stratigraphic units of interest in the Dukla Nappe are the Majdan Beds (upper Paleocene), the Hieroglyphic Beds (lower Eocene), the Variegated Shales (lower Eocene), and the Wielka Rawka Sandstones (occur intermittently in the Paleocene and Eocene). The main units of interest in the Silesian Nappe are the Istebna Shales (upper Paleocene), the Variegated Shales (lower Eocene), and the Ciężkowice Sandstones (occur intermittently in the Paleocene and Eocene).

The Majdan Beds are thin-to-medium-bedded black shales interbedded with sandstones (Cieszkowski, 2001). The Hieroglyphic Beds are also thin- to medium-bedded, but with alternating grey, green, and occasionally red shales which are occasionally arenaceous (Cieszkowski, 2004; Ślączka, 1971; Ślączka and Kaminski, 1998). Ksiazkiewicz (1956) referred to the green beds as being “glaucnite sandstones.” Lenses of turbidite sandstones may occur in either the Majdan or Hieroglyphic Beds and are referred to as the Wielka Rawka Sandstones (Ślączka and Kaminski, 1998). Occurrences of siderite nodules and sideritic marls occur in both the Majdan Beds and the Hieroglyphic Beds (Bąk, 2004). A relatively thin occurrence of the Variegated Shales occurs within the Hieroglyphic Beds in the Dukla Nappe, while in the Silesian Nappe the lower Eocene strata are dominated by
the Variegated Shales. The upper Paleocene of the Silesian Nappe is composed of Istebna Shales. Similar to the Wielka Rawka Sandstones of the Dukla Nappe, the Ciężkowice Sandstones of the Silesian Nappe occur sporadically throughout the upper Paleocene and lower Eocene, though they tend to be more thick-bedded in the lower Eocene.

3.2. Field Collection

Three sites with early Paleogene deep-marine sediments were sampled in southeastern Poland: the Moczarne and Szypowaty sections near Wetlina and the Stradomka section near Szczyrzyc. The first two sections are located in the Bieszczady Mountains within the Dukla Nappe while the third is in the Beskid Wyspowy Mountains within the Silesian Nappe (see Figure 4 and Table 1). The sections were predominantly silty shales with occasional sandstone layers and carbonate concretions (see Figures AII-1 through AII-8 in Appendix I).

In the Moczarne and Szypowaty sections of the Dukla Nappe, samples were taken from the Majdan Beds (Paleocene) and Hieroglyphic Beds (Eocene). In the Stradomka section of the Silesian Nappe, the Upper Istebna Shales (Paleocene) and the Variegated Shales (Eocene) were sampled. The largest coherent samples exhibiting minimal weathering were collected. For the purpose of generating meaningful isotopic data, care was taken to collect shale samples with minimal silt or sand content whenever possible. The aversion to arenaceous content was on account of the increased likelihood of fluid migration altering the isotopic composition of minerals through diagenesis and the potential contamination of the organic fraction with invading organic fluids of a different isotopic character. Carbonate nodules were occasionally encountered and collected when found.

Outcrop ages had been determined in advance based on deep-water agglutinated foraminifera (DWAF). The relevant DWAF biostratigraphic zones in the Dukla Nappe are the *Caudammina gigantea* partial range zone (Maastrichtian), *Remesella varians* interval
zone (Maastrichtian), *Rzehakina fissistomata* total range zone (Paleocene), *Glomospira* div. sp. acme zone (Ypresian), and *Saccaminoides carpathicus* interval zone (Eocene) (Bąk, 2004). The relevant DWAF biostratigraphic zones in the Silesian Nappe are the *Hormosina ovulum gigantea* interval zone (Campanian-Maastrichtian), *Rzehakina fissistomata* partial range zone (Danian), *Spiroplectammina spectabilis* partial range zone (Selandian-Thanetian), and the *Saccaminoides carpathicus* partial range zone (Ypresian) (Geroch and Nowak, 1984; Bąk, 2004).

4. Analytical Methods

4.1. Sample Preparation

Prior to running diagnostic tests requiring powdered samples, samples were processed to minimize contamination. Where little sample was available, half of the sample was preserved for thin sections and/or SEM analysis while the other half was set aside for milling. In the first step of preparation for milling, exposed outer surfaces and all weathered portions of the samples were removed using a rock saw. The ground sample surfaces were then briefly (~1 min) agitated in and rinsed with an organic solvent to remove rock flour and potential organic contamination. Cleansed samples were dried in an oven to remove any remaining solvent, allowed to cool, and milled in a cleaned SPEX mill equipped with a tungsten ring. A portion of the powdered samples was placed in pre-rinsed vials for isotopic analysis. The remainder of the powder was designated for XRD analysis, carbonate dissolution experiments, and carbonate bomb assays.

4.2. Isotopic Analysis

Isotopic analysis was performed on the carbonate mineral ($\delta^{13}C_{\text{xtal}}$ and $\delta^{18}O_{\text{xtal}}$) and organic ($\delta^{13}C_{\text{org}}$) constituents of the samples. Although most Paleocene/Eocene $\delta^{13}C$ curves in literature have been created using carbonate material from fossil remains (e.g., Zachos et
al., 2001), the majority of samples in this study did not contain carbonate material. Measurement of $\delta^{13}\text{C}_{\text{org}}$ was therefore pursued in an attempt to establish a proxy $\delta^{13}\text{C}$ curve.

Samples were sent to MSI Analytical Lab at the Marine Science Institute of U.C. Santa Barbara for isotopic analysis. In the case of the Moczarne samples, $\delta^{13}\text{C}_{\text{org}}$ analysis was initially performed by Dr. Mark Pagani at Yale University and then verified with MSI Lab data. Carbon weight percent was also calculated as part of the $\delta^{13}\text{C}_{\text{org}}$ analyses performed at the MSI Lab.

Inorganic isotopes ($\delta^{13}\text{C}_{\text{xtal}}$ and $\delta^{18}\text{O}_{\text{xtal}}$) were performed using a Finnigan Delta XP Isotope Ratio Mass Spectrometer with a Gas Bench. Calibration was performed using the NBS19 carbonate standard reference material. For each carbonate-bearing sample, 3 mg was loaded into vaccutainer vials which were then purged with helium gas. 103% H$_3$PO$_4$ was injected into each vial through a septum seal. The samples were allowed to equilibrate for approximately 24 hours at room temperature. The resulting CO$_2$ and H$_2$O reaction products were swept to the Gas Bench, the H$_2$O removed, and the CO$_2$ carried to the mass spectrometer where masses 44, 45, and 46 were collected simultaneously, representing the CO$_2$ combinations containing $^{12}\text{C}$, $^{13}\text{C}$, $^{16}\text{O}$, $^{17}\text{O}$ and/or $^{18}\text{O}$. Finally, the 45/44 and 46/44 ratio data were deconvoluted to estimate the $\delta^{13}\text{C}_{\text{xtal}}$ and $\delta^{18}\text{O}_{\text{xtal}}$ of the sample. Carbon isotope values were reported relative to vPDB. Oxygen isotope values were reported relative to vSMOW, then converted to vPDB using the equation $\delta^{PDB} = 0.970060 \cdot \delta^{SMOW} - 29.94$ (Friedman and O’Neil, 1977; Mozley and Burns, 1993). Measured data was normalized using repeated measurements of NBS19 and Getty Rock standards. Maximum error for both $\delta^{13}\text{C}_{\text{xtal}}$ and $\delta^{18}\text{O}_{\text{xtal}}$ was approximately ±0.6‰ with standard deviation of 0.1‰.

Organic isotopes ($\delta^{13}\text{C}_{\text{org}}$) were measured using a Finnigan Delta Advantage Isotope Ratio Mass Spectrometer with a Costech 4010 Elemental Combustion System. Calibration of the device was verified using acetonilide and NIST 8542, a sucrose standard reference material. The samples were acidified with 10% HCl to remove the inorganic carbon fraction, then dried at 60°C. In siderite-bearing samples, acidification was performed in
advance for a period of 6 days to insure full carbonate dissolution. 10 mg of the remaining material was then wrapped in tin capsules and combusted at 1000°C. The resulting combustion products were CO₂, H₂O, and NOₓ. The NOₓ was converted to N₂ in a reduction tube, and the H₂O was scrubbed out. Remaining CO₂ and N₂ were carried to a gas chromatograph column, separated, and introduced into a mass spectrometer instrument at different times. The instrument was tuned to collect masses 44 through 46 simultaneously, and the ratio data deconvoluted to estimate the δ¹³Corg of the sample. Isotope values were reported relative to vPDB. Measured data was normalized using repeated runs of acetylilide and NIST 8542 standards. Maximum error for δ¹³Corg was approximately ±0.6‰ with a standard deviation of 0.2‰. Since O₂ (g) was added during combustion, the resulting δ¹⁸Oorg data were contaminated and unusable.

4.3. Gas Chromatography Analysis

Since some of the sandstone units encountered are known hydrocarbon reservoirs in the subsurface (Cieszkowski, 2004) and since samples had been exposed to the modern biosphere in surface outcrops, several gas chromatography assays were conducted to investigate the potential for organic contamination. Assays were performed by Dr. Mark Pagani at Yale University using a Trace 2000 gas chromatograph.

4.4. X-Ray Diffraction Analysis

Powdered samples were analyzed by X-ray diffraction (XRD) using a Rigaku D/Max Ultima II with Cu Ka radiation in the X-ray Diffraction Lab of the Shared Equipment Authority at Rice University. Samples were mounted in standard back-fill aluminum sample holders to minimize biases in particle orientation. XRD patterns were scanned across a 2-Theta (2θ) range of 2°-100° using a step size of 0.02° 2θ and a scan speed of 2° 2θ/min.
Scans were initially preformed with pure sample, then repeated with an addition of 50 wt% \(\text{Al}_2\text{O}_3\) powder as an internal standard.

Qualitative mineral phase identification was achieved by analyzing scanned XRD patterns in Jade 8.5 processing software from Materials Data, Inc. Semi-quantitative mineral abundance determination was achieved through whole pattern fitting (WPF, also known as the Pawley method and the basis of the Rietveld method).

Whole pattern fitting did not include unidentified phases in calculating weight percent, was limited to a maximum of 16 identified mineral phases, and calculations summed to 100%. In cases where all mineral phases were identified and there were no additional amorphous phases present, WPF can be reasonably accurate. However, impurities or gradational changes in solid-solution series (e.g., carbonates, clays, and plagioclases) and the presence of multiple unidentifiable trace components reduce the effectiveness of WPF. Furthermore, inappropriate mineral identifications can cause significant errors, so vigilance was required during analysis.

Despite its pitfalls, whole-pattern fitting was useful in establishing the relative proportions of sample components as well as estimating potential weight percents. Compositions were further constrained by incorporating \(\text{Al}_2\text{O}_3\) as an internal standard, allowing sample-to-sample correlations and checking the quality of WPF analysis. XRD patterns were also exported to Excel spreadsheets for further analysis of peak areas. As a final step, results from carbonate dissolution, carbonate bomb measurements, and thin section observations were used to constrain quantitative estimates.

4.5. Carbonate Bomb Analysis

Carbonate bomb analysis (a.k.a., manometric analysis) was performed on samples with demonstrable carbonate content to determine percent carbonate. Since carbonate bomb assays are best done over short periods of time to minimize the effect of changing
barometric pressure and potential leaks (Müller and Gastner, 1971), measuring the full extent of siderite composition was impractical using a carbonate bomb. Siderite has a very slow dissolution rate, often requiring days to complete (Curtis et al., 1972; Al-Aasm et al., 2000; Bisutti et al., 2004; see Table 2). The use of carbonate bomb assays was nonetheless capable of measuring calcite content and setting lower limits to the potential amount of siderite contained in samples.

For each assay, between 1.00 and 1.50 g of sample was reacted with 10 mL of 1.2 N (10%) HCl acid in a sealed jar connected to a pressure gauge. Change in pressure was plotted against sample weight. Manometric measurements were taken at 30-second intervals until the reaction reached equilibrium or until 10 minutes elapsed. Calibration curves were established using a 100% CaCO$_3$ standard prior to measuring samples and verified by additional runs between every several samples. Standard measurements were consistent, plotting on a line with a $R^2$ value of 0.9997. Replicate analyses of samples containing no detectable siderite had a maximum error of 3%. The reaction chamber was rinsed with distilled water ($\geq$18 MΩ·cm) between experiments.

4.6. Carbonate Dissolution Analysis

For carbonate-bearing samples which did not equilibrate in carbonate bomb assays, long-term dissolution experiments were performed. For each sample, 5 g was put in vials with 50 mL of 10% HCl and allowed to dissolve for a period of 6 days while being agitated on a wrist-action shaker. Vial lids were kept loose and each vial was placed in a Whirl-Pak bag which was loosely sealed so as to allow the release of evolved gas while containing any potential vial spills. At the end of the dissolution period, samples were rinsed by centrifuging at 3,000 rpm for 20 minutes, removing the liquid, adding distilled water ($\geq$18 MΩ·cm), agitating with a vortexer, then repeating the process of centrifugation and liquid removal. The samples were then frozen, freeze-dried, and weighed to determine the amount of re-
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Table 2: Grain sizes of powdered siderite samples and reaction times used by different authors prior to isotopic analysis. *: authors claimed that the reaction was complete; †: room temperature assumed when not specified by publication.
remaining material. The difference between the original sample and remaining samples was used to calculate percent carbonate. Replicate analyses of samples had maximum error of 4%.

4.7. Thin Section Analysis

Key samples were sent to Texas Petrographic Services in Houston, TX, to prepare thin sections. Samples were impregnated with a blue epoxy in advance to stabilize the samples during cutting and polishing and to identify fractures and pore spaces within the samples. Samples were ground and polished to 30 mm thickness. No stain was applied to the samples.

Thin sections were analyzed using top-lit (up to 40x magnification) and back-lit (up to 400x magnification) petrographic microscopes.

4.8. SEM & EDAX Analysis

Preparation for SEM and EDAX analysis was done by attaching samples to a mount using carbon tape and applying a carbon-coating. In the case of mounted thin sections, carbon tape was wrapped around the sides of the slides to guarantee conductivity between the sample on top and the mount beneath.

Samples were analyzed using a FEI Quanta 400 high resolution field emission scanning electron microscope equipped with secondary electron (SE), backscatter electron (BSED), and energy dispersive spectroscopy (EDS or EDAX) detectors within the CNST Instrument Area managed by the Shared Equipment Authority at Rice University. SE and BSED images were acquired to determine grain morphologies and relationships. EDAX spot measurements and elemental mapping were performed to indentify grain compositions. Measurements were taken in high-vacuum conditions (~10⁻⁹ Torr) with 20 kV and a
beam spot size of 3-4 nm.

5. Results

5.1. Isotope Results

Isotope results are shown in Figures 5, 6, and 7 and Tables 3, 4, and 5. Of the 106 samples tested, $\delta^{13}C_{\text{org}}$ results ranged from -20.9‰ to -28.7‰ with a mean of -23.6‰ and a standard deviation of 1.4‰. Fourteen of the samples had siderite-dominated carbonate content with $\delta^{13}C_{\text{stal}}$ results between +1.0‰ and -15.9‰ with a mean of -7.6‰ and a standard deviation of 5.0‰. Twelve of the samples had calcite-dominated carbonate content with $\delta^{13}C_{\text{stal}}$ results between +1.6‰ and -18.7‰ with a mean of -1.1‰ and a standard deviation of 5.8‰. The $\delta^{18}O_{\text{stal}}$ values of all carbonates ranged from +0.2‰ to -16.0‰ with a mean of -6.1‰ and a standard deviation of 3.4‰.

5.2. Gas Chromatography Results

The gas chromatography (GC) scans are shown in Figure 8. The GC traces indicate that the organic material present in the Moczarne samples consists of a series of heavy alkanes. Such often remain after most other organic molecules have been metabolized, so it appears unlikely that modern organic sources were contaminating the samples. The n-alkanes also suggest exposure to high temperature and the presence of mature oils. Even so, the traces remain sufficiently different in character to support the idea that they do not have a common source. It is therefore possible that the organic material found in samples is syndepositional and not contaminated by migrating fluids.

5.3. XRD and Carbonate % Results

Mineral composition results are shown in Figures 5, 6, and 7 and Tables 3, 4, and
Moczarne Section
Bieszczady Mountains, Dukla Nappe, Polish Outer Carpathians

Figure 5: Inorganic δ¹³C and δ¹⁸O, organic δ¹³C, carbon weight %, and semi-quantitative mineral compositions based on XRD whole-pattern fitting, carbonate dissolution assays, and thin section analysis for samples from the Moczarne section.
Szypowaty Section
Bieszczady Mountains, Dukla Nappe, Polish Outer Carpathians

Figure 6: Inorganic δ¹³C and δ¹⁸O, organic δ¹³C, carbon weight %, and semi-quantitative mineral compositions based on XRD whole-pattern fitting, carbonate dissolution assays, and thin section analysis for samples from the Szypowaty section.
Figure 7: Inorganic δ¹³C and δ¹⁸O, organic δ¹³C, carbon weight %, and semi-quantitative mineral compositions based on XRD whole-pattern fitting, carbonate dissolution assays, and thin section analysis for samples from the Stradomka section.
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<td>-25.0</td>
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<td>53</td>
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Table 3: Isotopic and compositional data for the Moczarne section, Dukla Nappe. CO₂ (%) is from carbonate bomb or carbonate dissolution analysis. Mineral compositions based solely on XRD whole-pattern fitting are semi-quantitative. Mineral compositions less than 1% are not listed.
Table 4: Isotopic and compositional data for the Szypowaty section, Dukla Nappe. CO$_3$ (%) is from carbonate bomb or carbonate dissolution analysis. Mineral compositions based solely on XRD whole-pattern fitting are semi-quantitative. Mineral compositions less than 1% are not listed.
Figure 8: Gas chromatography curves for samples from the Moczarne section, Dukla Nappe.
5. X-ray diffraction analysis revealed that the primary constituents of samples were quartz, muscovite/illite, and occasionally calcite and/or siderite. Other minerals that were found in smaller or trace amounts included albite, montmorillonite, kaolinite, clinochlore, dolomite, ankerite, oligonite, rhodochrosite, rutile, anatase, ulvöspinel, pyrite, marcasite, and hauterite. Muscovite and illite commonly have nearly identical XRD responses and are therefore listed together. Glauconite is also included in the muscovite/illite category seeing as it is essentially an iron- and magnesium-rich variety of illite. A variety of cation substitutions resulted in many shifts in peak locations and intensities for the muscovite and illite minerals, complicating their evaluation. An example of a sample XRD curve juxtaposed over several of the commonly occurring mineral definitions is shown in Figure 9.

As mentioned before, WPF analysis did not compensate for unidentified phases in calculating weight percent and was limited in the number of mineral phases that could be integrated. Accuracy was improved where other assays helped to constrain the volume of specific components. Yet with the diversity of clays, carbonate minerals, metal oxides, presence of amorphous silica, etc., WPF analysis is regarded as merely being semi-quantitative.

5.4. Thin Section Results

Thin section analysis allowed for rough estimates of mineral abundances and attributes for the larger constituents in samples, but grains that required examination in magnifications above 200x were frequently obscured by mud-sized matrix and/or organic staining.

All samples bore significant amounts of quartz and mica clasts. Quartz grains were subangular to subrounded with poor sorting. Mica clasts were frequently fractured or contorted (see Figure 10), probably as a result of compaction. Small amounts of amorphous silica were found as groundmass or filling fossil cavities (see Figure 11).
Figure 9: (above) XRD scan of sample SP 12A. Increments on the y-axis correspond to intensity in counts (x1000). (below) Common XRD peaks for select minerals commonly identified in samples of this study, as defined by powder diffraction files (PDFs) of the International Centre for Diffraction Data (ICDD). Each mineral's strongest peak is reported as 100% with lesser peaks scaled accordingly.
Figure 10: Thin section photos of sample MO 7A in white light (above) and cross-polarized light (below) at 200x magnification. The bending and fracturing of the mica in the center probably occurred during compaction.
Figure 11: Thin section photos of MO 08C in (above) white light and (below) cross-polarized light at 400x magnification. Fossil chamber has been partially in-filled with siderite rhombs and amorphous silica (appears black in cross-polarized light in all orientations due to isotropy).
In siderite nodules, sedimentary structures were well preserved (see Figure 12). Siderite occurred predominately as subhedral rhombohedral crystals or amalgamations thereof (see Figures 13, 14, and 15). Calcite was found to occur in fossil remains (see Figures 15 and 16), nondescript clasts, and as cement in fractures (see Figure 12). In fossils, the calcite appears to have undergone recrystallization, pressure dissolution, and occasionally replacement.

Organic constituents were apparent as isolated particles, as a brown discoloration on other grains, or in-filling fractures. Pyrite was found to occur independently or as a replacing mineral in fossils (see Figure 16). Metal oxides were usually present in small or trace quantities.

5.5. SEM & EDAX Results

SEM and EDAX analysis served to document grain relationships, verify mineral abundances, and confirm the existence of trace minerals. However, the primary objective was to establish whether siderite and other carbonates were authigenic and syndepositional.

Three aspects of carbonate crystals were documented which provide evidence of primary deposition: involvement in compaction processes, sequential growth of multiple carbonate minerals, and the rimming of detrital grains with siderite.

Perhaps the most obvious evidence for siderite being authigenic and syndepositional was the involvement of siderite crystals in the mechanical fracturing of micas during compaction (see Figure 17). Siderite rhombs were also found to exist inside structurally-preserved fossil chambers where they may have provided internal support during compaction (see Figures 18).

Where sequential carbonate growth was observed, a gradational compositional change occurred between central anhedral to subhedral carbonate grains with compositions bordering between dolomite and ankerite being rimmed by a Mn-rich rim of rhodo-
Figure 12: Back-lit thin section of sample SP 17A at 1x magnification. Despite the presence of ~30% siderite, sedimentary structures remain relatively well preserved. White vein-filled fractures are filled with low-magnesian calcite. Blue areas are the epoxy used to mount the sample.
Figure 13: Thin section photos of SP 20A in white light at 40x (above) and 200x magnification (below). While subhedral siderite rhombs occur throughout the sample, they are occasionally concentrated locally such as on the vertical feature seen above.
Figure 14: Thin section photos of MO 08C at 200x magnification in white light (above) and cross-polarized light (below). The primary constituents in this view are a mud matrix with subhedral siderite rhombs scattered or grouped (e.g., upper left) throughout.
Figure 15: Thin section photo of MO 08C in white light at 400x magnification. What is potentially a foraminiferal chamber is visible in the center (marked with arrow) with recrystallized calcite within. Subhedral siderite rhombs, quartz grains, and occasional metal oxides occur throughout the clay matrix.
Figure 16: Thin section photo of MO 08A in top-sourced white light at 40x magnification. Shown fossil material is usually recrystallized low-magnesian calcite partially rimmed by pyrite (arrows), the latter possibly being an incipient stage of mineral replacement.
Figure 17: Backscatter electron (BSED) images from sample SP 17A. Image shows a mica (M) which was mechanically fractured by siderite (S) crystals, indicating that the siderite had formed prior to compaction. Pyrite (P) and quartz (Q) grains are also visible. Bright spots in the upper left are merely an electron-charging effect, not higher densities in the minerals.
Figure 18: Backscatter electron (BSED) images from sample SP 17A. Image shows siderite (S) infilling what is likely a foram chamber composed of calcite (C). The presence of the siderite may have helped preserve the chamber during compaction. Albite (A), mica (M), and clays (Cly) also visible. Partial rimming of detrital grains with siderite can be seen, as evidenced by siderite terminating against grains with orientations deviating from natural crystal faces (e.g., mica clast in upper right).
chrosite or oligonite which was in turn surrounded by siderite (see Figure 19). A similar compositional trend was documented by Dziubińska & Narębski (2004). This precipitation sequence is consistent with carbonate growth advancing through redox chemical zones during the initial and progressive burial of sediments.

Siderite was most commonly observed as subhedral rhombs scattered throughout the rock, consistent with the pervasive nucleation and growth discussed by Raiswell & Fisher (2000). Even so, they were occasionally found rimming detrital grains (e.g., see Figures 18 and 20) or occurring in concentrated groups, either by themselves (see Figure 21) or intergrown with pyrite (see Figures 20 and 22). The rimming of detrital grains with siderite was also documented by Dziubińska & Narębski (2004).

Calcite was found either as fossil material, filling fractures, or as amorphous grains. In certain fossils, remnant low-magnesian calcite is encased in silica which also fills the fossil chamber (see Figure 23). Thin section observations indicate that the silica is amorphous. No gradational compositional changes were observed between low-magnesian calcite and siderite, whether the calcite was in fossils or as cement in fractures. It is possible that pressure dissolution occurred where siderite rhombs or detrital grains contact calcite in fossils (e.g., see Figures 18 and 23). Where calcite filled fractures, gradational changes were observed between the initial fracture fill and the central fracture fill, with the low-magnesian calcite increasing in iron concentration toward the center of the vein-filled fractures (see Figure 24).

6. Discussion

Negative inorganic carbon isotope ($\delta^{13}C_{\text{calt}}$) ranges observed primarily in siderite samples indicate origins in the methanic zone or at the sulfidic-methanic interface. This interpretation is encouraged by the isotopic ranges and high concentration of dissolved inorganic carbon (DIC, a.k.a. carbonate alkalinity or $\Sigma CO_2$) typical of these zones (see
Figure 19: Secondary electron (SE), backscatter electron (BSED), and EDAX scans showing elemental distributions from sample SP 17A. Central calcium- and magnesium-rich carbonate grains (ankerite or dolomite) are rimmed by a manganese-rich carbonate (rhodochrosite or oligonite) which is in turn surrounded by siderite. Additional examples are shown in Figures AI-9 and AI-10 of Appendix I.
Figure 20: Secondary electron (SE) and backscatter electron (BSED) images from sample SP 20A. Image shows pyrite (P) replacing fossil material or intergrown with siderite (S). Deformed micas (M) and the partial or incipient rimming of detrital grains with siderite (arrows, lower right) may indicate that siderite precipitated prior to compaction.
Figure 21: Secondary electron (SE) and backscatter electron (BSED) images from sample SP 20A. Images shows subhedral siderite rhombs scattered randomly through the sample or grouped in masses (center and lower left).
Figure 22: Secondary electron (SE) and backscatter electron (BSED) images from sample SP 20A. Image shows pyrite (P) intergrown with siderite (S). In places, pyrite is pseudomorphous where it mimics rhombohedra. This indicates replacement, possibly of more soluble carbonates such as dolomite, ankerite, rhodochrosite, or oligonite.
Figure 23: Secondary electron (SE), backscatter electron (BSED), and EDAX scans showing elemental distributions in sample MO 8C. Calcite fossil fragment is visible in center with voids being in-filled with siderite rhombs and amorphous silica. Siderite rhombs may also be replacing calcite material or inducing pressure dissolution. Mg and Mn scans showed no prominent patterns.
Figure 24: Secondary electron (SE) and backscatter electron (BSED) images from sample SP 17A. Image shows low-magnesian calcite vein-filled fracture (vff). The BSED scan shows that the calcite became increasingly dense (lighter hue) in the inner part of the vein as more impurities (mainly Fe) were incorporated. The inclusion of subhedral siderite rhombs along with other detrital grains within the fracture indicates that the siderite rhombs formed prior to the calcite fill.
Figure 3), especially since the later would encourage the precipitation of carbonates. Due to the complexities involved in methane cycling and DIC sources, it is likely that the resulting carbonate $\delta^{13}$C values are a product of multiple sources and various, probably repeated, isotopic fractionations. The range of siderite $\delta^{13}$C$_{\text{stal}}$ values are nonetheless considered typical of methanogenic-related origins (see Figure 25 and Table 6). While most of the calcite-dominated samples had $\delta^{13}$C$_{\text{stal}}$ values that were unordinary, a few of them did exhibit sufficiently negative values to suggest methane-related origins.

Siderite and occasionally other carbonates in this study were also found to be authigenic and syndepositional as manifested by their role in compaction, internal compositional evolution consistent with evolving redox chemical zones, and rimming of detrital grains. This combined with their characteristically methanogenic-related isotopic values suggests that they precipitated in sediments where methane was being actively produced. Given depositional depths exceeding 2000 mbsl (Bak, 2004) and a hydrate stability boundary of 1400 mbsl or deeper (Dickens, 2001), methane hydrates were probably forming in these sediments along with the concretions during the late Paleocene and early Eocene.

Although most P/E $\delta^{13}$C curves have been created using inorganic carbonate material from fossil remains (e.g., Zachos et al., 2001), most samples in this study did not contain carbonate minerals. It was hoped that $\delta^{13}$C curves derived from the organic fraction of samples would reflect global $\delta^{13}$C shifts during the late Paleocene and early Eocene. Unfortunately, no correlation was apparent between the $\delta^{13}$C$_{\text{org}}$ data and published $\delta^{13}$C curves. A variety of processes could have masked the global $\delta^{13}$C signature in the organic fraction including early methane cycling, migration of fluids, or some other form of diagenesis or contamination not resolved by our limited GC analysis.

The negative trend in oxygen isotopes of this study could result from a combination of factors including $^{18}$O-depletion in the sulfate-reducing zone, precipitation at elevated temperatures, belated precipitation in a closed system, rapid precipitation in an open system, recrystallization, and water-sediment interactions (Mozley and Burns, 1993). Isolat-
Figure 25: Histogram comparing methanogenic-related CO₂ and siderite δ¹³C values listed in literature (adapted from Raiswell & Fisher, 2000; see Table 6) to isotopic ranges observed in this study. Siderite and calcite are shown in terms of number of samples dominated by each and by a sum of percentages (Σ%). Since average carbonate % is approximately 30% for carbonate-bearing samples, percentage sums were multiplied by 3 to improve visual comparison with the other categories. For example, where the -4 ±1‰ δ¹³C range contains two samples with 8% and 43% siderite, respectively, the Σ% value plotted on the y-axis (frequency) is (.08 + .43) x 3 = 1.53. The Σ% plots therefore represent δ¹³C distributions in terms of weight percent. The δ¹³C values in this study are bulk values, so some error is introduced by assuming the same isotopic ratios for samples containing multiple varieties of carbonate. Even so, the δ¹³C range of siderite in this study overlaps nicely with the range of methanogenic-related siderite reported in literature.
<table>
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<th>Publication</th>
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<td>Curtis et al., 1972</td>
<td>freshwater; Atchafalaya River Basin, Louisiana</td>
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<td>lower Miocene</td>
<td>-</td>
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<td>-</td>
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<td>Pearson &amp; Nelson, 2005</td>
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<td>70.7-84%</td>
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<td>Claypool et al., 2004</td>
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<td>51.2-82.7%</td>
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<td>Mackem &amp; Hutcheon, 1988**</td>
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<td>Fritz et al., 1971</td>
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<td>Mozley &amp; Carothers, 1992**</td>
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<td>Cretaceous (Neocomian)</td>
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<td>-</td>
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<td>U. Jurassic</td>
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<td>Fisher et al., 1998*</td>
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<td>freshwater; England</td>
<td>Pennsylvania</td>
<td>-</td>
<td>-3.09 to +10.35%</td>
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Table 6: Known inorganic $\delta^{13}$C ranges of siderite concretions associated with methanogenesis. *: Referenced by Raiswell & Fisher (2000); **: referenced by Mozley & Burns (1993). Frequency plots for data from these and other sources are shown in Figure 25.
ing a single cause to explain the $\delta^{18}$O data herein is impractical. Among the more likely factors is the release of $^{18}$O-depleted oxygen from sulfate and organic material as organic matter decomposes in the sulfate-reducing zone (Sass et al., 1991; Mozley and Burns, 1993). Increasing temperatures can also contribute to $^{18}$O-depletion. Carbonates precipitating in sediments moving deeper through the geothermal gradient inherit progressive levels of $^{18}$O-depletion (Mozley and Burns, 1993). Biogenic heat (e.g., from methanogens and sulfate-reducing bacteria) could also contribute to higher temperatures provided that heat generation exceeded heat diffusion (e.g., El-Fadel et al., 1996). Alternatively, preferential incorporation of $^{18}$O during initial authigenic mineral precipitation within a closed system will lead to decreased $\delta^{18}$O pore water values which could be inherited by siderite and other minerals which precipitate more slowly (Berner, 1981; Mozley and Burns, 1993). The decreasing of pore water $\delta^{18}$O can also be accomplished in an open system if precipitation occurs more rapidly than diffusion (Mozley and Burns, 1993). Recrystallization can also allow carbonates to equilibrate with the $\delta^{18}$O of pore water. The relative stability of siderite and low-magnesium calcite make them resilient to recrystallization, so the contribution of recrystallization is questionable. As for water-sediment interactions, they can lower $\delta^{18}$O by $> 7\%_{o}$ PDB as $^{18}$O is exchanged between minerals and pore waters, usually as volcanic ash or basalts alter into smectite (e.g., montmorillonite). An additional yet unlikely mechanism for depleting $^{18}$O in carbonates is exposure to meteoric water. While the most common explanation for substantially negatively-shifted $\delta^{18}$O values involves flushing sediments with meteoric water during diagenesis (Mozley and Burns, 1993), the depth of deposition for these sediments would likely preclude such a possibility.

Permeable conduits may have facilitated the formation of concentrated masses of authigenic minerals. Siderite, sometimes mixed with pyrite, is periodically found in amalgamated masses which are usually elongate (e.g., Figures 13 and 22). It is not unreasonable to suppose that the migration of enriched solutions through permeable sediments or fractures facilitated their precipitation.
Siderite will not form while sulfides are available to react with divalent iron, leading to the preferential formation of pyrite (Berner, 1991; Coleman et al., 1993; Appelo and Postma, 2005). When pyrite is found intergrown with and surrounded by siderite crystals, it either preceded the precipitation of siderite or diagenetically replaced carbonate material after the fact, probably dolomite, rhodochrosite, or another carbonate mineral with a higher solubility than siderite. This latter option of replacement seems viable where pyrite occurs in pseudomorphous rhombs (see Figure 22).

The occurrence of amorphous silica within microfossil cavities or as groundmass in deep-sea sediments is not uncommon (Calvert et al., 1977). Amorphous silica identified in this study through thin-section and EDAX analysis is therefore in harmony with the interpreted depositional environment.

While distinctive changes in clay mineralogy across the Paleocene-Eocene boundary have been documented in some areas (e.g., Gibson et al., 2000; Robert and Chamley, 1991; Robert and Kennett, 1992; Robert and Kennett, 1994), no notable changes in clay mineralogy were observed in these sections. Although changes in clay mineralogy can be induced by climatic changes, clays remain crude paleoclimate indicators. Shifts in chemical weathering processes that produce different clays are often slower than depositional processes, and erosion can mobilize clayey soil horizons that were produced millions of years in advance (Chamley, 1989; Gingele et al., 2001, Thiry, 2000; Thiry and Dupuis, 2000; Weaver, 1989). The lack of changes in clay mineralogy from the Paleocene to Eocene possibly signifies that erosion was keeping pace or exceeding chemical weathering in sediment source areas.

7. Conclusions

Siderite and occasionally other carbonates found in Paleocene and Eocene sediments of the Dukla Nappe are authigenic and furthermore likely originated in sediments where
methane cycling was active. This supports the idea that biogenic methane was being actively produced in continental margins during the Paleocene and Eocene. In turn, hydrate accumulations would have been able to accumulate on the margins where sufficient depth and frigid temperatures existed. By supporting the possibility of methane hydrates accumulating on continental margins, authigenic carbonates from this study provide supporting evidence for the hydrate dissolution hypothesis used to explain hyperthermals at the Paleocene-Eocene boundary and in the early Eocene.
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Appendix I: Supplemental Figures

Figure AI-1: Location of sample MO 3, Majdan Beds (Paleocene), Dukla Nappe.
Figure AI-2: Location of sample MO 5, Majdan Beds (Paleocene), Dukla Nappe.

Figure AI-3: Location of sample MO 7A, Hieroglyphic Beds (Paleocene-Eocene), Dukla Nappe.
Figure A1-4: Location of samples SP 9 and SP 9A, Majdan Beds (Paleocene), Dukla Nappe.

Figure A1-5: Location of sample SP 17A, Hieroglyphic Beds (Eocene), Dukla Nappe.
Figure A1-6: Location of sample S 5, Upper Istebla Shales (Paleocene), Silesian Nappe.

Figure A1-7: Location of samples S 14 and S 15, Upper Istebla Shales (Paleocene), Silesian Nappe.
Figure A1-8: Location of sample S 29, Variegated Shales (Eocene), Silesian Nappe.
Figure A1-9: Secondary electron (SE), backscatter electron (BSED), and EDAX scans showing elemental distributions from sample SP 17A. A calcium- and magnesium-rich carbonate grain (ankerite or dolomite) is rimmed by manganese-rich carbonate (rhodochrosite or oligonite) which is in turn surrounded by siderite. The grain in the upper left is quartz.
Figure A1-10: Secondary electron (SE), backscatter electron (BSED), and EDAX scans showing elemental distributions from sample SP 17A. Despite the rough surface being scanned, it is still apparent that a calcium- and magnesium-rich carbonate grain (ankerite or dolomite) is rimmed by manganese-rich carbonate (rhodochrosite or oligonite) which is in turn surrounded by siderite.