Carbon and oxygen isotope records of Permian brachiopods from relatively low and high palaeolatitudes: climatic seasonality and evaporation

Jesper Kresten Nielsen, Blazej Blazejowski, Piotr Gieszcz and Jan Kresten Nielsen

Geological Society, London, Special Publications v.376, first published November 26, 2012; doi 10.1144/SP376.6
Carbon and oxygen isotope records of Permian brachiopods from relatively low and high palaeolatitudes: climatic seasonality and evaporation

JESPER KRESTEN NIELSEN1,2*, BŁAŻEJ BŁAŻEJOWSKI3, PIOTR GIESZCZ4 & JAN KRESTEN NIELSEN5

1North Energy ASA, Kunnskapsparken, Markveien 38 B, NO-9504 Alta, Norway
2Department of Geology, University of Tromsø, Dramsveien 201, NO-9037 Tromsø, Norway
3Institute of Paleobiology, Polish Academy of Sciences, Twarda 51/55, PL 00-818 Warszawa, Poland
4Association of Polish Climatologists, ul. Międzynarodowa 58/36, PL03-922 Warszawa, Poland
5Statoil ASA, Field Development North, P.O. 273, NO-7501 Stjørdal, Norway

*Corresponding author (e-mail: jesperknielsen@gmail.com)

Abstract: Several brachiopods which belong to the same genus *Horridonia* of late Early and early Late Permian age in Spitsbergen and Poland, respectively, have been petrographically and geochemically analysed to verify seasonal variation in stable carbon and oxygen isotope values for palaeoclimatological implications. The specimens of *Horridonia timanica* from Spitsbergen show distinct cyclicity reflective of seasonal pattern, while those of *Horridonia horrida* from Poland do not. These differences are explained by the fact that the former lived at high palaeolatitudes at the northern margin of the supercontinent Pangaea where the seawater temperature differences between winter and summer seasons were greater, as expressed in the isotopic composition of the skeletal materials. In contrast, the shell growth of *Horridonia horrida* was subjected to strong evaporative influence by climatic variations in the eastern area of Pangaea.

Carbon, oxygen and strontium isotopes of brachiopods of a wide range of ages are often used to determine seawater isotopic composition chemostratigraphic correlation and characteristics of their living habitat such as seawater temperature and thereby palaeoclimate. Studies of brachiopods include: the Wegener Halvø Formation of Permian age in East Greenland (Scholle et al. 1991; Scholle 1995); the Carboniferous and Permian of Kansas, Texas and New Mexico (Magaritz et al. 1983; Given & Lohmann 1986; Grossman et al. 1991, 1993, 1996; Mii & Grossman 1994); Silurian brachiopods from Gotland in Sweden (Bickert et al. 1997); Upper Pleistocene brachiopods from New Zealand (Curry & Falllick 2002); Late Palaeozoic brachiopods from North America (Popp et al. 1986; Brand 1989); Early–Middle Permian bivalves and brachiopods from Australia (Korte et al. 2008; Ivany & Runnegar 2010; Mii et al. 2012) and the Kapp Starostin Formation on Spitsbergen of the archipelago Svalbard (Gruszczyn’ski et al. 1992; Mii et al. 1997); and more geographically widespread studies (Grossman 1994; Veizer et al. 1997; Korte et al. 2005; Korte & Kozur 2010) and studies of modern brachiopods (Lowenstam 1961; Barbin & Gaspard 1995; Carpenter & Lohmann 1995; James et al. 1997; Auclair et al. 2003; Brand et al. 2003). The majority of brachiopod species have shells that are composed of low-magnesium calcite, which is the most stable skeletal carbonate over geological timescales; such brachiopod shells are therefore less susceptible to diagenetic alteration. Advanced petrography such as cathodoluminescence and scanning electron microscopy of shell material and its microstructure is crucial for exploring the possibility of fabric-retentive and non-luminescent materials, that is, well-preserved primary shell materials (e.g. Rush & Chafetz 1990; Barbin & Gaspard 1995; Mii et al. 1997). Isotopic compositions of brachiopods have often shown to be comparable to those of marine cements and thereby seawater (Given & Lohmann 1985; Scholle et al. 1991). A detailed sub-sampling of growth bands of brachiopods can be utilized to obtain the carbon and oxygen (and strontium) isotope values of past seawater, especially for chemostratigraphic correlations. Such isotope

studies of brachiopods can be placed in a biogeo-
ographic and palaeoclimatic context (e.g. Shen &
Shi 2000, 2004) to unravel seasonality during
growth of the brachiopods (Grossman et al. 1996).
To investigate whether the isotopic compositions
of late Early and early Late Permian brachiopods
of the same genus from Spitsbergen and Poland
can be used to determine seasonal variation, we
have carried out a series of carbon and oxygen
isotope analyses on increment level. It is shown
that the analysis of preserved microstructures of
the productid brachiopods of Horridonia horrida
(Sowerby 1823) and H. timanica (Stuckenberg
1875) are useful in determining the palaeoclimate
and, to some extent, the palaeoceanographic con-
ditions during the Permian. The specimens from
the northern margin of Pangea show distinct cycli-
city (seasonal pattern), while those from Poland
do not.

Geological setting
A marked change in the lithofacies and biofacies
encountered for the Tempelfjorden Group (late
Artinskian–Wuchiapingian, possibly Changhsin-
gian) and the underlying Gipsdalen Group (late
Serpukhovian–early Artinskian) and Bjarmeland
Group (late Sakmarian–early Kungurian) on Sval-
bard and in the Norwegian Barents Sea (Figs 1 & 2)
characterizes a major climatic change as the super-
continent Pangea drifted northwards and the oceanic
current systems underwent change related to rifting
(Beauchamp 1994; Stemmerik & Worsley 2005;
Stemmerik 2008; Worsley 2008). Intracratonic rift
systems developed to the west of Svalbard and the
Boreal Realm became connected via the Green-
land–Norway Sea, forming the Zechstein seaway
to the central European Zechstein basins (the North-
eren Permian Basin and Southern Permian Basin;
Ziegler 1990; Stemmerik et al. 1991; Ziegler et al.
1997; Figs 3–5). During the Late Carboniferous–
Late Permian, the present-day Spitsbergen drifted
approximately from 20° N to 45° N (Stemmerik 2000;
Golonka 2011; Fig. 1) while the Southern Perm-
ian Basin was located c. 30° further to the south.
Along this south–north-trending seaway, the climate
changed from arid evaporative subtropical environ-
ment at low palaeolatitudes to temperate colder
environment further north (Stemmerik 1995, 2000).
Along the Norwegian–Greenland seaway, the
Ravnefjeld Formation (onshore East Greenland)
and the offshore Mid Norway of Wuchiapingian
age are regarded to be time-equivalent to the Kup-
ferschiefer (Stemmerik 1995; Stemmerik et al.
2001; Bugge et al. 2002; Menning et al. 2006)
and, further north, roughly equivalent to the Kapp
Starostin, Røye and Ørret formations (Stemmerik
& Worsley 2005; Figs 2 & 5). As for the Kup-
ferschiefer, Ravnefjeld, Kapp Starostin and Ørret
Formations, dysoxic to anoxic sulphidic bottom-
water conditions existed in deeper waters of the
European Zechstein basins (Pancost et al. 2002),
the East Greenland Basin (Nielsen & Shen 2004;
Nielsen et al. 2010) and the Barents Shelf and Spits-
bergen (Nielsen et al. 2012).

Fig. 1. Palaeogeographic map of the Guadalupian time. Modified from Golonka (2011). Blue: deep basin; pale
blue: shelf area; orange: topographic highs, inactive tectonically; pale brownish: topographic medium to low,
inactive tectonically.
Boreal realm (Spitsbergen)

Cutbill & Challinor (1965) introduced the term Tempelfjorden Group (equivalent to the Russian name Starostinskaya Svita) for a suite of spiculites (spiculitic chert), siliceous (spiculitic) shales and siltstones with intercalated minor glauconitic sandstones and silicified skeletal limestones of late Early–Late Permian age (late Artinskian–Kazanian) in the onshore areas (Stemmerik 1988; Nakrem 1991, 2005; Mangerud 1994; Fig. 2). The carbonates contain a fauna often dominated by brachiopods, sponges, bryozoans and crinoids. The type area for the Tempelfjorden Group is in the innermost part of Isfjorden in central Spitsbergen (Cutbill & Challinor 1965; Dallmann et al. 1999). The Kapp Starostin Formation of the Tempelfjorden Group has its type section in the Festningen section (Frebold 1937; Orvin 1940; Dallmann et al. 1999). The lowermost part of the Kapp Starostin Formation is dominated by sandy bioclastic limestone with a rich brachiopod and bryozoan fauna in the up to 20 m thick Vøringen Member (the so-called ‘Spirifer limestone’; late Artinskian–early Kungurian age), overlaid by alternating shales, siltstones and cherts and siliceous limestones of the Svenskeegga Member (Kungurian–Kazanian). The uppermost unit, the c. 50 m thick Hovtinden Member (Kazanian–Tatarian), is composed of shales and siltstones with few fossils (Nakamura et al. 1987; Małkowski 1988; Stemmerik 1988; Mangerud & Konieczny 1993; Nakrem 1995; Dallmann et al. 1999). The age of the Vøringen Member is based on conodonts (Szaniawski & Małkowski 1979), non-fusulinid foraminifers in the underlying Gipsdalen Group (Sosiptrova 1967, 1969; Błaz˙ejowski 2009), palyynomorphs (Mangerud & Konieczny 1993) and bryozoans (Nakrem 1995). Although the age of the upper part of the Kapp Starostin Formation is somewhat problematic, Nakrem et al. (1992) indicate a Kazanian age (see also Nakrem 2005). Based on the similarities of the brachiopod faunas between the upper part of the Kapp Starostin Formation and the Foldvik Creek Group in East Greenland, the
The upper part of the Kapp Starostin Formation may be of Kazanian–early Tatarian age (Stemmerik 1988; Fig. 2). Time-equivalent deposits are found offshore in the Norwegian Barents Sea where the spiculitic deposits of the Røye Formation and shales of the Ørret Formation are especially well described from the eastern Finnmark Platform (southeastern Norwegian Barents Sea; Henriksen et al. 2011). The Tempelfjorden Group usually thins over local structural highs, where the exposures on Bjørnøya on the Stapp High (western Norwegian Barents Sea), for example, show an extremely condensed development of c. 115 m in thickness development. Highly condensed exposures on the margins of the Sørkapp-Hornsund High of Spitsbergen are only a few metres thick and pinch out over the structure (Hellem & Worsley 1978). The thickness of the Kapp Starostin Formation reaches up to 460 m; it is 380 m in the type section at Isfjorden (the Festningen section) and becomes highly condensed and pinches out on the eastern margin of the Sørkapp-Hornsund High (Malkowski 1982, 1988; Steel & Worsley 1984; Dallmann et al. 1999). The Tempelfjorden Group was deposited during an overall transgression accompanied by retrogradation of the coastline (Fig. 2). The main accumulations of spiculites of the Kapp Starostin Formation are related to transgressive periods when favourable environmental conditions for sponges prevailed over most of the shelf. Cool-water bryozoan carbonates formed along the margins and formed low-relief platforms during sea level highstand (Larssen et al. 2005). Above the Vøringen Member, abundant trace fossils such as Zoophycos and Chondrites indicate low-energy as well as oxic to dysoxic bottom waters well below normal

Fig. 3. Palaeogeographic map of the Greenland–Norwegian seaway, Norwegian Barents Sea and Svalbard (Kazanian time). Slightly modified from Stemmerik (2000).
wave base (Małkowski 1988; Nakrem 2005; Nielsen et al. 2012). Such depositional conditions were punctuated by the development of a stratified water column where anoxic and sulphidic bottom waters persisted for a shorter time, based on sedimentological, palaeoecological and geochemical evidence (Małkowski & Hoffman 1979; Małkowski 1982, 1988; Nielsen et al. 2012). Other factors controlling the distribution of the brachiopods may also be substrate mobility, particularly of the spiculitic deposits found above the Vøringen Member (Małkowski 1988) where brachiopods are only occasionally found in coquinas which may represent storm rework (Nakrem 2005).

The main groups of fossils in the Kapp Starostin Formation comprise brachiopods, sponges (mainly siliceous), bryozoans, foraminifers, ostracods, echi-noderms (crinoids), bivalves, gastropods, echinoderms (crinoids), bivalves, gastropods, corals and algae (e.g. Siedlecka 1970; Małkowski 1988; Nakrem 2005; Błaz´ejowski 2008). The fine-grained sediments are dominated by abundant delicate bryo-zoans, trepostomids, rhabdomesids, cryptostomids and fenestellids, while the more robust trepostomids, Polyposa, Acanthocladia and Reteporidra, dominate the partially silicified limestones (Nakrem 1994, 1995). Most of the fossils are typical cool-to cold-water forms while the occurrence of temperate to warm-water forms of corals, trilobites and ammonoids are rare, according to Nakrem (2005).

Assemblages of brachiopods from ten outcrops of the Kapp Starostin Formation in central and southern Spitsbergen have been comprehensively described by Małkowski (1988) (Figs 2 & 6). The majority of the over 2500 specimens are well preserved, often with clearly visible morphology, growth bands, inner structure and microstructure of the shell (Figs 6–8), except for a few partially silicified (Małkowski 1988) and/or partially replaced with blocky low-Mg calcite (Figs 6 & 7) specimens. At the Vindodden section (Fig. 9), the Vøringen Member (c. 40 m thick) is composed of fossiliferous biocalcarenites and biomicrites interbedded with non-fossiliferous marly sediments with some gravel. The fossil assemblage is dominated by abundant productids, such as Horridonia timanica, and other brachiopods such as spiriferoids including mostly broken bryo-zoans, crinoids and bivalves. The Svenskeegga Member (c. 180 m thick) is dominated by spiculitic deposits and some marly limestones containing bryo-zoans, cystoid crinoids, pectenid bivalves, solitary corals and rare gastropods, but somewhat fewer brachiopods (Małkowski 1988). The latter are mainly confined to the storm-induced coquinas and platform edge bars above normal wave base during lower sea level (Nakrem 2005). Dark shales and locally developed glauconitic porous sandstones of the Hovtinden Member (c. 110 m thick) contain some productids, spirifer- ids, bryo-zoans, bivalves and solitary corals. Size of the Horridonia timanica varies somewhat throughout the formation, often well preserved in or close...
to life position. Their disappearances and reappearance are related to facies zones and most likely to fluctuations in oxygen deficiency and substrate properties (most likely substrate nature), as they have been found in northeastern Spitsbergen (Małkowski 1988). The lifestyle of *Horridonia timanica*, *Svalbardoproductus arctius* and *Anemosaria pseudohorrida* was stabilization in the sediment, commonly on coarse-grained loose substrates rich in skeletal debris, by anchoring and supporting it with their long and straight spines. The spines grow mainly on the margins of the ventral valve and on the auricle edges (Małkowski 1988). Małkowski (1988) also indicates that the *Horridonia timanica* is valuable as an indicator of the environment.

The mode of life of brachiopods such as Waagenoconcha irginae and Kochiproductus porrectus was floating at the surface of the soft substrate and such as Linoproductus dorotheevi that was velum-bearing forms within the sediment. Waagenoconcha irginae lived between the skeletal banks dominated by *Horridonia timanica* and *Svalbardoproductus arctius*. Other brachiopods achieve stability of the shell by the resistance of the ventral valve, but lack spines (Małkowski 1988).
Southern Permian Basin (Poland)

The Rotliegend of Germany, Netherlands and Poland begins in the latest Carboniferous Gzhelian Stage and continues into the Late Permian Wuchiapingian Stage, while the overlying Zechstein can be correlated with the Middle Wuchiapingian and most of the Changhsingian Stage (Figs 4 & 5) (Wagner 1994; Johnson et al. 1994; Kiersnowski et al. 1995; Geluk 1999; Brauns et al. 2003; McCann et al. 2008). The Zechstein–Buntsandstein boundary does not coincide with the Permian–Triassic boundary but is still latest Permian in age based on conchostracans, palaeomagnetic and palynological data (e.g. Geluk & Röhling 1997; Kozur 1999; Szurlies et al. 2003; Menning et al. 2006). Megasporas, conchostracans and magneetostratigraphy indicate that the Permian–Triassic boundary is located c. 30 m above the base of the Lower Buntsandstein (in the M2 cycle; Kozur 1999; Szurlies et al. 2003), that is, the Zechstein–Buntsandstein boundary is about 0.1 Ma older than the Changhsingian–Indusian (i.e. Permo-Triassic?) boundary (Menning et al. 2006).

During the Permian, the Norwegian–Greenland seaway was established by southwards transgression preceded by intra-Kungurian pulses of rifting which, in combination with glacio-eustatic sea level rise due to the deglaciation in Gondwana, reached the Northern Permian and Southern Permian basins (Surlyk et al. 1986; Ziegler 1990; Stemmerik 1995; Ziegler et al. 1997). These basins were topographic lows and became rapidly flooded (Glennie & Buller 1983). An arid climate and a repeated tectonic and glacio-eustatic restriction on renewal supply of marine waters from the north resulted in deposition of the cyclical Zechstein Group (Fig. 5). The Zechstein Group is very variable in thickness, partly as a result of post-depositional salt movements (halokinesis). The cycles typically comprise transgressive anoxic shales of the Kupferschiefer followed by carbonates and thick evaporites (mostly anhydrite and halite), occasionally intercalated with local clastic rocks. Evaporites such as halite...
dominate the basin-centre sequences, while limestones, dolomites and some anhydrites prevail along the basin margins (Fig. 4; Wagner 1994; Kiersnowski et al. 1995; Geluk 2007; McCann et al. 2008; Peryt et al. 2010). After the initial transgression, the Southern Permian Basin reached 200–300 m of water depth (Ziegler 1990). Each cycle becomes progressively more evaporitic, finally ending with potash deposits. We have investigated brachiopods from limestones of the oldest cyclothem (PZ1, Poland), which is time-equivalent to the Z1 Werra cycle in NW Germany (Fig. 5). The limestones are confined to shallow waters in basin margin areas and on intra-basinal highs, where a

Fig. 7. Photomicrographs of the microstructures of the brachiopods. (a) Primary microstructure of Horridonia horrida (Sowerby 1823), Kajetanów quarry, Poland (ZPAL Bp. IX/1 K). (b–f) Microstructures of the Horridonia timanica (Stuckenber 1875), Vindodden section, Spitsbergen (ZPAL Bp. XXX/V-414). (b, c) Well-preserved primary microstructure. (d) Surface structures. (e, f) Blocky calcite has replaced smaller parts of the shell.
rich fauna with a close affinity to the Norwegian–Greenland seaway and the Boreal Realm lived. The deposits sequence of Z1 is considered as being formed in an arid climate within a shallow intra-continental sea (Wagner & Peryt 1997; Słowakiewicz et al. 2009).

Fig. 8. Cathodoluminescence of the brachiopods. The non-luminescent to slightly luminescent (dark grey to black) is that part of the skeleton which holds its origin. (a–d) Horridonia horrida (Sowerby 1823), Kajetanów quarry, Poland. Sample ZPAL Bp. IX/65 K. The shells are slightly to non-luminescence except for a very few yellowish luminescing calcite infilled fractures. Some of the shells have worked as umbrella for early diagenetic yellow to brownish luminescing calcite cements. Examples of (a) umbo, (b) central portion of valve, (c) non-luminescing outer layer of central portion of valve and (d) hinge area. (e) Horridonia timanica (Stuckenbergen 1875), Vindodden section, Spitsbergen. Sample ZPAL Bp. XXX/V-5. The shell is non-luminescing except for a slightly luminescing calcite infilled fracture. Samples for isotope analysis were taken from non-luminescing parts containing a seawater isotope signature (avoiding sampling of the luminescing diagenetic-influenced parts).
Brachiopods from the Lower Zechstein black limestones, Kajetano´w, Poland

Investigated material was collected from abandoned quarry in Kajetano´w village which is situated c. 10 km northward of Kielce (Holly Cross Mountains region, central Poland) (Figs 4 & 5). Dark and black limestones and marls bedded rhythmically dipping northwards at 12–15° are cut by minor faults and appear in the western wall of the Kajetano´w quarry. The name Kajetano´w Limestones was introduced by Pawłowska (1978); at present they form a succession of up to 8 m thick. The limestones are medium- and thin-bedded, and show discrete horizontal and wavy lamination. An admixture of quartz grains, mica flakes and scattered pyrite as well as small sandstone clasts accompanied by pyritized bioclasts and fragments of plants are visible in thin sections. The lower part of the profile – the Productus Limestones – consists of medium- and thick-bedded limestones intercalated by marls (c. 1.5 m thick), dated by the occurrence of brachiopod Horridonia horrida (Sowerby 1823). The upper part of the profile pass into stratified medium- and thin-bedded limestones and marls (c. 4 m thick, the Strophalosia Marls) with abundant macro- and microfossils that are represented by Horridonia horrida (Sowerby), Strophalosia morrisiana King, Dielasma elongatum Schlotheim, Lingula credneri Geinitz, Bakewella ceratophaga Schlotheim, B. antiqua Verneull, Nucula beyrichi Schlotheim, Stenopora columnaria Schlotheim, Acanthocladia anceps Schlotheim and Agathamina pusilla Geinitz (after Fijałkowska-Mader 2010; see also Jurkiewicz 1962; Kaz´mierczak 1967).

Materials and methods

For the purposes of this study, we have chosen to investigate two species Horridonia horrida (Sowerby 1823) and Horridonia timanica (Stuckenberg 1875) based on their abundance and preservation, including the evidence of autochthonous (i.e. isotopically analysed) specimens which were collected in their life position.

The specimens of Horridonia horrida come from the Lower Zechstein black (bituminous) limestones from Kajetanów, Holly Cross Mountains, Poland (Kaz´mierczak 1967; Figs 4, 5 & 10). The material was collected by J. Kaz´mierczak during summer 1964 in the Kajetanów quarry and in several outcrops in the western part of Gałe ˛zice-Kowala syncline in the Holy Cross Mountains, southern Poland. The collection is housed in the Institute of Palaeobiology, Polish Academy of Sciences, and has unique value since the outcrops no longer exist. The collection, which numbers a total
of 89 specimens as well as a few separate valves, is marked with the catalogue numbers ZPAL Bp. IX/1–137 (Kazmierczak 1967).

The brachiopods *Horridonia timanica* are from the Vøringen Member of the Kapp Starostin Formation (Tempelfjorden Group, late Early–Late Permian), Vindodden, central Spitsbergen (Figs 2 & 9). The material examined in this paper is from the Vindodden section, one of 10 sections of the Kapp Starostin Formation from where K. Małkowski collected his brachiopods (described in detail in 1988). Małkowski’s collection is housed in the Institute of Palaeobiology of the Polish Academy of Sciences, Warsaw, labelled ZPAL Bp. 1–2500 (Małkowski 1988).

To exclude the possibility of diagenetic overprint in the investigated fossil shells (e.g. Popp et al. 1986; Brand et al. 2003), we examined the chosen samples using scanning electron microscopy (SEM) with an energy-dispersive spectrometer (EDS). Carbon-coated fragments and polished thin sections of the samples were examined in secondary electron (SE) and backscatter electron (BSE) operational modes, respectively. In that way, we could examine microstructure and composition in two and three dimensions.

Thick polished sections of *H. horrida* and *H. timanica* shell were examined using plane light and cathodoluminescence (CL) microscopy. CL analyses were carried out on a Technosyn Model 4000.

Table 1. Carbon and oxygen isotopic composition of Horridonia timanica (Stuckenberg 1875) from Spitsbergen

<table>
<thead>
<tr>
<th>Sample ZPAL Bp. XXX/V-42</th>
<th>Sample ZPAL Bp. XXX/V-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subsample No.</td>
<td>δ¹³C (‰)</td>
</tr>
<tr>
<td>1</td>
<td>3.40</td>
</tr>
<tr>
<td>2</td>
<td>3.78</td>
</tr>
<tr>
<td>3</td>
<td>3.71</td>
</tr>
<tr>
<td>4</td>
<td>3.84</td>
</tr>
<tr>
<td>5</td>
<td>4.20</td>
</tr>
<tr>
<td>6</td>
<td>4.46</td>
</tr>
<tr>
<td>7</td>
<td>4.05</td>
</tr>
<tr>
<td>8</td>
<td>3.81</td>
</tr>
<tr>
<td>9</td>
<td>4.08</td>
</tr>
<tr>
<td>10</td>
<td>4.42</td>
</tr>
<tr>
<td>11</td>
<td>4.81</td>
</tr>
<tr>
<td>12</td>
<td>3.92</td>
</tr>
<tr>
<td>13</td>
<td>3.79</td>
</tr>
<tr>
<td>14</td>
<td>4.34</td>
</tr>
<tr>
<td>15</td>
<td>4.33</td>
</tr>
<tr>
<td>16</td>
<td>4.25</td>
</tr>
<tr>
<td>17</td>
<td>3.88</td>
</tr>
<tr>
<td>18</td>
<td>4.06</td>
</tr>
<tr>
<td>19</td>
<td>4.46</td>
</tr>
<tr>
<td>20</td>
<td>4.17</td>
</tr>
<tr>
<td>21</td>
<td>4.48</td>
</tr>
<tr>
<td>22</td>
<td>4.59</td>
</tr>
<tr>
<td>23</td>
<td>4.34</td>
</tr>
<tr>
<td>24</td>
<td>3.98</td>
</tr>
<tr>
<td>25</td>
<td>4.03</td>
</tr>
<tr>
<td>26</td>
<td>4.18</td>
</tr>
<tr>
<td>27</td>
<td>4.03</td>
</tr>
<tr>
<td>28</td>
<td>3.77</td>
</tr>
<tr>
<td>29</td>
<td>4.13</td>
</tr>
<tr>
<td>30</td>
<td>4.19</td>
</tr>
<tr>
<td>31</td>
<td>3.87</td>
</tr>
<tr>
<td>32</td>
<td>3.72</td>
</tr>
<tr>
<td>33</td>
<td>3.38</td>
</tr>
<tr>
<td>34</td>
<td>3.54</td>
</tr>
<tr>
<td>35</td>
<td>3.16</td>
</tr>
</tbody>
</table>
8200 MK II CL stage coupled to an Olympus microscope (Grossman et al. 1993). The digital images were taken with Nikon DS-Ri1 camera. Any diagenetically altered shell materials were eliminated from further analyses.

Prior to taking carbonate samples, the shell was cleaned to remove any surface contamination. Individual carbonate powder samples (>50 µg) were millcut under the microscope sequentially from the outer layer along the axis of maximum growth from the interior area less influenced by diagenesis. Spatial resolution was c. 1 mm.

For stable isotope analysis, the carbonate powder was reacted with 100% orthophosphoric acid under vacuum at 70 °C in a KIEL IV carbonate device, which was coupled to a Finnigan MAT Delta Plus isotope ratio mass spectrometer. Isotope ratios are reported in per mil (‰) in the usual delta notation relative to the VPDB (Vienna Peedee Belemnite) standard (defined via NBS 19). The spectrometer external error amounts to less than ±0.08 ‰. Experiments carried out on sample replicates showed that the average difference between replicates was less than ±0.15 ‰ for δ13C and δ18O.

Shell morphology

*Horridonia timanica* (Stuckenberg 1875) has a large trapezoid shell with auricles, where the ornamentation is absent or granular (Figs 6 & 7). There is a narrow umbo and a distinct sinus. The spines are thick and straight according to Małkowski (1988). As shown in Małkowski’s figure (1988, fig. 7), the phenotypic variation of *H. timanica* in the Kapp Starostin Formation may include the following variable features: shell size, shell coiling, auricle size, ornamentation density, spine distribution and the presence or absence of growth lines. The size of *H. timanica* ranges from 18.2 to 83.3 mm in width and from 14.8 to 74.0 mm in length (Małkowski 1988).

*Horridonia horrida* (Sowerby 1823) is generally sub-pentagonal to sometimes sub-oval in outline, with the largest convexity occurring in the middle part and large triangular ears (Fig. 6). The anterior margin is bent and forms a single fold. The ventral valve is strongly convex. The umbo is large and broad and the sulcus is broad and shallow. The dorsal valve is slightly concave and almost flat, but with a slightly outlined broad fold. The ornamentation is smooth, although concentric irregular wrinkles are clearly visible. Growth lines are often rather densely distributed and may show disturbances along the anterior margin. The ventral valves are thickest at umbo and the areas of muscle fields. On both valves, spines are distributed along the hinge margin and thick long auricular spines occur on the ears. The microstructure of hollow spines is similar to the valves. The external morphology may vary by differences in shell coiling and in width of the ears related to the length of hinge margin. The size of *H. horrida* ranges from 26 to 56 mm in width and from 16 to 47 mm in length, according to Kaźmierczak (1967).

*Horridonia horrida* is strongly characterized by the costae on the anterior part of the ventral valve (Dunbar 1955, 1961; Kaźmierczak 1967). *Horridonia timanica* differs from *H. horrida* in the lack of hinge and auricular spines on the ventral valve, granular ornamentation, more massive hinge and generally larger dimensions (Kaźmierczak 1967).

*Horridonia horrida* from the Holy Cross Mountains, Poland is identical to those described from: the Lower Zechstein (Werra cyclothem) of the Outer...
Sudetic Basin and the Fore-Sudetic Monocline, Poland; the Zechstein of Middle England (Marl Slate, Magnesian Limestone); the Lower Zechstein of Germany (Kupferschiefer shales and Zechsteinkalk limestones); the Zechstein of Lithuania (Kaźmierczak 1967); and Late Permian of East Greenland (Dunbar 1955, 1961). H. horrida has however not been found in the Arctic Europe and Russia (Kaźmierczak 1967).

H. timanica has been described from the Permian of Spitsbergen.

Table 2. Carbon and oxygen isotopic composition of Horridonia horrida (Sowerby 1823) from Poland

<table>
<thead>
<tr>
<th>Subsample No.</th>
<th>δ¹³C (‰)</th>
<th>δ¹⁸O (‰)</th>
<th>Subsample No.</th>
<th>δ¹³C (‰)</th>
<th>δ¹⁸O (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.41</td>
<td>-4.30</td>
<td>1</td>
<td>3.33</td>
<td>-3.48</td>
</tr>
<tr>
<td>2</td>
<td>4.83</td>
<td>-4.45</td>
<td>2</td>
<td>2.91</td>
<td>-3.75</td>
</tr>
<tr>
<td>3</td>
<td>4.84</td>
<td>-4.21</td>
<td>3</td>
<td>2.63</td>
<td>-4.33</td>
</tr>
<tr>
<td>4</td>
<td>4.93</td>
<td>-4.09</td>
<td>4</td>
<td>3.57</td>
<td>-4.67</td>
</tr>
<tr>
<td>5</td>
<td>4.94</td>
<td>-3.76</td>
<td>5</td>
<td>3.89</td>
<td>-4.54</td>
</tr>
<tr>
<td>6</td>
<td>4.79</td>
<td>-3.67</td>
<td>6</td>
<td>3.63</td>
<td>-4.32</td>
</tr>
<tr>
<td>7</td>
<td>4.47</td>
<td>-3.35</td>
<td>7</td>
<td>3.59</td>
<td>-3.28</td>
</tr>
<tr>
<td>8</td>
<td>4.33</td>
<td>-3.17</td>
<td>8</td>
<td>3.97</td>
<td>-2.72</td>
</tr>
<tr>
<td>9</td>
<td>4.29</td>
<td>-3.25</td>
<td>9</td>
<td>4.32</td>
<td>-2.48</td>
</tr>
<tr>
<td>10</td>
<td>4.41</td>
<td>-2.95</td>
<td>10</td>
<td>4.54</td>
<td>-2.51</td>
</tr>
<tr>
<td>11</td>
<td>4.44</td>
<td>-2.81</td>
<td>11</td>
<td>4.48</td>
<td>-3.00</td>
</tr>
<tr>
<td>12</td>
<td>4.28</td>
<td>-2.75</td>
<td>12</td>
<td>4.34</td>
<td>-3.39</td>
</tr>
<tr>
<td>13</td>
<td>4.40</td>
<td>-2.35</td>
<td>13</td>
<td>3.70</td>
<td>-2.22</td>
</tr>
<tr>
<td>14</td>
<td>3.89</td>
<td>-2.49</td>
<td>14</td>
<td>4.68</td>
<td>-2.47</td>
</tr>
<tr>
<td>15</td>
<td>4.59</td>
<td>-1.94</td>
<td>15</td>
<td>4.30</td>
<td>-2.65</td>
</tr>
<tr>
<td>16</td>
<td>3.84</td>
<td>-2.15</td>
<td>16</td>
<td>4.04</td>
<td>-1.97</td>
</tr>
<tr>
<td>17</td>
<td>3.98</td>
<td>-2.14</td>
<td>17</td>
<td>4.37</td>
<td>-2.41</td>
</tr>
<tr>
<td>18</td>
<td>4.27</td>
<td>-1.62</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>4.26</td>
<td>-1.44</td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>4.38</td>
<td>-1.90</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>4.65</td>
<td>-1.89</td>
<td>21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>4.08</td>
<td>-2.45</td>
<td>22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>2.62</td>
<td>-2.75</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>3.36</td>
<td>-2.79</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>3.17</td>
<td>-3.90</td>
<td>25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Main statistical parameters and Pearson correlation coefficients of the isotopic compositions shown in Tables 1 and 2

<table>
<thead>
<tr>
<th>Horridonia timanica</th>
<th>Horridonia timanica</th>
<th>Horridonia horrida</th>
<th>Horridonia horrida</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample ZPAL Bp. XXX/V-42</td>
<td>n = 35</td>
<td>Sample ZPAL Bp. XXX/V-5</td>
<td>n = 30</td>
</tr>
<tr>
<td>δ¹³C (‰)</td>
<td>δ¹⁸O (‰)</td>
<td>δ¹³C (‰)</td>
<td>δ¹⁸O (‰)</td>
</tr>
<tr>
<td>Maximum</td>
<td>4.81</td>
<td>-4.37</td>
<td>5.66</td>
</tr>
<tr>
<td>Mean</td>
<td>4.03</td>
<td>-5.93</td>
<td>5.10</td>
</tr>
<tr>
<td>Minimum</td>
<td>3.16</td>
<td>-8.19</td>
<td>4.34</td>
</tr>
<tr>
<td>Correlation coefficient</td>
<td>0.69</td>
<td>0.44</td>
<td>-0.24</td>
</tr>
</tbody>
</table>
Stable isotopic composition

Carbon and oxygen isotopes have been analysed from two valves of *Horridonia timanica* (Table 1). The subsamples have δ¹³C values ranging from 3.16 to 5.66‰. The δ¹⁸O values are between −8.19 and −3.43‰. The correlation coefficients between δ¹³C and δ¹⁸O are 0.69 and 0.44 in the valves ZPAL Bp. XXX/V-42 and ZPAL Bp. XXX/V-5, respectively. The correlation is moderately positive, and the curves of δ¹³C and δ¹⁸O indicate some cyclical pattern (Fig. 11).

Two valves of *Horridonia horrida* have also been analysed isotopically (Table 2). The subsamples show δ¹³C values between 2.62 and 4.94‰ (Table 3). δ¹⁸O values vary between −4.67 and −1.44‰. Concerning the valve ZPAL Bp. IX/1 K, the correlation coefficient between δ¹³C and δ¹⁸O is −0.24 and indicates no significant relationship. In contrast, the correlation coefficient is moderately positive (0.61) for the valve ZPAL Bp. IX/7 K. There is no distinct cyclical nature in the sets of isotope values from *H. horrida* (Fig. 12).

Seasonality and evaporation

The δ¹⁸O values within *Horridonia timanica* show a recurring pattern that may be interpreted in terms of seawater temperature in the habitat. It assumes that the salinity was constant during the life duration of the sampled growth increments. This method of interpretation requires that the so-called vital effect upon oxygen isotopic fractionation was insignificant or even absent. Recent articulated brachiopods have nearly no vital effect and the calcite phase is in isotopic equilibrium with ambient water (Wefer & Berger 1991, fig. 30; Carpenter & Lohmann 1995; James et al. 1997); we assume that this was the case for the *Horridonia* specimens. The δ¹⁸O cycles are therefore interpreted as reflective of seasonal changes in the isotopic composition caused by temperature variations. Previous studies have interpreted seasonal cycles in the oxygen isotopic composition of brachiopods. For instance, Mii & Grossman (1994) recognized seasonality in the brachiopod *Neospirifer dunbari* from the tropical epicontinental sea of Kansas during Late Pennsylvanian. Annual seasonal changes have also been recognized in other invertebrate groups such as in the Atlantic surf clam *Spisula solidissima* (Jones et al. 1983) and the geoduck *Panopea generosa* (Nielsen & Nielsen 2009), corresponding to instrumental records of sea surface temperature.

The above-mentioned δ¹⁸O values from *Horridonia horrida* do not show such cyclicity; the curves are more irregular in course (Fig. 12). The δ¹⁸O mean values for *H. horrida* are higher than those from *H. timanica* (Table 3), which preliminarily suggest that the former species lived in lower-temperature water in the Southern Permian Basin. Because the Southern Permian Basin was located at lower latitude than the northern entrance of the Greenland–Norway seaway, the interpretation solely in terms of temperature seems less likely. The Southern Permian Basin was an epicontinental sea characterized by a narrow entrance that restricted rejuvenation with normal marine water.
from the Greenland–Norway seaway (Figs 1 & 4). The salinity and therefore the oxygen isotopic composition varied with shell crystallization/precipitation, river outlets and evaporation in the region. Increased evaporation would have resulted in higher salinity as well as higher δ18O values. Changes in the salinity could have blurred any seasonal pattern. The fact that the evaporative process can be reflected in the shell isotopic ratio was demonstrated by, for example, Bickert et al. (1997). Silurian brachiopods from Gotland (Sweden) have isotopic ratios indicating palaeoenvironmental changes between a humid and an arid climate. The arid conditions yielded higher salinity as well as δ13C and δ18O values (Bickert et al. 1997).

The oxygen isotope ratio in Horridonia timanica correlates moderately with δ13C values, showing a partial in-phase relation (Fig. 11; Table 3). The latter was probably related to the isotopic composition of the available food such as phytoplankton that was dependent upon the water temperature. The δ13C ratio in H. horrida was irregular during growth time (Fig. 12) and could have been distorted because of changes in the isotopic fractionation within the food items. The phytoplankton and zooplankton may have been sensitive to salinity changes so that the floral composition and its isotopic ratios altered gradually over the years. The minimum of the δ13C values is higher in H. horrida than in H. timanica (Table 3). The cause of this is speculative and needs further investigation.

Conclusions

Comparative analysis of the results gives interesting clues about the differences in the record of environmental parameters at distant places and at slightly different times. We have performed precise and careful analysis, which is consistent with the large palaeolatitudinal distance between Boreal realm (Spitsbergen) and the Southern Permian Basin (Poland) during the Permian (Fig. 1). On Spitsbergen there is clearly a seasonal pattern, both on carbon and oxygen isotopes, supporting the fact that the habitat of the brachiopods was located at relatively high palaeolatitudes.

In the brachiopod shells from Poland however, we do not observe such seasonal regularities. The stable isotope pattern appears to be related to the effect of regional evaporative processes at much lower palaeolatitudes. Most likely, the somewhat distorted carbon isotope pattern was caused by available food sources and their sensitivity to salinity changes over time. Any diagenetically altered shells materials were eliminated prior to analysis; diagenetic processes therefore cannot explain the recorded isotope patterns.

The Institute of Palaeobiology, Polish Academy of Sciences (PAS), Warszawa kindly granted permission to carry out the analysis on the brachiopods collected by J. Kazmierczak (1967) and K. Malikowski (1988). We would like to sincerely thank K. Malikowski for many helpful suggestions during the early phase of this investigation. We are grateful to W. Trela for fruitful discussions and the permission to use the picture of the Kajenów quarry. N.-M. Hanken is thanked for fruitful discussions during fieldwork on Spitsbergen. We thank the editors, M. Sone and an anonymous reviewer for constructive comments which improved the manuscript.

References


Brauns, C. M., Patzold, T. & Hack, U. 2003. A Re–Os study bearing on the age of the Kupferschiefer black shale at Sangerhausen (Germany). Abstracts of the
XVth International Congress on Carboniferous and Permian Stratigraphy, Utrecht.


SŁOWIAKIEWICZ, M., KIERSNOWSKI, H. & WAGNER, R. 2009. Correlation of the Middle and Upper Permian marine and terrestrial sedimentary sequences in Polish, German, and USA Western Interior Basins with reference to global time markers. Palaeoworld, 18, 193–211.


SOWERBY, J. 1823. The Mineral Conchology of Great Britain: or Coloured Figures and Descriptions of those Remains of Testaceous Animals or Shells, which have been Preserved at Various Times and Depths in the Earth. Volume 4. W. Arding, London.


