Chemosymbiotic bivalves and stable carbon isotopes indicate hydrocarbon seepage at four unusual Cenozoic fossil localities

STEFFEN KIEL AND JÖRN PECKMANN

LETHAIA

Four unusual Cenozoic fossil localities are identified here as ancient hydrocarbon seep sites using palaeontological, petrological, and stable carbon isotope data. Late Eocene carbonate-cemented sandstone bodies in the Wagonwheel Mountains in California were previously suspected to represent ancient hydrocarbon seep sites, but the relatively high $\delta^{13}C_{\text{carbo}}$ values (−12.2 to −5.0‰) suggest oil rather than methane seepage. The Oligocene fauna of the Elmira asphalt mine, Cuba, was previously interpreted as a mix of freshwater and marine taxa, but all species are here identified as belonging to marine groups, including the bivalve families Lucinidae and Vesicomyidae, whose extant members live largely in symbiosis with chemoautotrophic endosymbionts. A carbonate concretion from this site showed $\delta^{13}C_{\text{carbo}}$ values as low as −32.2‰, which most likely indicates methane seepage. A previously unpublished Oligocene fossil locality in Atlántico, northern Colombia, is dominated by large solemyid, mytilid, lucinid, and vesicomyid bivalves, which most likely lived with chemotrophic endosymbionts. Seepage of biogenic methane without a significant contribution of thermogenic methane is indicated by $\delta^{13}C_{\text{carbo}}$ values as low as −51.3‰. We confirm that the Pleurophopsis-dominated sites of the Heath Shale and Lomitos Chert in northern Peru are ancient seep sites, although the previous identification of Pleurophopsis peruiana as a vesicomyid is doubtful.

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Seeping methane and subsequently generated sulphide can fuel highly productive invertebrate communities on the deep-sea floor that rely on the microbial oxidation of these reduced compounds (Pauli et al. 1985; Levin 2005). The dominant invertebrates live either in symbiosis with methane and/or sulphide-oxidizing bacteria, or graze on free-living bacterial mats. The anaerobic oxidation of methane by archaea and bacteria in the sediment (Boetius et al. 2000) facilitates the precipitation of calcium carbonate (Ritger et al. 1987) and can result in large limestone bodies that enclose the associated invertebrate communities. Such limestone bodies in deep-water sedimentary strata and their associated fauna have often been described as curiosities in the geological and palaeontological literature. Their true nature, however, was only recognized after living hydrocarbon seep communities were found in the Gulf of Mexico in the mid-1980s (Paul et al. 1985). Since then, fossil seeps have been searched for in literature surveys and in the field using palaeontological, stable isotope, petrographical, and more recently, molecular geochemical methods (Gaillard et al. 1985; Campbell 1992; Bottjer et al. 1995; Peckmann et al. 1999).

Palaeontological indicators for possible fossil seep sites are worm tubes resembling tubes of vestimentiferan worms and five bivalve groups with modern representatives relying partly or entirely on chemotrophic endosymbionts: bathymodiolins, solemyids, thyasirids, lucinids, and vesicomyids (Fisher 1990; Campbell 2006). Members of the latter four families have very distinctive shells that are morphologically conservative, which makes them easy to recognize. However, the same morphological conservatism makes detailed systematic work within these groups (e.g. genus or species level) difficult.

Here we discuss the nature of four Cenozoic deposits (Fig. 1) in which several of these chemosymbiotic bivalve groups occur. Two of the deposits had previously been suspected to represent seep limestones,
the other two were recognised during surveys of the literature and the Cenozoic mollusc collection of the US National Museum of Natural History. We confirm their formation at hydrocarbon seeps and clarify the identity of their inhabitants. The confirmation of the palaeoenvironmental interpretation is based on petrographical and isotope geochemical analyses of carbonate adhering to the fossils stored in collections. We need to stress that the very limited amount of carbonate rock available for these analyses cannot be sufficient to document the likely complexity of the respective seep deposits.

Material and methods

The material from three of the four localities is located in the Smithsonian Natural History Museum (USNM) in Washington, D.C. This includes type and voucher material from the Elmira asphalt mine in Cuba, voucher material from the Lomitos Chert and Heath Shale in northern Peru, and undescribed material from a site on the Palmar-Molinera-Road in Colombia. Material from Wagonwheel Mountain in southern California is located in the Los Angeles County Museum of Natural History, Invertebrate Palaeontology section (LACMIP) in Los Angeles. The macrofossils were prepared using air scribes and a kerosene-based tar remover in the case of the Cuban specimens. Material for shell microstructure studies was mechanically broken off the specimen, cleaned using an ultrasound bath and 70% ethanol, coated with gold–palladium and photographed using a Philips XL30 ESEM scanning electron microscope. Larger specimens were photographed using an Olympus Camedia C-3040 Zoom or a JVC KY-F75U digital camera. To avoid redundancy, we only figure specimens or features of specimens that have not previously been illustrated.

Thin sections were studied with a Zeiss Axioskop 40 optical microscope. Powdered samples for oxygen and carbon stable isotopic analyses were taken from the surfaces of polished blocks using a hand-held microdrill. Samples were reacted with 100% orthophosphoric acid in a vacuum at 75°C, and the evolved CO₂ gas was analysed with a Finnigan MAT 251 mass spectrometer at the University of Bremen. The Δ¹³C and Δ¹⁸O results are reported relative to the V-PDB standard (SD < 0.04%) and appropriate correction factors were applied.

The Wagonwheel sites, California

Squires & Gring (1996) described two isolated 'anomalous calcareous sandstone bodies rich in lucinid
bivalves' in the Late Eocene Wagonwheel Formation in Kern County, southern California (Fig. 1). The assemblages (see Table 1 for a faunal list) were interpreted as chemosynthesis-based communities that utilized a diffuse flow of organic-rich waters seeping through sandy areas in submarine channels. Foraminifera in the surrounding mud- and siltstone indicate deposition at the shelf break or in upper bathyal depths (Smith 1956; Squires & Gring 1996). The material for Squires & Gring’s study was originally housed in the Collection of the California State University at Northridge, which has now been moved to the LACMIP (Groves et al. 2002).

### Petrology and geochemistry

Two bivalve specimens from Squires & Gring’s original collection, both with little shell material preserved but with golf ball-sized pieces of carbonate sandstone matrix adhering to them, were selected for thin section preparation and stable isotope work. The dominant carbonate phases of the calcareous sandstone sample are homogenous and clotted micrite, microspar, and minor calcite cement. The carbonate matrix cements abundant detrital quartz, foraminifera, shell debris, and faecal pellets. The micrite was affected by a corrosion event (Fig. 2A), a phenomenon commonly observed in seep limestones (e.g. Campbell et al. 2002).

Four samples of micrite yielded $\delta^{13}$C values ranging from $-12.2$ to $-5.0\%$ and $\delta^{18}$O values ranging from $-0.1$ to $+0.9\%$ (Fig. 3). The rather high $\delta^{18}$O values indicate that the limestones experienced little late diageneric alteration and probably no significant burial.

### Palaeontology

Three bivalve species were reported from the Wagonwheel sites by Squires & Gring (1996): *Epilucina*

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**Table 1.** Faunal list from the Wagonwheel sites, California.

<table>
<thead>
<tr>
<th>Taxon</th>
<th>Remarks</th>
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<tbody>
<tr>
<td><em>Tyasira folgeri</em> Wagner &amp; Schilling, 1923</td>
<td>Described as <em>Conchocele bisecta</em> by Squires &amp; Gring (1996)</td>
</tr>
<tr>
<td><em>Vesicomya aff. tschudi</em> Olsson, 1931</td>
<td></td>
</tr>
<tr>
<td><em>Epilucina washingtoniana</em> (Clark, 1925)</td>
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Fig. 2. Petrography of seep deposits. Plane-polarized light. □A. Calcareous sandstone, Wagonwheel site. Homogenous micrite (m) and clotted micrite (cm) enclosing detrital quartz (bright). The arrow points to a corrosion front. ms: microspar; □B. Pyritiferous carbonate concretion with detrital quartz, Elmira asphalt mine, Cuba. The arrow points to a foraminiferan; □C. Fossiliferous limestone, Heath Shale, Peru. The arrow points to fibrous carbonate cement; □D. Limestone, Lomitios Chert, Peru. m: micrite, cm: clotted micrite, Cc: calcite cement.
A Matrix micrite- Wagonwheel, CA
Matrix micrite, Cuba
'Mytilus' shell, Cuba
'Mytilus (?)' shell, Cuba
Elmira conraditex shell, Cuba
Matrix micrite, Colombia
Matrix micrite, Heath Shale, Peru
Matrix micrite, Lomitos Chert, Peru

Fig. 3. Cross-plot of δ¹³C and δ¹⁸O values of micrite and shell material.

...in Weaver 1942 and pl. 23, figs 8, 14, 15 in Moore 1963) differs from the Recent specimens assigned to *C. bisecta* mainly by having a significantly more curved posterior ridge (Coan et al. 2000; Kamenev et al. 2001; and observations by SK on material in the USNM and LACM collections). Ontogenetic changes in shell shape of *C. bisecta* were pointed out by Kamenev et al. (2001) and Squires & Gring (1996) but the more curved character of the posterior ridge in the Miocene type species can also be observed when Recent and Miocene specimens of the same size are compared.

*Thyasira folgeri* was originally described from the Wagonwheel Formation (Wagner & Schilling 1923) but later considered to represent immature specimens of *C. bisecta* by several authors (see Squires & Gring 1996). But the posterior ridge of *T. folgeri* specimens from the Wagonwheel sites is positioned in a much narrower angle to the anterior shell margin than in Recent or Miocene specimens of *C. bisecta*, suggesting that *T. folgeri* represents a distinct species. *Thyasira folgeri* was also described from a Mid- to Late Eocene seep carbonate in the Humptulips Formation in Washington (Goedert & Squires 1990). Many specimens have subsequently been collected at this site, and they are consistently more inflated than the Wagonwheel specimens, and also than Recent and Miocene specimens of *C. bisecta*.

We conclude that the thyasirid at the Wagonwheel sites should be referred to as *T. folgeri*, and that there is a higher diversity of thyasirids in the Cenozoic of the US Pacific Northwest than currently appreciated.

**Palaeoenvironment**

An evaluation of the palaeoenvironmental setting of the Wagonwheel deposits is not as straightforward as for the other examples under consideration in this study. However, the sum of the observed palaeontological, petrographical, and geochemical patterns is best explained by the former existence of an oil seep (see discussion below).

**The Elmira asphalt mine, Cuba**

In a survey of the palaeontology of the West Indies, Cooke (1919) reported the occurrence of an unusual mixture of freshwater and marine taxa from the Oligocene Elmira asphalt mine near Bejucal, Cuba. The supposed freshwater taxa included *'Unio' bitumen*, and viviparid and thyarid gastropods, the marine taxa were lucinid and solemyid bivalves, and trochid, cypraeid and buccinid gastropods (Table 2). Type and...
vouchers material of Cooke’s work was examined in the USNM and showed that his published drawings of the specimens are largely accurate. The USGS locality descriptions associated with the material (USGS Cenozoic localities 3652 and 5312) did not contain any additional information than in Cooke (1919).

**Petrology and geochemistry**

Among the voucher material, in the same box as additional specimens of ‘Unio’ bitumen, were two small (< 4 cm diameter) elongate-spherical carbonate concretions. The smaller of these was thin sectioned. Its matrix consists of pyritiferous micrite that encloses detrital quartz and foraminifera (Fig. 2B). The mostly framoidal pyrite is particularly abundant at the margin of the concretion, which resembles pyritiferous carbonate nodules of Jurassic seep Umestones from southern France (cf. Peckmann & Thiel 2004).

Isotope analysis of two samples of micrite yielded δ13C values of −32.2 and −23.5%, and δ18O values of +0.1 and +0.3%, respectively (Fig. 3). Additionally, four shells of bivalve molluscs have been analysed. Shell material of two specimens of ‘Myrtacea’ asphalctica yielded δ13C values of −1.3 and −0.6%, and δ18O values of −0.4 and −0.9%. Similar values were found for shell samples of ‘Unio’ bitumen (δ13C: −0.9%; δ18O: +1.0%) and Elmira cornuarietis (δ13C: 0.0%; δ18O: −0.8%).

**Palaeontology**

The hinge plate of ‘Unio’ bitumen is moderately strong and has a sharp top edge that borders the outer margin of the dorsal and anterodorsal part of the shell (Fig. 4A, B). The sub-umbonal tooth is bifid, most of the posterior part (2b in the terminology of Cosel & Salas, 2001) is broken off but was apparently strong, 2a is weak and parallel to the shell margin. The posterior tooth is absent; the anterior lateral (AII) tooth is merely a thickening of the inner shell margin and has a shallow socket above it. The anterior adductor muscle attachment scar is triangular with broadly rounded margins; the posterior margin is demarcated by a strong ridge. Vescimyid affinities of ‘Unio’ bitumen have long been suspected (Olsson 1931; Goedert & Squires 1993). ‘Unio’ bitumen has a generalized, elongated vescimyid-like shell shape resembling that of the enigmatic Pleurophopsis’ unionides from Miocene seeps of nearby Trinidad (Van Winkle 1919; Gill et al. 2005). But the hinge dentition of Unio’ bitumen resembles that of Callogonia, as the teeth are arranged more or less in one line (Cosel & Salas 2001), whereas Pleurophopsis’ unionides has an Adulomya-like hinge (Kiel in press; Amano & Kiel, unpublished). In sum, ‘Unio’ bitumen is certainly a vescimyid, but cannot presently be assigned to an existing genus due to its contradicting hinge and shell characters, and must await a thorough revision of the Vescimyidae.

The largest species in the assemblage is the lucinid Myrtacea (?)asphalctica. Cooke (1919) was uncertain about his assignment of this species to Myrtacea and we agree with his misgivings. The species most likely belongs to a new genus due to its large size and unusual hinge dentition (Fig. 4C, D).

The most conspicuous gastropod in the Elmira assemblage is the large (> 40 mm diameter) E. cornuarietis, which (Cooke 1919) interpreted as a new genus of the freshwater family Viviparidae. The combination of a low turbiniform shell and crossed lamellar shell microstructure (Fig. 4E) considerably restricts the possible taxonomic affinities of this genus. These include the mainly intertidal littorinids (Reid 2002), the deep-water family Trichotropidae, especially the genus Torellia (see Dell 1990), and the vent/seep endemic clade Neomphalina, among which the ‘scaly foot’ snail (Warén et al. 2003) is strikingly similar regarding size, shape and sculpture. However, E. cornuarietis lacks the shell pores that are characteristic for many neomphalids (Kiel 2004).

Cooke (1919) assigned two gastropod species to the freshwater genus Hemisinus (Thiaridae): H. bituminifer and H. costatus. The two species are represented by one specimen each and differ only marginally in size and the number of ribs per whorl. They most likely represent the same species and are here interpreted to belong to the deep-water genus Abyssochrysos, that builds very similar shells and is also known for ontogenetic changes in its sculpture (Houbrick 1979; Bouchet 1991; Killeen & Oliver 2000). Specimens of Abyssochrysos sp. were described from other Cenozoic Caribbean seeps (Gill et al. 2005), but these specimens

### Table 2. Faunal list from the Elmira asphalt mine, Cuba.

<table>
<thead>
<tr>
<th>Taxon</th>
<th>Remarks</th>
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<tbody>
<tr>
<td>Solemya sulcifera Cooke, 1919</td>
<td>New genus of Lucinidae; Fig. 4C, D</td>
</tr>
<tr>
<td><em>Myrtacea</em> asphalctica Cooke, 1919</td>
<td>Vesimyid, genus uncertain; Fig. 4A, B</td>
</tr>
<tr>
<td>‘Unio’ bitumen Cooke, 1919</td>
<td>Littorinid, trichotropid, or neomphalid?; Fig. 4E</td>
</tr>
<tr>
<td>Margarites naticoides Cooke, 1919</td>
<td>Originally assigned to Hemisinus; synonymous with H. costatus Cooke, 1919 from the same locality</td>
</tr>
<tr>
<td>Elmira cornuarietis Cooke, 1919</td>
<td></td>
</tr>
<tr>
<td>Abyssochrysos bituminifer Cooke, 1919 n. comb.</td>
<td></td>
</tr>
<tr>
<td>Cypraea semen Cooke, 1919</td>
<td></td>
</tr>
<tr>
<td>Levifusus angelicus Cooke, 1919</td>
<td></td>
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differ from Cooke's specimens by having a subsutural constriction. More similar to the Cuban *H. bituminifer* and *H. costatus* is the 'zygopleurid sp. A' of Gill *et al.* (2005, fig. 4J) from seep carbonates in the Sub-Oceanic Fault Zone on Barbados, which might even represent the same species.

Among the remaining gastropod species reported by Cooke (1919), *Margarita naticoides* has nacreous shell (Fig. 4F), which clearly places it in the Trochoidea. Although the strong subsutural ridge is somewhat unusual for that genus, this species might well belong to *Margarites* (see Hickman & McLean 1990). The other two species, *Levifusus? angelicus* and *Cypraea semen*, are predatory gastropods. They are neither seep-related nor strictly deep-sea groups, but instead are indicators for more shallow water environments.

**Palaeoenvironment**

'Unio' *bitumen* is here clearly identified as a vesicomyid. Together with the lucinid *Myrthaea* (?)asperlctica and the solemyid, the fauna of the Elmira asphalt mine locality is dominated by three large bivalve species whose extant relatives live in symbiosis with chemoautotrophic endosymbionts. Whereas lucinids and solemysids occur in many reducing environments, extant members of the Vesicomyidae having the size of 'Unio' *bitumen* live exclusively at hydrothermal vents, hydrocarbon seeps, or at whale carcases in the sulphophilic stage. This and the very negative δ²⁶²⁶ values of the carbonate concretion provide evidence that the Elmira asphalt mine locality represents an ancient methane seep site (see discussion below).

The discrepancy between low δ²⁶²⁶ values in the carbonate concretion and 'normal marine' values in the molluscan shells results from the fact that the carbon in the calcium carbonate used for shell formation is taken from the ambient seawater rather than from metabolic products (Paull *et al.* 1989; Fisher 1995).

Asphalt-soaked seep fossils like those from the Elmira asphalt mine have been reported from other...
sites in the Caribbean region (Gill et al. 2005). This does not necessarily indicate an ancient analogue to the modern asphalt seep sites inhabited by tube worms and vesicomyid bivalves like the Campeche Knolls in the Gulf of Mexico (MacDonald et al. 2004), because the asphalt could have infiltrated pre-existing seep carbonates at any time since their formation. Nevertheless, it is plausible that the methane and crude oil generating the asphalt are derived from the same reservoir.

The Palmar-Molinera-Road site, Colombia

When Boss & Turner (1980) described Calyptogena magnifica from hydrothermal vent sites on the Galapagos Rift, they discussed several possibly related fossil species. Among them they mentioned 'exceptionally large specimens of an unnamed species of Pleurophopsis from presumed Oligocene strata of Colombia, USGS locality 11253, ¼ mile N of junction Arroyo Piadras Palmar and Palmar-Molinera-Road, Atlántico, Colombia.' (Boss & Turner 1980, p. 164) The material from this site has now been re-examined and has revealed four seep-related bivalve species and three other taxa (Table 3). Material for carbon isotope analysis was also available.

Geochemistry

Carbonate rock adhering to fossils was sufficient for a preliminary isotope study, but did not allow the preparation of thin sections. Three samples of what is apparently the microcrystalline matrix of the rock yielded δ13C values ranging from −51.3 to −45.6‰ and δ18O values ranging from −5.5 to −4.1 (Fig. 3), the latter indicating that the limestone was affected to some degree by late diagenesis.

Palaeontology

Two of the bivalve species in the USNM collection of USGS Site 11253 reach the 200 mm of the presumed Pleurophopsis reported by Boss & Turner (1980). It is unclear which of these two species, if either, was referred to as 'large Pleurophopsis' by these authors. Both species differ significantly from the type species of Pleurophopsis and most other large vesicomyids by having the umbo in a central position. Both have an oval outline, recrystallized fragments of shell material show commarginal growth ribs, and no data are available on the pallial line or muscle attachment scars. One of the species has a pronounced, prosogyrate beak and resembles a vesicomyid, but has no hinge dentition preserved. This species vaguely resembles the 'vesicomyid sp. B' reported from a Miocene seep in Venezuela (Gill et al. 2005), except that the Venezuelan species has the umbo in a more anterior position.

The other species is almost orthogyrate, the beak extents only minimally over the dorsal shell margin, and preparation of a fragmentary right valve revealed a narrow, edentulous hinge (Fig. 5A, B). In dorsal view the posterior area tapers towards the umbo and is separated from the outer side of the shell by a thin groove. On the interior of the shell, this area shows fine horizontal striae that extend slightly beyond the umbo. Just anterior to the umbo the hinge forms a sharp ridge. Internal moulds show that fine radial striations were present on the interior of the shells, typical for lucinids (Fig. 5C, D).

Regarding its size and edentulous hinge, this species is similar to several seep-related Cretaceous to Early Cenozoic species. The presumed lucinid Cryptolucina elassodyseides from Eocene hydrocarbon seep carbonates in Washington State, USA (Saul et al. 1996), is more elongate than the Colombian species and also has a straight or even concave ventral margin. Also similar is a species that was mentioned but not figured by Olsson (1931, p. 119) as 'large Cyprina-Isocardia-like shell 190 mm in length' from the Lomitos Chert in northern Peru. Such a shell from Olsson's Peruvian collection was examined in the USNM; the specimen has very little shell material preserved, but seems to have a slightly more prosogyrate beak than the Colombian species. The 'lucinid sp. B' from a Miocene seep in Venezuela (Gill et al. 2005) has a more pronounced beak. Also similar regarding shell outline and hinge dentition are Cryptolucina kuhnpassetensis from Early Cretaceous seeps in Northeast Greenland (Kelly et al. 2000) and the enigmatic fossil 'chemosynthetic thraciid' Nipponothracia from Early Cretaceous and Miocene strata of Japan (Kanie & Sakai 1997). This may be synonymous with Cryptolucina (Goedert et al. 2003), but as the taxonomically important muscle attachment scars of Nipponothracia are not known, this appraisal remains tentative. In sum, one of the two species that could

<table>
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<th>Taxon</th>
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<tr>
<td>Solemyid</td>
<td>Fig. 5J</td>
</tr>
<tr>
<td>Bathymodiolus? n. sp.</td>
<td>Fig. 5K-1</td>
</tr>
<tr>
<td>Lucinid</td>
<td>Fig. 5A, B</td>
</tr>
<tr>
<td>Skeneiform gastropod</td>
<td></td>
</tr>
<tr>
<td>Naticid</td>
<td></td>
</tr>
<tr>
<td>Serpulid tube</td>
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Fig. 5. Bivalves from the Palmar-Molinera-Road site, Colombia. A–D. Lucinid; E, A. Lateral and dorsal view of hinge, USNM 533985; E, C. Exterior of left valve, USNM 533986; F, D. Detail showing commarginal growth lines on the shell's exterior and radial striation on the interior, same specimen as C. G–I. Bathymodiolus? n. sp.; G, E. Smallest specimen, USNM 533982; H, F. USNM 533983; I, G. Detail showing commarginal growth lines on the shell's exterior and radial striation on the interior, USNM 533981; J, H. Complete view of same specimen as G; K, I. Largest specimen, USNM 533984; K, J. Solemyid, right valve, USNM 533987.

represent Boss and Turner's 'large Pleurophopsis' may indeed represent a vesicomyid, the other has an edentulous hinge and could well belong to the mostly seep-related lucinid Cryptolucina.

The third Colombian species in the USNM collection is an elongate mytilid (Fig. 5E–I) that is very similar to the suspected or confirmed fossil bathymodiolins Bathymodiolus willapaensis (Squires & Goedert 1991; Kiel 2006) from the Eocene–Oligocene of Washington, USA; 'Modiolus exbrocci' from the Miocene Calcari a Lucina, Italy (Taviani 1994), the Cenozoic Caribbean bathymodiolines of Gill et al. (2005), and 'Volsella akamadaensis' and Bathymodiolus? sp. from the Japanese Miocene and Pliocene (Majima et al. 2005). However, the Colombian specimens are more elongate than any of these species. The four available specimens range in size from 38 to 60 mm and most likely belong to a new species of Bathymodiolus. In addition to these more common species, there is a poorly preserved solemyid of 31 mm in length (Fig. 5J).

Embedded in the carbonate matrix adhering to one of the presumed Bathymodiolus specimens are rather brittle specimens of a smooth, low-spired skeleform gastropod, two naticiform gastropods, and a serpulid tube with a diameter of 2.5 mm. Although these specimens seem to have fine details preserved, they were too brittle to be extracted from the hard matrix. Small wood fragments can be seen in the matrix adhering to the largest bathymodiolin and the solemyid.

**Palaeoenvironment**

The Palmar-Molinera-Road site in Colombia is here identified as an ancient methane seep. The very negative carbon isotope values clearly show that the carbonates formed under the influence of methane oxidation, and the four dominant bivalves (lucinids, bathymodiolins, solemyids, and vesicomyids) belong to groups with extant relatives that contain chemotrophic endosymbionts.
The Heath Shale and Lomitos Chert, Peru

The Lomitos Chert was first described as a ‘curious occurrence of cherty limestones’ within the shales of the Middle Eocene Talara Formation in northern Peru (Olsson 1931, p. 118). These limestones contain chemosymbiotic bivalves like lucinids, solemyids, thyasirids, and vesicomyids, including the enigmatic genus *Pleurophopsis*. Boss & Turner (1980) used the presence of these taxa as additional evidence for a close relationship between *Pleurophopsis* and the vent and seep vesicomyid *Calyptogena*. In subsequent studies, the Lomitos Chert was considered as a seep limestone (Goedert et al. 1995, 2003; Squires & Gring 1996; Campbell 2006).

A very similar *Pleurophopsis* fauna was reported by Olsson (1931) from the Late Oligocene Heath Shale, or ‘Cone Hill facies’. These fossils were found in thin-bedded yellow limestones along with shark teeth and large skeletons of toothed whales. Despite the similarity of this faunal assemblage to that of the Lomitos Chert, the *Pleurophopsis* fauna of the Heath Shale never attracted the same attention from seep researchers as the Lomitos Chert. For complete faunal lists for the Lomitos Chert and Heath Shale, see Olsson (1931, pp. 118, 119).

Material from Olsson’s collection in the USNM that is clearly associated with both localities under consideration consists of numerous specimens of *Pleurophopsis peruviana* from the Heath Shale, labelled USGS loc. 21219. The description of this locality in the USGS locality register reads as follows: ‘6½ km northeast of Quebrada Mancora and 3½ km southeast of the mouth of Quebrada Seca. Limestone lens in middle of Heath Shale.’ In addition, one box with several specimens of *Thyasira staujni* contained a label saying ‘Lomitos’.

Based on the similarity of the fauna to those of the Heath Shale, Olsson (1931) considered the age of the Lomitos Chert as Oligocene, and speculated that the overlying Oligocene sediments, which accordingly yielded the Lomitos Chert, had been eroded away. Campbell (2006), however, disagreed with this view and assigned the Middle Eocene age of the Talara Formation to the Lomitos Chert. No new data are currently available, and the age of the Lomitos Chert remains unresolved.

Petrology and geochemistry

**Heath Shale.** – One stored specimen of *P. peruviana* with little shell preserved but with a substantial amount of adhering carbonate rock was used to produce a thin section. The matrix of the limestone consists of homogenous and clotted micrite. It contains abundant shell debris including gastropods (Fig. 2C). Former cavities including shelter cavities are partly filled by fibrous carbonate cement. Samples of micrite for isotope analysis were taken from the same piece of rock from which the thin section was produced. The two obtained δ13C values are very low (−37.9 and −35.5‰). The low δ18O values of −6.0 and −5.5‰ indicate that the micrite was affected by meteoric or burial diagenesis.

**Lomitos Chert.** – Petrography and isotope analysis were performed on the carbonate matrix adhering to a stored specimen of *T. staujnii*. The dominant phase in the limestone sample is clotted micrite accompanied by homogenous micrite and at least two generations of calcite cement (Fig. 2D). The δ13C values of micrite are not as low as those from the Heath Shale carbonates, but are still significantly 13C-depleted (−25.3 and −25.0‰). As for the Heath Shale limestone, low δ18O values (−8.1 and −6.7‰) indicate that the rock was affected by later diagenesis altering a previous marine isotope signature.

Palaeontology

A specimen of *P. peruviana* from USGS loc. 21219 (Heath Shale) revealed that the hinge is moderately strong but virtually edentulous (Fig. 6A, B). Only two shallow indentations can be seen in the lower margin of the hinge line below the posteriormost part of the umbo. The anterior adductor muscle attachment scar is strong, and almost round except for a small indentation on the posterior side (Fig. 6C). It is posteriorly bordered by a ridge, which is especially strong on the dorsal side and flattens toward the ventral side. Although this species is remarkably similar in general shell shape to the type of *Pleurophopsis*, *P. unionides*, and also to *Unio* ‘bitumen’ from the Cuban locality, the lack of hinge dentition does not support a position within the Vesicomyidae. However, this conclusion is based on a single adult specimen with a coarsely recrystallized shell. As dissolution of hinge teeth among living vesicomyids has been reported (Cosel & Salas 2001) examination of additional material is required to prove taxonomic affinities.

Palaeoenvironment

The δ13C values of micrites from the Peruvian limestone deposits indicate that the bivalve molluscs lived at hydrocarbon seeps. The dominant carbonate phases observed in two thin sections agree with this interpretation. The seepage fluids of the Heath Shale deposit were probably dominated by methane. Fluid composition of the Lomitos Chert seeps is not as
Fig. 6. Pleurophopsis peruviana Olsson, 1931 from the Heath Shale, Peru. □A. View of the dorsal interior of a left valve, USNM 530295; □B. Close-up of hinge of same specimen; □C. Anterior portion of a right valve, showing the deeply impressed anterior muscle attachment scar and the ridge posterior to it; USNM 530294.

Discussion and conclusions

Composition of seepage fluids

This study confirms that the limestone deposits from California, Cuba, Colombia, and Peru, formed at hydrocarbon seeps, as previously suspected. Although the petrographical and isotopic data sets are rather limited, some preliminary inferences can be drawn regarding the mode of seepage and the composition of seepage fluids in particular.

Mostly based on the fauna, Squires & Gring (1996) suspected that the Wagonwheel deposits formed at hydrocarbon seeps. This interpretation can be refined by our petrographical observations and carbon isotope data. The lowest $\delta^{13}C_{\text{carbonate}}$ value of $-12\%_\circ$ is not negative enough to exclude carbon sources other than hydrocarbons. It needs to be stressed that seep carbonates do not just reflect the isotopic composition of their parent hydrocarbons. Instead, their isotopic composition reflects a mixing of hydrocarbon and other sources (Peckmann & Thiel 2004). As hydrocarbons have lower $\delta^{13}C$ values than other sources (e.g. marine carbonate), carbonate phases induced by hydrocarbon oxidation have higher $\delta^{13}C$ values than their parent hydrocarbons. Crude oil, for example, has $\delta^{13}C$ values ranging from $-35$ to $-25\%_\circ$ (Roberts & Aharon 1994). Carbonates forming today at oil seeps in the Gulf of Mexico with high seepage rates exhibit values between $-25$ to $-15\%_\circ$, whereas low seepage rates lead to higher values of around $-10\%_\circ$ (Joye et al. 2004). Remarkably, Squires & Gring (1996) suggested that seepage in the Wagonwheel Formation was diffusive. These authors report that the carbonate-bearing deposits have a petroliferous odour. Considering these lines of evidence and the palaeontological and petrographical observations provided above, the existence of large articulated bivalve molluscs associated with lenses of calcareous sandstone embedded in deep-water mudstones is best explained by oil seepage. Oil seepage was also suggested to explain a Late Devonian high-abundance but low-diversity assemblage of dimerelloid brachiopods (Peckmann et al. 2007). $\delta^{13}C$ values as low as $-12\%_\circ$ found for the Devonian limestones are very similar to the values of the Wagonwheel carbonate.

The lowest value of micrite of $-25\%_\circ$ from the Peruvian Lomitos Chert is too low to be explained by carbon sources other than hydrocarbons. But as the degree of mixing involved in the formation of the carbonates cannot be assessed, it is difficult to decide if seepage fluids contained mostly oil or methane. The isotopic composition of methane varies based on its genesis. Thermogenic methane shows $\delta^{13}C$ values between $-50$ and $-30\%_\circ$ (Sackett 1978), whereas
biogenic methane is even more $^{13}$C-depleted and typically exhibits values between $-110$ and $-50\%$ (Whiticar 1999); abiogenic methane is an unlikely source in the sedimentary settings of the examples discussed here. Mixing of different hydrocarbon sources, as observed at some modern seeps, is an additional factor that needs to be considered when assessing the fluid composition of ancient seeps. The lowest $\delta^{13}$C values found for the Cuban carbonates of $-32\%$ most likely indicates methane seepage. Considering the typical offset in $\delta^{13}$C values between parent hydrocarbons and seep carbonates observed at modern seeps (cf. Peckmann & Thiel 2004), oil seepage seems unlikely. Limestones in the Peruvian Heath Shale can be confidently interpreted to have formed at methane seeps based on $\delta^{13}$C values of $-38$ and $-36\%$. This also applies to the Colombian carbonates that exhibit $\delta^{13}$C values negative enough (as low as $-51\%$) to indicate seepage of biogenic methane, and excluding a significant contribution from thermogenic methane.

To sum up, all the deposits examined in this study are interpreted to have formed at hydrocarbon seeps. The composition of seepage fluids varied from site to site. The Californian example from the Wagonwheel Formation is believed to represent an oil seep. The Colombian, Peruvian Heath Shale, and the Cuban deposits all formed at methane seeps, but the origin and isotopic composition of methane were probably very different. It remains unresolved if fossiliferous limestones in the Peruvian Lomitos Chert formed at methane or oil seeps.

**Palaeobiogeographic relationships**

Assessing biogeographic relationships between these sites and other known Cenozoic seep faunas is difficult because of the varying and often poor state of preservation, and the limited numbers of species or generic identifications. For example, in a comparison of molluscan genera at 45 Eocene to Miocene seeps sites in Washington State, USA, and Japan, using cluster analysis, Kiel & Goedert (2006) revealed few distinct biogeographic patterns.

However, a few general remarks are possible. The Colombian and Cuban sites share large lucinids, vesicomyids, and mytilids, and *Abyssochrysea* with other Cenozoic seep sites in Barbados, Trinidad, and Venezuela (Harding 1998; Gill et al. 2005), but the enigmatic gastropod *Elmira* does not occur at any of the latter sites. The Peruvian sites share with those in the Caribbean the large lucinid and *Pleurophosis*-like shells, although these similarities might be superficial, because in both cases the taxonomic affinities are unclear. The Californian Wagonwheel sites and the Peruvian sites share the medium-sized, truncate *Vesicomya tschudi*; similar shells occur in Eocene to Miocene seeps in Washington (Goedert & Kaler 1996; Amano & Kiel, unpublished), and also the 'veneroid indet.' reported from Barbados and Trinidad (Gill 2005) has a similar shell shape, but the systematic affinities of these species need to be confirmed based on hinge dentition.

The Japanese Eocene to Oligocene sites are (at least superficially) more similar to seep communities from the Oligocene of Washington than to the Miocene Caribbean ones. They contain mainly *Conchocele*-like shells that are similar to most large thyasirids from this time period, and short Calyptrgona-like shells that resemble the *Vesicomya tschudi* group from Peru and the North American west coast. Seeps from the Japanese Miocene are dominated by recurrent Calyptrgona, Vesicomya, Conchocele, and Lucinoma communities with very few gastropods (Majima et al. 2005).

**Acknowledgements.** We thank Anna Disture, Yuangao Qu, both Bremen, and Jonathan Wingerath, Washington, D.C., for preparing thin-sections and Monika Segl, Bremen, for stable isotope analyses; Warren Blow [deceased] Mark Florence, Steve Jabo, Pete Kroehler, Jann Thompson, and Thomas A. Waller, Washington, D.C., for their help with the collection at the USNM; Richard L. Squires, Northbridge, and Harry Filkorn, Los Angeles, for their help in the collection at LACMIP, John D. Taylor and Emily A. Glover, London, for their help with lucinid systematics, and Jim Goedert, Wauna, and Cris Little, Leeds, for critically reading the manuscript. Ian Harding and an anonymous reviewer provided valuable comments. SK carried out most of his work for this study during a post-doctoral fellowship (Charles D. and Mary V. Walcott fellowship) at the Smithsonian Institution, Washington, D.C., and during an Intra-European Marie-Curie Fellowship of the European Commission at the University of Leeds, which is gratefully acknowledged. This work was supported by the 'Deutsche Forschungsgemeinschaft' through the DFG-Research Center for Ocean Margins, Bremen (contribution no. RCOM0506).

**References**


