

Carbon cycling at ancient methane–seeps

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Abstract

The oldest known seep deposits with macroinvertebrate taxa are Devonian in age. Although more and more examples continue to be discovered, the Palaeozoic and Mesozoic record of methane–seeps is still fragmentary. The relationship of ancient carbonate deposits to methane seepage is established by (i) the geological setting and structural features, (ii) the occurrence of low diversity but high abundance faunal assemblages, (iii) carbonate fabrics, (iv) low $\delta^{13}\text{C}$ values of early diagenetic carbonate phases, and (v) characteristic ^{13}C -depleted biomarkers. In this review, special emphasis is placed on biogeochemical processes at ancient methane–seeps. Specific carbonate fabrics and phases include, in order of decreasing significance for seep-dominated environments, (i) inverted stromatolite cavities, (ii) upside-down stromatolites, (iii) globular fabrics, (iv) botryoidal aragonite, (v) micritic nodules, (vi) fractures, (vii) clotted micrites, and (viii) constructive seams representing fossilised biofilms. The carbon of the early diagenetic carbonate phases was derived predominantly from the oxidation of methane which resulted in low $\delta^{13}\text{C}$ values. Pyrites enclosed in the seep limestones generally show low $\delta^{34}\text{S}$ values and a significant variability of their isotopic composition on a small scale, both indicating bacterial sulphate reduction as the sulphide-supplying process. ^{13}C -depleted lipid biomarkers characterise the microbial populations involved in the cycling of carbon at ancient methane–seeps. Typical compounds include isoprene-based lipids from archaea, and linear and monomethyl-branched carbon skeletons assigned to sulphate-reducing bacteria (SRB), consistent with the syntrophic relationship of these microbes in the anaerobic oxidation of methane (AOM).

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1. Introduction

Methane–seeps are typical features of ocean margins. Modern seep deposits occur in a variety of

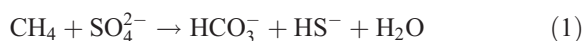
different marine geotectonic settings (Campbell et al., 2002) and commonly sustain dense chemosymbiotic invertebrate communities (Sibuet and Olu, 1998). To locate ancient seep deposits, a ‘seep-search strategy’ was proposed by Campbell and Bottjer (1993). Similarly, Kelly et al. (1995) listed typical features to recognize seep-related limestones, and several studies used lipid biomarkers to track microbial methane oxidation in ancient seep environments (e.g. Thiel et al., 1999; Burhan et al., 2002; Peckmann et al., 2002).

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In contrast to numerous seep deposits that have been described in Cenozoic strata, the record of Mesozoic seep deposits is sparse (Gaillard et al., 1992; Campbell and Bottjer, 1993; Kelly et al., 1995, 2000; Kauffman et al., 1996; Campbell et al., 2002), and becomes even more fragmentary in the Palaeozoic. To date, only two Palaeozoic deposits have been shown by geochemical and other evidence to represent ancient seep environments (Peckmann et al., 1999a, 2001a). Other Palaeozoic deposits have been tentatively interpreted to be related to methane seepage on the basis of specific high abundance but low diversity faunal assemblages (Campbell and Bottjer, 1995; different types of chemoautotrophic assemblages are discussed by Little et al., 2002).

Carbonate formation at methane-seeps results from the anaerobic oxidation of methane (AOM), because AOM causes an increase in alkalinity (Ritger et al., 1987; Paull et al., 1992).



Recently, molecular, isotopic, and phylogenetic evidence revealed that AOM is performed by a consortium of methanotrophic archaea and sulphate-reducing bacteria (SRB), although the exact biochemical pathway of AOM still remains to be elucidated (e.g. Elvert et al., 1999, 2000; Hinrichs et al., 1999, 2000; Thiel et al., 1999, 2001a; Boetius et al., 2000; Pancost et al., 2000, 2001a; Valentine and Reeburgh, 2000; Bian et al., 2001; Lanoil et al., 2001; Orphan et al., 2001a, 2002; Thomsen et al., 2001; Hinrichs and Boetius, 2002; Michaelis et al., 2002; Nauhaus et al., 2002; Teske et al., 2002; Zhang et al., 2002; for a recent, comprehensive review on the biogeochemistry of AOM, see Valentine, 2002). Likewise, carbonate formation results from the metabolic activity of AOM-performing microbes and is confined to anoxic environments (Aloisi et al., 2000; Peckmann et al., 2001b).

Methane-seeps are sometimes linked to shallow gas hydrate occurrences. Gas hydrates are widely distributed along continental margins (Kvenvolden, 1988, 1998; Suess et al., 2001). They are stable at water depth greater than 300 to 500 m and burial depth lower than 100 to 1100 m (Kvenvolden, 1993). The water in the gas hydrate cages is enriched in ^{18}O by 2‰ to 3‰ relative to the primary pore-waters (Davidson et al., 1983; Ussler and Paull, 1995). Consequently, unusual-

ly high $\delta^{18}\text{O}$ values of seep carbonates have been used to trace gas hydrate destabilisation (Bohrmann et al., 1998). A significant ^{18}O -enrichment of carbonates (relative to a composition in equilibrium with ambient waters) at methane-seeps in the Mediterranean Sea was attributed to ^{18}O -rich fluids, possibly related to destabilisation of gas hydrates (Aloisi et al., 2000). It has been suggested that stratabound (non-seep) dolomites, which formed in Tortonian marls in the Lorca Basin (SE Spain) prior to the Messinian salinity crisis, are related to gas hydrate dissociation (Pierre et al., 2002). This was based on high $\delta^{18}\text{O}$ values and both high and low $\delta^{13}\text{C}$ values of the dolomites and deformation structures in the Tortonian sediments. The latter include slumps and faults often associated with the breakdown of gas hydrates (cf. Kvenvolden, 1998; Paull et al., 2003).

In this review, we apply the term ‘methane-seep’ to sites that have been imprinted by seepage of reduced carbon-compounds. However, we need to stress that there is some uncertainty regarding the fluid composition of some of the ancient seeps. In three instances, $\delta^{13}\text{C}_{\text{carbonate}}$ values not negative enough to exclude carbon sources other than methane (e.g. petroleum) or inclusions of metamorphosed petroleum within seep limestones suggest that methane might not have been the dominating or at least not the sole carbon-compound of the respective seepage fluids (Peckmann et al., 1999a,b, 2001a).

The purpose of this paper is not to present a general compilation on ancient methane-seep deposits, but to review the knowledge on the biogeochemistry of ancient seep-influenced environments. Therefore, we concentrate on (i) only those carbonate fabrics that are indicative of ancient biogeochemical processes, (ii) stable isotope signatures, and (iii) biomarker patterns. Furthermore, we discuss potential signatures for gas hydrate-destabilisation that might have been recorded in ancient seep deposits.

2. Sedimentary fabrics

2.1. Clotted micrites, pyritiferous carbonate nodules, and pyrite rims

Authigenic, microcrystalline carbonates are the volumetrically dominant phases of methane-seep

deposits. The most common variety is micrite (microcrystalline calcite), but microcrystalline aragonite and dolomite occur as well (Roberts and Aharon, 1994; Peckmann et al., 2001b). Microcrystalline carbonates typically form the matrix of the seep deposits and several generations within one deposit are common. Most micrites are homogenous, but clotted microfibrils also have been reported (Roberts and Aharon, 1994; Naehr et al., 2000; Peckmann et al., 1999a, 2001b, 2002; Campbell et al., 2002). The expression ‘clotted micrite’ is used for an aggregate of microscopic, irregular, microcrystalline clots with calcite spar crystals that fill the spaces between clots (Peckmann et al., 2002). An analogous carbonate phase of modern methane–seep deposits from the Black Sea consists of micritic clots, but lacks the cement filling up the pore space (Peckmann et al., 2001b). This reveals that the clotted fabric of ancient seep deposits is a primary one and does not result from recrystallisation. Clotted fabrics of different scales are considered to represent typical features of microbial carbonates (Burne and Moore, 1987). Therefore, the common occurrence of clotted microfibrils in seep deposits may be related to small-scale variations in the chemical environment during carbonate precipitation caused by microbial metabolism.

Characteristic components of some seep deposits are pyritiferous carbonate nodules (Peckmann et al., 1999b, 2003). The smoothly shaped, spheroidal nodules are formed of micrite which usually consists of smaller crystals than the surrounding matrix micrite or microspar. Some nodules show a zonation with significant amounts of framboidal pyrite particularly abundant in concentric layers (Fig. 1). In others, pyrite becomes more abundant toward the nodule margins. The nodules are believed to have formed in a manner analogous to the formation of carbonate concretions, which they resemble (Peckmann et al., 2003). It is widely accepted that concretions are the result of microbial activity (Coleman, 1993; Raiswell and Fisher, 2000) and that their carbonate phases record the biogeochemical processes involved in their genesis (Kiriakoulakis et al., 2000). In seep-limestone nodules, the close association of micrite and iron sulphide, and particularly the concentric enrichment of the latter are suspicious. It has been pointed out that the modes of iron sulphide formation, including the transformation processes from monosulphides to py-

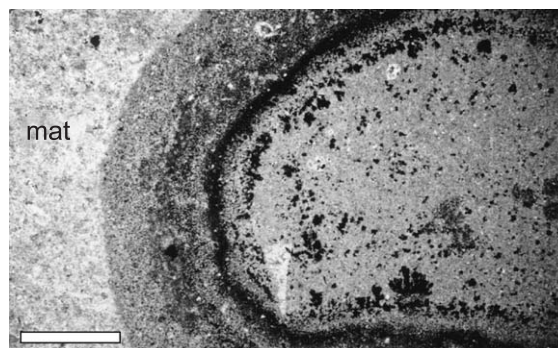
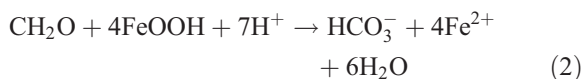
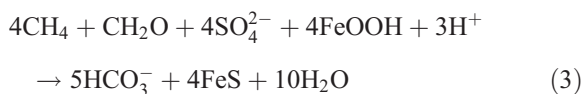


Fig. 1. Pyritiferous carbonate nodule enclosed in the matrix (mat) of a Late Jurassic (Oxfordian) seep limestone from Beauvoisin, southeastern France. Pyrite (dark) is enriched in concentric layers. Plane-polarized light. The scale bar corresponds to 1 mm.

rite, have distinct effects on the carbonate buffer and, thus, on carbonate precipitation (Coleman and Raiswell, 1995). Where iron reduction:



and sulphate reduction (coupled to AOM at seeps; Eq. (1)) occurred contemporaneously, and in close proximity, alkalinity would have been increased by (i) the consumption of protons and (ii) the production of bicarbonate ions:



This scenario (Eq. (3); Peckmann et al., 2003) does not necessarily imply that AOM by sulphate and iron reduction are coupled, but if these processes occur in close proximity, carbonate formation is even more favoured than by AOM alone (Eq. (1)). To date, no evidence exists that iron reduction can be directly coupled to AOM. Although no electron acceptors other than sulphate have yet been demonstrated to oxidise methane under anoxic conditions, it should be noted that the free energy yield of methane oxidation coupled to iron reduction would be greater than that of sulphate-dependent methane oxidation (Valentine, 2002). Remarkably, some sulphate-reducing bacteria have been found to be capable of performing iron reduction in salt-marsh sediments using hydrogen as a substrate (Coleman et al., 1993).

Pyrite rims common in some seep limestones are often associated with corrosion surfaces. [Campbell et al. \(2002\)](#) reported corroded carbonate surfaces encrusted with pyrite. Similarly, nodular, pyrite-rimmed carbonate aggregates have been interpreted to result from corrosion ([Peckmann et al., 2003](#)). Although it is possible that pyrite precipitation is postdating corrosion, a relationship between sulphide-rich fluids inducing iron sulphide formation and the dissolution of carbonate is likely. The interdependence of carbonate corrosion and sulphide precipitation could have been due to the migration of Fe^{2+} and H_2S to the reaction site (cf. [Coleman and Raiswell, 1995](#)). In this scenario, iron sulphide formation results in an increase of acidity:



Different modes of iron sulphide formation have an opposite effect on the carbonate system. Whether carbonate is precipitated or dissolved can be simply a function of the proximity of iron reduction and sulphate reduction to the formation site of iron sulphide.

2.2. Inverted stromatactoid cavities and stromatolitic fabrics

Inverted stromatactoid cavities typify a metre-sized methane–seep deposit from the Oligocene Lincoln Creek Formation of western Washington State ([Peckmann et al., 2002](#)). These cavities are similar to stromatactis, a common structural element of Palaeozoic mud mounds ([Monty, 1995](#)). However, compared to stromatactis, the ‘Lincoln Creek’ cavities are inverted, having a digitate lower surface and a smooth upper surface ([Fig. 2](#)). This inversion is believed to result from an opposite growth direction of the seep deposit compared to mud mounds ([Peckmann et al., 2002](#)). Palaeozoic mud mounds, like modern carbonate mounds, showed a predominantly upward-directed carbonate aggregation. The growth of seep deposits, on the other hand, is fuelled by ascending methane. AOM proceeding below pre-existing carbonate crusts results in a downward-directed carbonate aggregation on the lower surface of the crusts.

Stromatolitic fabrics have been found in some seep deposits ([Kelly et al., 1995](#); [Peckmann et al., 2001a](#)). A downward-directed growth of stromatolitic carbo-

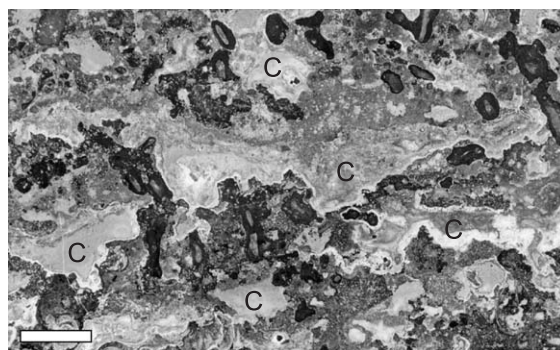


Fig. 2. Polished slab of the Lincoln Creek Formation limestone with inverted stromatactoid cavities, Oligocene, western Washington State. The former cavities (C), now filled by authigenic carbonate phases, exhibit a smooth upper and an irregular, digitate lower surface. The widest cavity is in the centre, smaller ones are at the centre-right and -left, and in the centre-below. The scale bar corresponds to 2 cm.

nates at methane–seeps on the Aleutian accretionary margin was proposed by [Greinert et al. \(2002\)](#). It is widely accepted that seep carbonates form within the sediment ([Gaillard et al., 1992](#); [Peckmann et al., 2001b](#)) which leads to a complex growth pattern. The mode of carbonate aggregation depends on (i) the intensity of seepage, (ii) the shape of the pre-existing deposit, (iii) the rate of AOM, and (iv) the potential diffusion of the resultant carbonate species prior to precipitation. It may vary significantly, e.g. from lateral to preferentially downward or upward aggregation, as all the crucial parameters are not constant.

2.3. Fossilised biofilms

A Miocene methane-derived carbonate rock from the Apennines in northern Italy was found to contain fossilised biofilms ([Peckmann et al., 1999b](#)). The rock is intensely brecciated, with its microcrystalline dolomitic matrix crosscut by fractures filled with calcite cement. At the contact to the calcite cement, the dolomitic matrix is overgrown by coatings ([Fig. 3a](#)). These coatings are rich in organic substances, as indicated by their intense autofluorescence ([Fig. 3b](#)), and consist of dolomitic crystal-aggregates including hemispheroidal crusts ([Fig. 3c](#)), rods with brush-like terminations ([Fig. 3c](#)), and dumbbells ([Fig. 3d](#)). Similar crystal-aggregates were induced by bacterial ac-

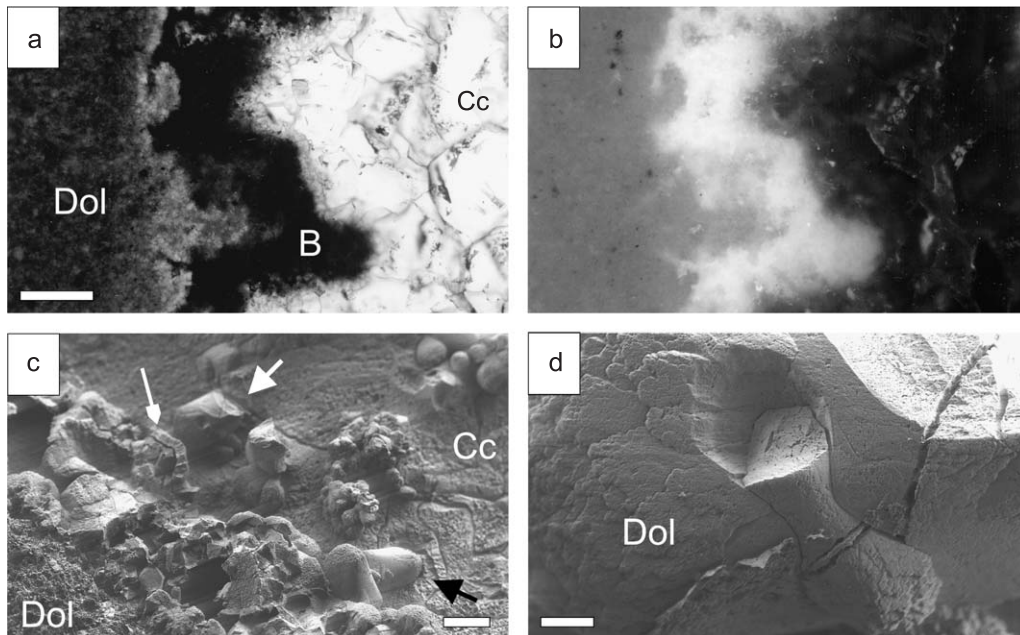


Fig. 3. Fossilised biofilms of the Marmorito limestone, Miocene, northern Italy. (a) Dolomitic seam (B) representing a fossilised biofilm coating the dolomitic matrix (Dol). Calcite cement (Cc) is filling the fracture. Plane-polarized light. The scale bar corresponds to 200 μm . (b) Same section as (a). The fossilised biofilm exhibits an intense autofluorescence. Fluorescence image. (c) The fossilised biofilm consists of hemispheroidal crusts (thin arrow) and rods with brush-like terminations (thick black arrow). The thick white arrow points to the detail shown in (d). Dol=dolomitic matrix; Cc=fracture-filling calcite cement. Field emission—SEM image. The scale bar corresponds to 50 μm . (d) Dumbbell-shaped crystal aggregate in the centre of a rod-shaped crystal aggregate (Dol). Field emission—SEM image. The scale bar corresponds to 5 μm .

tivity in laboratory experiments using undifferentiated marine bacteria or sulphate-reducing bacteria, respectively (Buczynski and Chafetz, 1991; Warthmann et al., 2000). The Marmorito coatings match the typical size of biofilms (cf. Riding, 2002) and are clearly constructive in origin. Therefore, and because of their low $\delta^{13}\text{C}_{\text{dolomite}}$ values, they have been interpreted to represent fossilised biofilms of methanotrophic microbes (Peckmann et al., 1999b). The occurrence of isolated remains of these fossilised biofilms within the dolomitic matrix of the rock further indicates an involvement of biofilms in carbonate formation.

2.4. Gas hydrate-associated carbonates

Carbonate phases intercalated with gas hydrates in sediments of the Cascadia margin consist of aragonite and high-Mg-calcite (Bohrmann et al., 1998). Bedding-parallel gas hydrate layers up to 10 cm in thickness have been found. Cross sections through the gas

hydrate/sediment mixture revealed a globular texture (Bohrmann et al., 1998). The globular cavities that are partly filled by gas hydrate have been interpreted as former gas bubbles indicating the existence of free gas prior to hydrate precipitation. Moreover, the surface of an aragonite precipitate, which formed in a massive gas hydrate layer, outlined the globular texture of the hydrate (Bohrmann et al., 1998). The observation that the surface morphology of the mineral phase mimics the globular texture of the gas hydrate implies that similar fossil carbonate precipitates could indicate a former association with gas hydrates. However, similar fabrics are formed by botryoidal aragonite, a common component of seep limestones that is not necessarily associated with gas hydrates (Roberts and Aharon, 1994; Peckmann et al., 2001b). Individual botryoids may be up to several centimetres in diameter (Peckmann et al., 1999b) and their aggregates inevitably have a globular fabric that could easily be misinterpreted as being related to gas hydrates.

2.5. *In situ* brecciation

Many methane-seep limestones are intensively fractured (Beauchamp and Savard, 1992; Kelly et al., 1995; Peckmann et al., 1999b). Fracturing of carbonate deposits in pockmarks of the North Sea has been interpreted to result from a rise in pressure due to the accumulation of methane gas below the limestone crusts and the subsequent vigorous gas release causing the crusts to break (Hovland et al., 1987).

The formation and dissociation of gas hydrate are the main processes that cause short-term and small-scale disruption of the seafloor at shallow seeps in the Gulf of Mexico (MacDonald et al., 2003). Bohrmann et al. (1998) reported that in modern sediments of the Cascadia margin, offshore Oregon, brecciation-like deformation is caused by the growth of gas hydrates and subsequent fracturing. Moreover, it has been shown that a porous gas hydrate variety from the Cascadia margin has a low bulk density, which may cause episodic release of large hydrate aggregates from the sea floor (Suess et al., 2001). When the buoyancy of the hydrates exceeds the loading of the overlying sediments, chunks of hydrate detach and float to the sea surface. Chunks of up to a cubic metre in size have been observed (Suess et al., 2001). This is a further mechanism that may cause sediment deformation in methane-rich, hydrate-bearing environments. The resulting sedimentary fabric might well resemble early *in situ* brecciation, as the carbonate layers associated with the hydrate will be fractured by this process.

3. Stable isotopes

3.1. Carbon and oxygen stable isotope ratios of carbonates

Biogenic methane is strongly depleted in ^{13}C and exhibits $\delta^{13}\text{C}$ values in the range from -50‰ to -110‰ (Whiticar et al., 1986; Whiticar, 1999). Thermogenic methane typically has values ranging from -30‰ to -50‰ (Sackett, 1978). Values even higher than -20‰ have been reported for hydrothermal fluids (Botz et al., 2002 and references therein). Petroleum usually exhibits $\delta^{13}\text{C}$ values in

the range from -25‰ to -35‰ (Roberts and Aharon, 1994).

The $\delta^{13}\text{C}$ values of ancient hydrocarbon-derived carbonates, which inherit their stable isotope composition from their carbon sources, have been used to evaluate the origin of the fluids. However, as the extent of mixing among different carbon sources (e.g. marine carbonate vs. decomposition of organic matter vs. hydrocarbons) is not known, an evaluation of fluid composition based on the $\delta^{13}\text{C}_{\text{carbonate}}$ values alone is ambiguous. Because carbon sources other than hydrocarbons usually contain relatively more ^{13}C , $\delta^{13}\text{C}$ values of seep carbonates will generally be higher than those of the seeping hydrocarbons. Accordingly, very low $\delta^{13}\text{C}$ values of ancient seep carbonates (-58‰ , Terzi et al., 1994; -62‰ , Shibasaki and Majima, 1997; -69‰ , Campbell et al., 2002) indicate a biogenic methane source.

Where both carbonate minerals and methane gas have been analysed at modern seeps, an enrichment of ^{13}C in the carbonate relative to the gas was usually found. Comparing the most negative $\delta^{13}\text{C}_{\text{carbonate}}$ values of each deposit with the respective $\delta^{13}\text{C}_{\text{methane}}$ values, it appears that most of the $\text{C}_{\text{carbonate}}$ derived from methane, but other carbon sources are still significant (Table 1). Only methane from the North Sea yielded exclusively higher $\delta^{13}\text{C}$ values than associated seep carbonates (Hovland et al., 1987). The authors suggested that the isotopic composition of the trace amounts of interstitial methane analysed does not reflect the composition of the parent gas. It needs to be stressed that $\delta^{13}\text{C}_{\text{methane}}$ values may vary significantly at the same seep site, with a trend toward higher values with decreasing sediment depth due to fractionation associated with AOM (Tsunogai et al., 2002).

As discussed above, methane-seep carbonates generally are typified by low $\delta^{13}\text{C}$ values. However, $\delta^{13}\text{C}$ values higher than $+5\text{‰}$ have been reported for some individual carbonate phases from ancient seep deposits (Gaillard et al., 1992; Peckmann et al., 1999b, 2002, 2003). Highly positive $\delta^{13}\text{C}$ values indicate methane formation rather than oxidation, because of the ^{13}C -enrichment in the CO_2 pool utilized by archaeal methanogenesis (Irwin et al., 1977; Boehme et al., 1996). The ^{13}C -enriched carbonate phases formed later in the diagenetic sequence than the early diagenetic ^{13}C -depleted carbonate

Table 1

The most negative $\delta^{13}\text{C}_{\text{carbonate}}$ values of some modern methane–seep deposits compared with the respective $\delta^{13}\text{C}_{\text{methane}}$ values (relative to the PDB standard in ‰)

$\delta^{13}\text{C}_{\text{carbonate}}$	$\delta^{13}\text{C}_{\text{methane}}$	Localities	References
– 54	– 63 to – 66	Cascadia subduction zone off Oregon	Bohrmann et al. (1998)
– 49	– 80 to – 84	Florida Escarpment, Gulf of Mexico	Paull et al. (1989)
– 53	– 43 to – 71	Northern Gulf of Mexico	Aharon et al. (1997), Brooks et al. (1986)
– 48	– 63 to – 71	Blake Ridge, Carolina continental rise	Naehr et al. (2000), Lorenson and Collett (2000)
– 30	– 58 to – 68	Håkon Mosby mud volcano, off Norway	Damm and Budéus (2003), Lein et al. (1999), Lein et al. (2000)
– 61	– 40 to – 44	North Sea off Norway	Hovland et al. (1987)
– 46	– 32 to – 63	Gulf of Cádiz, eastern Atlantic Ocean	Díaz-del-Río et al. (2003)
– 41	– 62 to – 68	northwestern Black Sea	Peckmann et al. (2001b), Michaelis et al. (2002)
– 44	– 78	Makran accretionary prism off Pakistan	Von Rad et al. (1996)
– 40	– 47 to – 58	New Ireland fore-arc basin, Papua New Guinea	Schmidt et al. (2002)
– 41	– 59 to – 71	Sunda fore-arc basin, off Java	Wiedicke et al. (2002)

phases induced by methane oxidation. This illustrates the potential of ancient seep limestones to record the changes in biogeochemical processes during increasing burial.

Campbell et al. (2002) compiled stable carbon and oxygen isotopic data for 33 globally distributed seep carbonates, ranging in age from Devonian to Holocene. Three stable isotopic fields were defined, including (i) a ^{13}C -, ^{18}O -depleted field containing most Mesozoic and Palaeozoic examples, (ii) a variably ^{13}C -depleted, but ^{18}O -enriched field with most Cenozoic and modern occurrences, and (iii) a scattered, ^{13}C -enriched field, with variable ^{18}O contents. A trend

from low $\delta^{18}\text{O}$ values of matrix-forming microcrystalline carbonates to higher values in later, but still early diagenetic phases has been reported for several seep or vent deposits (Monji et al., 1998; Campbell et al., 2002). Monji et al. (1998) suggested that micrite making up conical mud-mounds in the AntiAtlas (Morocco) was precipitated from hydrothermal fluids; alternative explanations for low $\delta^{18}\text{O}$ values of early diagenetic micrites are discussed by Peckmann et al. (2003).

Due to the enrichment of ^{18}O in gas hydrates, anomalously positive $\delta^{18}\text{O}_{\text{carbonate}}$ values could argue in favour of gas hydrate destabilisation at methane–seep sites. However, although high $\delta^{18}\text{O}$ values of carbonate phases have successfully been used to track the destabilisation of gas hydrates at modern seeps (Bohrmann et al., 1998; Aloisi et al., 2000), this approach has not been applied to ancient seep deposits. Oxygen isotopes are much more prone to exchange than carbon isotopes in carbonate rocks. The oxygen isotope ratio is believed to shift towards lower $\delta^{18}\text{O}$ values during rock alterations, because meteoric waters are usually significantly depleted in ^{18}O relative to marine waters. Therefore, it is possible that signatures of gas hydrate destabilisation have been obscured in some ancient seep carbonates. The significance of the general trend to lower $\delta^{18}\text{O}$ values with increasing age found in any kind of carbonates is questionable as demonstrated by the ongoing debate on whether this trend is caused by isotope exchange or variations in the ocean water isotopic composition during earth history (Hoefs, 1997 and references therein; Lécuyer and Allemand, 1999; Wallmann, 2001).

3.2. Stable isotopes of sulphur in pyrite

Pyrite, typically occurring as a framboidal crystal aggregate, is the most common non-carbonate mineral in methane–seep limestones. It forms by the reaction of hydrogen sulphide with reactive detrital iron minerals (Berner, 1974) and inherits the stable isotopic composition of the H_2S (Price and Shieh, 1979; Böttcher et al., 1998). The formation of pyrite in sedimentary environments results from the metabolism of sulphate-reducing bacteria (SRB) which produce H_2S strongly depleted in ^{34}S . Detmers et al. (2001) observed that the fractionation capacity of

different strains of SRB varies strongly. They reported a range from 2‰ to 42‰. In other experiments, pure cultures of SRB have been found to produce maximal isotope fractionations of 46‰ (Kaplan and Rittenberg, 1964) and 47‰ (Bolliger et al., 2001). In natural environments, the degree of fractionation also depends on substrate availability and sulphate concentrations, with substrate-limited conditions favouring intense fractionation and low sulphate concentrations leading to minimal fractionations (Canfield, 2001). At methane-seeps in the Gulf of Mexico, sulphate reduction rates have been found to be up to 600 times higher than in a non-seep reference sediment, indicating that sulphate reduction is a key biogeochemical process at seep sites (Aharon and Fu, 2000). Here, $\delta^{34}\text{S}$ values of residual sulphate up to +71‰ have been documented (Aharon and Fu, 2003).

Considering the importance of bacterial sulphate reduction in seep environments, the associated pyrite received little attention. As sulphate reduction and methane oxidation are coupled in seep environments, systematic studies on the sulphur isotopic composition of pyrite may not only yield patterns diagnostic for bacterial sulphate reduction, but also for AOM. Kohn et al. (1998) analysed pyrite from sediments at a methane-seep in Monterey Bay, coastal California. The authors achieved a high spatial resolution by using an ion microprobe. The $\delta^{34}\text{S}$ values showed a range from -41‰ to -5‰, and variations in $\delta^{34}\text{S}$ values between different pyrite aggregates in the same sediment were as high as 35‰. Even individual aggregates exhibited a considerable variability of up to 15‰. Zoning within grains indicated an increase in ^{34}S through time (Kohn et al., 1998).

Only very few data are available on the isotopic composition of pyrite from ancient methane-seep deposits. Beauchamp and Savard (1992) found an average value of -18‰ for five samples of pyrite enclosed in a Cretaceous seep-carbonate from the Canadian arctic. A wide range of $\delta^{34}\text{S}$ values has been reported for pyrite from an Eocene seep limestone in Washington State (Peckmann et al., 2003). Using conventional preparation techniques, a range of 15‰ was found on a cm-scale within the same limestone sample and the total range of $\delta^{34}\text{S}_{\text{pyrite}}$ values for all samples analysed was 20‰. The lowest $\delta^{34}\text{S}$ value obtained was -15‰. The wide range of

$\delta^{34}\text{S}$ values found by Kohn et al. (1998) and, to a lesser degree, by Peckmann et al. (2003) is consistent with Rayleigh fractionation of sulphur isotopes in a closed system. It most likely results from bacterial sulphate reduction in microenvironments, where small, residual pools of seawater-sulphate are utilised. A comparison with pyrite from oceanic spreading centres reveals that the thermochemically formed sulphide exhibits a much smaller isotope variability (cf. Shanks, 2001) than the seep-associated pyrite. Being derived from two virtually unlimited sources, i.e. MORB-derived sulphides ($\delta^{34}\text{S}$ of $+0.1 \pm 0.5$ ‰ Sakai et al., 1984) and reduced seawater-sulphate ($\delta^{34}\text{S}$ of +21‰, Rees et al., 1978), thermochemically formed pyrites display a rather homogenous isotope composition.

Therefore, not only low $\delta^{34}\text{S}$ values, but also isotopic heterogeneity may be used as a proxy for the biogenic formation of pyrite. Remarkably, the lowest $\delta^{34}\text{S}$ values reported for seep-associated pyrites (as low as -41‰, Kohn et al., 1998) are too low to be explained by a single-step process, considering the maximal known fractionation capacity of SRB (47‰, Bolliger et al., 2001) and the isotopic composition of marine sulphate ($\delta^{34}\text{S}$ of +21‰ Rees et al., 1978). Moreover, as sulphate reduction coupled to AOM is not thought to be substrate (i.e. methane) limited in methane-seep areas (Aharon and Fu, 2000), no such extreme fractionation can be expected. $\delta^{34}\text{S}_{\text{pyrite}}$ values too low to be explained by sulphate reduction alone could be linked with sulphide oxidation and subsequent bacterial disproportionation of the intermediate sulphur species (elemental sulphur, thio-sulphate, or sulphite), producing ^{34}S -enriched sulphate and ^{34}S -depleted sulphide (Canfield and Thamdrup, 1994). The lowest $\delta^{34}\text{S}$ values of seep-associated pyrite either indicate that bacterial disproportionation was involved in the cycling of sulphur at the seep sites (cf. Aharon and Fu, 2003) or that yet unknown strains of SRB are capable of such a fractionation.

In summary, both the wide range of $\delta^{34}\text{S}$ values and strong depletions in ^{34}S relative to seawater-sulphate point to bacterial sulphate reduction as the sulphide-generating process in methane-seep environments. Stable sulphur isotopes are a useful tool to reconstruct the biogeochemical cycling of sulphur at ancient seep sites. With hopefully more systematic

studies becoming available in the future, characteristic isotope patterns might be recognized not only for bacterial sulphate reduction in general, but also for AOM by sulphate.

4. Biomarkers

Compared to other methods, the particular strength of the biomarker concept is its potential to evaluate the persistence of distinctive methane-utilising taxa on a geological time scale. Compound-specific isotopic measurements have become essential for the recognition of relevant tracer compounds. As methane is strongly depleted in ^{13}C , the isotopic signatures of specific lipids can testify to the biological uptake of methane carbon and differentiate indigenous substances from allochthonous compounds and contaminants.

The current ‘fossil database’ includes five ancient methane–seep carbonates (Table 2). In the following, previous biomarker reports on these materials are reviewed and, in some instances, complemented by

additional data. The fossil seep deposits show very low to moderate thermal maturities and give an idea of postdepositional alterations that modify the original lipid distributions.

4.1. Lipid patterns of modern seeps

Numerous studies on modern environments provide information on the compound inventories associated with methane–seeps (for references, see Table 3; recent compilations are provided by Hinrichs and Boetius, 2002; Pancost and Sinninghe Damsté, 2003). Strong variations in the patterns reported indicate considerable diversity of the microbial taxa involved in methane consumption. However, most of the biomarkers fall into the following categories, according to their chemical structures and most likely biological sources.

- (1) Isoprene-based archaeal lipids, namely (i) tail-to-tail linked, irregular isoprenoid hydrocarbons (Fig. 4, structures I, II, III, and unsaturated

Table 2
Description of samples from recent reference sites (Black Sea, R1–3), and fossil seeps for which biomarker data exist (F1–9)

Location	Sample	Age	Literature	Maturity	Parameter
NW Black Sea, Ukrainian shelf	Microbial mats, R1, R2, Seep carbonate, R3	Recent	Pimenov et al. (1997) M; Peckmann et al. (2001b) P; Thiel et al. (2001a, b) B; Lein et al. (2002) P; Michaelis et al. (2002) B, M; Tourova et al. (2002) M	–	–
Be’eri, Israel	Microbial mat, sandstone	Pleistocene	Burhan et al. (2002) B	Very low	$\beta\beta\text{-}\gg\alpha\beta\text{-}$ hopanoids, intact aminobacteriohopanetriol
Marmorito, N-Italy	Marmorito limestone, F1 Tubeworm limestone, F2 Siltstone embedding seep carbonates F3	Miocene	Peckmann et al. (1999b) P, B; Thiel et al. (1999) B this study	Very low Low	$\beta\beta\text{-}\gg\alpha\beta\text{-}$ hopanoids, Hop-17(21)-ene present Hop-17(21)-ene prominent $\beta\beta\text{-}\lt\alpha\beta\text{-}$ hopanoids, 20S/(S+R) C_{29} steranes = 0.3
Lincoln Creek Fm., WA, USA	Seep carbonates (CR3, CR2, SR4), F4, F5, F6	Oligocene	Rigby and Goedert (1996) P; Thiel et al. (2001a) B; Peckmann et al. (2002) P, B	Very low	$\beta\beta\text{-}\gt\alpha\beta\text{-}$ hopanoids, Hop-17(21)-ene prominent
Whiskey Creek, WA, USA	Seep carbonate, F7	Eocene	Goedert et al. (2003) P, B	Low to moderate	22S/(S+R) homohopanes = 0.5, $\beta\beta\text{-}$ hopanoids absent, 20S/(S+R) C_{29} steranes = 0.3
Beauvoisin, S-France	Seep carbonates, F8, F9	Jurassic Oxfordian	Gaillard et al. (1985) P; Peckmann et al. (1999b) P, B	Moderate	22S/(S+R) homohopanes = 0.56, Ts/(Ts+Tm) = 0.32

Capital letters in the ‘Literature’ column refer to studies on microbiology (M), geology–palaeontology and petrography (P) and biomarkers (B), respectively. For details on the maturity parameters used, see Peters and Moldowan (1993).

Table 3

Characteristic ^{13}C -depleted biomarkers reported from recent methane-rich environments, likely biological sources, and inferred diagenetic products (HC=hydrocarbons)

Compound/structure (Fig. 4)		Biological source	Literature	Putative diagenetic products
Crocetane (2,6,11,15-tetramethylhexadecane), crocetenes	I	Archaea?	Boetius et al. (2000), Elvert et al. (2000, 2001), Hinrichs et al. (2000), Pancost et al. (2000, 2001a), Bian et al. (2001), Orphan et al. (2001b), Thiel et al. (1999, 2001a), Michaelis et al. (2002), Zhang et al. (2003)	Crocetane, $\leq \text{C}_{20}$ tail-to-tail isoprenoid HC
PMI (2,6,10,15,19-pentamethylcosane), PMIA	II	Archaea (Methanosarcinales?)	Boetius et al. (2000), Elvert et al. (2000, 2001), Hinrichs et al. (2000), Pancost et al. (2000, 2001a, 2001b), Bian et al. (2001), Orphan et al. (2001b), Thiel et al. (1999, 2001a), Michaelis et al. (2002), Zhang et al. (2003)	PMI, $\leq \text{C}_{25}$ tail-to-tail isoprenoid HC
Squalane (2,6,10,15,19,23-hexamethyltetracosane), squalenes	III	Archaea, bacteria, widespread	Elvert et al. (2000)	Squalane, $\leq \text{C}_{30}$ tail-to-tail isoprenoid HC
Archaeol (2,3-di- <i>O</i> - phytanyl- <i>sn</i> -glycerol)	VIII	Archaea	Hinrichs et al. (1999, 2000), Boetius et al. (2000), Elvert et al. (2000, 2001), Pancost et al. (2000, 2001a, 2001b), Orphan et al. (2001b, 2002), Michaelis et al. (2002), Werne et al. (2002), Zhang et al. (2003)	Phytanol, phytanic acid, $\leq \text{C}_{20}$ head-to-tail isoprenoid HC (e.g. phytane, pristane, nor-pristane) as above
<i>sn</i> -3- and/or <i>sn</i> -2- Hydroxyarchaeol (2- <i>O</i> -3-hydroxyphytanyl- 3- <i>O</i> -phytanyl- <i>sn</i> -glycerol)	IX	Archaea (Methanosarcinales <i>sn</i> -2-?; Methanoaeta <i>sn</i> -3~)	Hinrichs et al. (1999), Boetius et al. (2000), Pancost et al. (2000, 2001a, 2001b), Orphan et al. (2001b, 2002), Michaelis et al. (2002), Werne et al. (2002), Zhang et al. (2003)	as above
Biphytanyl tetraethers	X	Archaea	Pancost et al. (2000, 2001a*), Schouten et al. (2001), Thiel et al. (2001a**), Michaelis et al. (2002**), Wakeham et al. (2003), Zhang et al. (2003)*=biphytanyl α,ω -diols; **=hydrocarbons after ether cleavage	α,ω -Diols, and -diacids, $\leq \text{C}_{40}$ head-to-head isoprenoid HC
Mono- and dialkyl- glycerolethers (non isoprenoidal); <i>n</i> -, mono-methyl (<i>i</i> -, <i>ai</i> -, mid-chain), ω -cyclohexyl, cyclopropyl carbon chains	e.g. XIII	SRB	Hinrichs et al. (2000), Pancost et al. (2001b), Orphan et al. (2001b, 2002), Michaelis et al. (2002), Teske et al. (2002), Werne et al. (2002)	Corresponding alkan-1-ols, alkanoic acids, and alkanes
Ester-bound fatty acids; <i>n</i> -, mono-methyl (<i>i</i> -, <i>ai</i> -, mid-chain), ω -cyclohexyl, cyclopropyl carbon chains	e.g. XI	SRB	Boetius et al. (2000), Hinrichs et al. (2000), Pancost et al. (2000, 2001b), Orphan et al. (2001b), Thiel et al. (2001a), Zhang et al. (2002), Elvert et al. (2003)	Corresponding alkan-1-ols and alkanes
Diploptene/diplopterol (hop-22(29)-ene, hopan-22-ol)	XIV	Bacteria (methanotrophs?)	Spooner et al. (1994), Elvert et al. (2000), Pancost et al. (2000), Hinrichs (2001), Thiel et al. (2001a, 2003), Werne et al. (2002)	Hopanoide HC $\leq \text{C}_{30}$
Extended hopanoids, e.g. <i>bis</i> -homohopanol, <i>bis</i> -homohopanoic acid	e.g. XVI	Bacteria	Pancost et al. (2000), Thiel et al. (2003)	Hopanoide HC $\leq \text{C}_{35}$
<i>n</i> -Tricos-10-ene	XVII	Bacteria?	Thiel et al. (2001b), Michaelis et al. (2002)	<i>n</i> -Tricosane, < C_{23} alkanes,

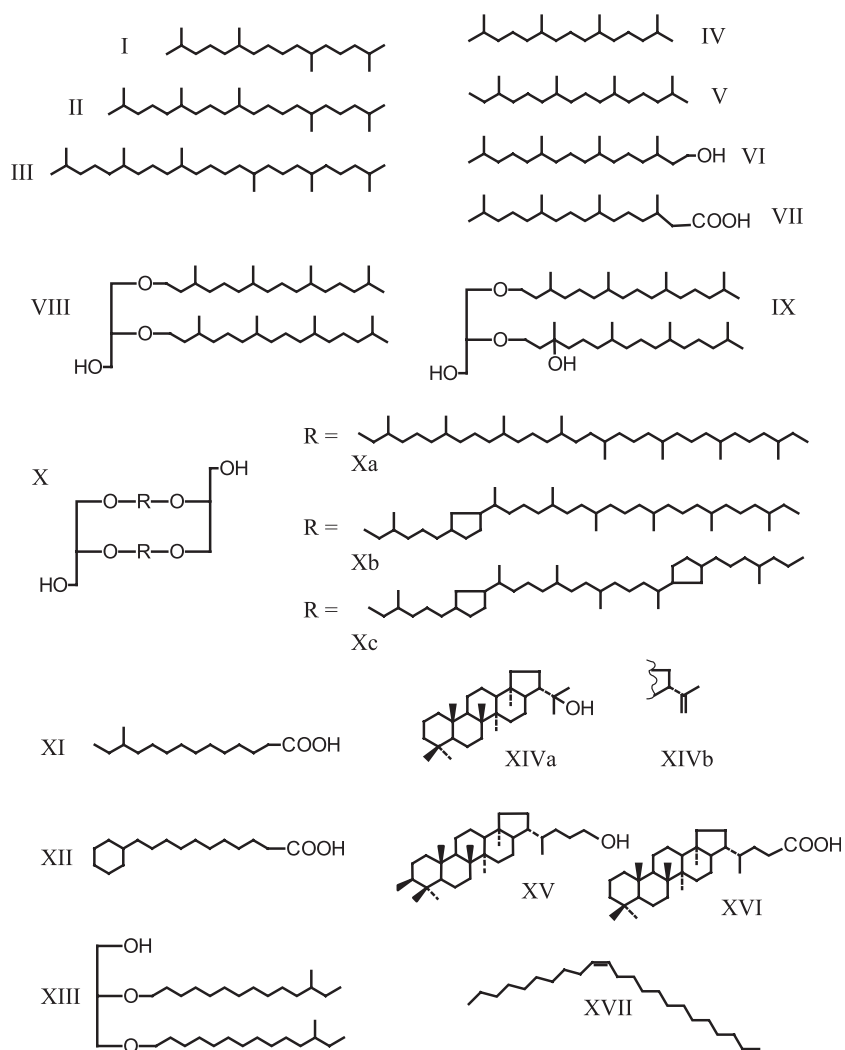


Fig. 4. Structures cited in the text.

derivatives), (ii) glycerol diethers with regular head-to-tail linked C_{20} isopranyl (phytanyl-) moieties, namely archaeol (VIII), *sn*-2- (IX) and *sn*-3-hydroxyarchaeol, (iii) phytanol and phytanic acid (VI, VII), and (iv) glycerol tetraethers carrying head-to-head linked acyclic and cyclic phytane dimers (C_{40} biphytanes; Xa-c), and the corresponding C_{40} α,ω -diols and diacids.

- (2) Acetate-based lipids carrying non-isoprenoid carbon chains. These compounds are thought to originate from bacteria, particularly from SRB.

The structures comprise various ester-bound C_{14} to C_{18} fatty acids. Most abundant are saturated and monoenoic *n*-homologues, terminally branched (*anteiso*- C_{15} , XI), and to a lesser extent, cyclic carbon chains (10,11-cyclopropyl- and ω -cyclohexyl-, XII). The fatty acids are accompanied by corresponding non-isoprenoid alcohols, monoalkylglycerolethers (MAGE), and 1,2-dialkylglycerolethers (DAGE, e.g. XIII).

- (3) Hopanoids, namely the C_{30} compounds diplopterol and diploptene (XIV), and extended

homologues, such as *bis*-homohopanol and *bis*-homohopanoic acid (XVI). These lipids may derive from bacteria other than SRB, including aerobic methanotrophs.

- (4) Compounds of unknown affiliation, such as *n*-tricosane derivatives (XVII).
- (5) Allochthonous components, e.g. high molecular weight *n*-alkanes and carboxylic acids derived from land-plants, and steroids derived from phytoplankton.

In methane-rich settings, these compounds, except those listed in (5), typically show strong to extreme depletions in ^{13}C ($\delta^{13}\text{C}$ values as low as $\sim -130\text{‰}$; Elvert et al., 2000) in contrast to values normally observed for marine lipids of about -25‰ . The ^{13}C depletions are indicative for an anabolic uptake of methane-derived carbon by the source biota and are believed to reflect in situ activity of syntrophic archaea/SRB consortia mediating AOM.

4.2. Postdepositional processes: general remarks

As in recent sediments, the admixture of allochthonous organic substances and biodegradation influences the fossil biomarker inventory of rocks. It is additionally diluted by secondary migration and progressively altered by thermal maturation. These processes obscure to a varying degree the information archived and must be addressed in the interpretation of the patterns observed. Nevertheless, many fossil seep carbonates show a remarkable preservation of their indigenous biomarker inventory. Unlike other carbonate rocks (e.g. reefs), seep carbonates are commonly embedded in fine-grained, hemipelagic sediments which may, to a certain extent, provide an effective sealing against diagenetic alterations caused by migrating fluids. Moreover, carbonate precipitation fuelled by AOM (Aloisi et al., 2000; Peckmann et al., 2001b; Lein et al., 2002; Michaelis et al., 2002) may also result in an early 'self-lithification' of the organisms involved and appears to be crucial for the protection of organic compounds (Thiel et al., 1999). A third important factor may be the sulphate-dependence of AOM, leaving no sulphate available for further oxidation and thus protecting the organic matter of AOM-performing microbes from destruction (Hinrichs et al., 2000).

4.3. Lipid patterns of ancient seeps

4.3.1. Archaeal isoprenoids

Tail-to-tail linked isoprenoid carbon chains occur only as free hydrocarbons. It is unclear, whether these compounds are metabolic by-products or have a distinct function among the archaeal lipids. The PMI skeleton (II) has been identified in the lipid fractions of methanogenic and thermoacidophilic archaea and is widely used as a sedimentary biomarker for archaea, specifically methanogens. PMI derivatives have been found in pure cultures of methanogens of the order Methanosarcinales (Schouten et al., 1997). This is consistent with the ubiquitous occurrence of ^{13}C -depleted PMI derivatives at modern methane-seeps, where members of the Methanosarcinales are regarded as an archaeal partner involved in AOM (Table 3). At modern seeps, like in the cultured archaea, PMI is accompanied by unsaturated derivatives (PMI Δ) with up to five double bonds (Table 3; Fig. 5a). During diagenesis, PMI Δ rapidly disappear, possibly because of binding to macromolecules or reductive conversion to the saturated hydrocarbon. This may explain the lack of PMI Δ , and in turn, often enhanced relative concentrations of PMI in fossil sediments (Table 4; Fig. 5b–d). ^{13}C -depleted PMI is, as indicated by our database, the most widespread and persistent hydrocarbon biomarker for AOM-performing archaea (Table 4). Remarkably, PMI as well as crocetane are missing in a Pleistocene seep deposit (Be'eri, Israel), where the ancient microbial population was based on aerobic (i.e. bacterial) methanotrophy rather than on AOM (Burhan et al., 2002).

^{13}C -depleted crocetane (I) is a specific biomarker for AOM at seeps. However, compared to PMI, crocetane shows a more scattered distribution, and its absence has been reported in several cases (Hinrichs et al., 1999; Thiel et al., 2001a), possibly indicating independent sources for these compounds (Bian et al., 2001). Sediments as old as Precambrian have been reported to contain crocetane (McCarthy, 1967; Greenwood and Summons, 2003), but in this early work, no isotopic data were available. Recently, crocetane with a normal isotopic composition was found in Ordovician crude oil from Australia by Barber et al. (2001). These authors suggested an origin of crocetane from the thermal degradation of PMI.

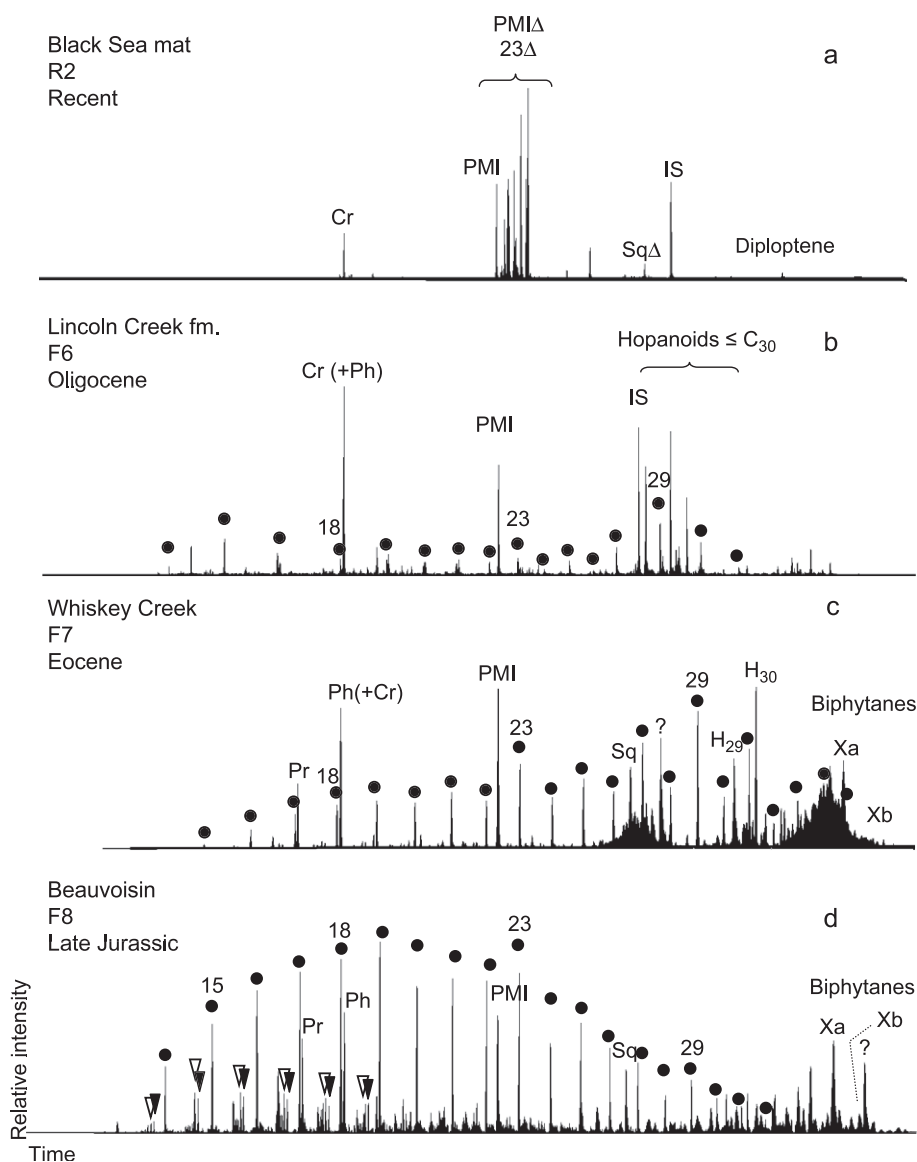


Fig. 5. Total ion current chromatograms (subtracted for background) of hydrocarbons (C_{15+}) extracted from selected seep deposits. Age and thermal maturity increase from (a) to (d). Filled circles/numbers indicate n -alkanes of the respective carbon chain length. Pr = pristane (IV); Cr = crocetane (I); Ph = phytane (V, partly coeluting with Cr); 23 = n -tricosane; PMI = 2,6,10,15,19-pentamethylcosane (II); Sq = squalane (III); Δ = unsaturated derivatives; H_{29} , H_{30} = 17 α (H),21 β (H)-30-norhopane, 17 α (H),21 β (H)-hopane, respectively; open and filled triangles = 2-methyl- (*i*-) alkanes and 3-methyl- (*ai*-) alkanes. IS = internal standard.

Archaea are the widely accepted source of ^{13}C -depleted crocetane at modern seeps. Crocetane occurrences in fossil seep deposits indicate the persistence of the source organisms through geological time. If present, crocetane is always accompanied by PMI and

is similarly depleted in ^{13}C (Table 4). Prior to the thermal generation of hydrocarbons, crocetane may represent a main compound of the hydrocarbon fractions, as observed for several Cenozoic seeps (Table 4, Fig. 5b). Upon thermal stress, crocetane tends to get

Table 4

Occurrence and isotopic compositions of methane-related biomarkers from fossil seeps and recent reference samples (Black Sea, R1–3)

Sample	Ph									PMI		Sq HC sat./Δ	C ₄₀ Biphytanes (# = cycles)						ai-15			
	23 HC	Pr HC	Cr HC	HC	OH	Acid	-O-	-O- OH	HC sat.	HC Δ	HC		HC	HC	-O-	-O-	-O-	HC	OH	Acid	-O-	
																						0
R1	■ -73 ¹	T	∅	T	∅	T	■	∅	■	■	T	∅	∅	∅	■	■	■	∅	∅	■	■	
R2	■	T	■ -95	∅	∅	T	■	■	■	■	■	∅	∅	∅	■	■	■	∅	∅	■	■	
R3	■	T	■ -107	T	■	■	■	■	■	■	■	∅	∅	∅	■	■	■	∅	∅	■	■	
Be'eri ²			∅				■ →*	∅	∅	∅	∅	∅	∅	∅	∅	■	■					
F1 ²	■ -87	T	T	T	T	■	∅	∅	■	∅	T	■	∅	∅				∅	■	T	■	
F2	■ -72	T	■ -116	?	■	■	■	∅	■	∅	■	T	∅	∅					■	■	∅	
F3	■ -81	T	?	■		■			■	∅	■	∅	∅	∅				∅		■	■	
F4	■	■ -81	■ -110	■	■	■	■	T	■	∅	■	■	T	∅	T	T	∅	∅	■	■	■	
F5	■ -33	■ -39	■	■	■	■	■	∅	■	∅	■	■	■	T				T	■	■	∅	
F6	■ -68	■	■	■	■	■	■	∅	■	∅	■	■	∅	∅				■		■	■	
F7	■ -55	■ -42	T	■ -80		■	∅	∅	■	∅	■	■	■	T				■		■	■	
F8	■ -44	■ -45	∅	■ -66		T	∅	∅	■	∅	■	■	T	∅	∅	∅	∅	■		T	∅	
F9	■	■	∅	■			∅		■	∅	■	■	∅	∅				■			■	

Sample denotations accord to the code given in Table 2. ■=high abundance, ■=moderate or low abundance, T=traces, ∅=not present, no entry=not analysed, or not reported. Numbers denote $\delta^{13}\text{C}$ values [‰ vs. PDB]. Values given in italics have not been previously reported, otherwise see Table 2 for references. Carbon skeletons are denoted as follows: 23=*n*-tricosane (F1–F9) and *n*-tricosene (R1–R3 only); Pr=pristane (IV); Cr=crocetane (II); Ph=phytane derivatives (V–IX); PMI=2,6,10,15,19-pentamethylcosane (II) and -icosenes; Sq=squalane (III); ai-15=*anteiso*-pentadecane derivatives (XI, XIII), as representatives for non-isoprenoid lipids. Derivatives appear as: HC=hydrocarbon (sat.=saturated, Δ=unsaturated); OH=alcohols; Acid=monocarboxylic acid; -O-=glycerol ether; -O-OH=hydroxylated glycerol ether; 0,1,2=numbers of cyclopentyl rings in biphytanyl moieties. ¹Hydrogenation product. ²Seep site influenced by aerobic methanotrophy. ³Major coelution with crocetane or phytane, respectively.

progressively masked by phytane. Using conventional GC-columns, it may therefore become increasingly difficult to recognize the presence of crocetane in mature sediments.

Archaeol (VIII) shows a considerable diagenetic stability, as it occurs in the majority of the Cenozoic deposits studied. It is absent from the thermally altered Whiskey Creek and the Late Jurassic seep carbonates. Like archaeol, *sn*-2- (IX) and/or *sn*-3-hydroxyarchaeol are often prominent at modern seeps, but appear to be more susceptible to degradation and have not been reported from ancient sediments. This may be due to the additional functional group involving a tertiary carbon atom. Nevertheless, traces of

hydroxyarchaeol occur in one of the Tertiary Lincoln Creek Formation samples; a finding which may further highlight the high preservation potential of seep carbonates.

Unlike archaeol derivatives, the isoprenoid hydrocarbons phytane (C₂₀, V), pristane (C₁₉, IV) and norpristane (C₁₈) are not common in modern AOM environments, but are ubiquitous in fossil seep deposits (Table 4). The abundance of phytane obviously increases with thermal maturity and it tends to successively mimic the presence of its coeluting pendant, crocetane (Fig. 5). Strong ¹³C-depletions in fossil seep deposits indicate that a major portion of the phytane derives from lipids of methane-utilising archaea. The

most plausible biological precursors are archaeol (VIII) and hydroxyarchaeol derivatives (e.g., IX). A similar scenario may be valid for pristane (IV), although it is generally less prominent in the fossil seep samples than phytane and always shows higher ^{13}C contents. Nevertheless, $\delta^{13}\text{C}$ values in the range of -50‰ to -30‰ (Table 4) suggest major inputs from photoautotrophic sources, but additional contributions from ^{13}C -depleted archaeal lipids. An analogous observation was made for *nor*-pristane in the Whiskey Creek deposit ($\delta^{13}\text{C}$: -55‰). The isotopic signatures indicate an origin of regular C_{18} , C_{19} , and C_{20} isoprenoids from archaeal isopranyl lipids, with possible implications for the interpretation of these widespread compounds in other ancient sediments and oils.

Archaeal dibiphytanyl diglycerol tetraethers (X) are not amenable to conventional GC-MS and their direct study requires more advanced analytical techniques (HPLC-MS). Recently, cyclic and acyclic tetraethers have been found in modern marine settings (Hopmans et al., 2000; Sinninghe Damsté et al., 2000) including methane-seeps (Pancost et al., 2001a; Zhang et al., 2003), and even in Cretaceous black shales (Kuypers et al., 2001). These compounds were also detected indirectly through chemical degradation techniques (e.g. HI/LiAlH_4 -treatment) releasing the head-to-head linked C_{40} isoprenoid hydrocarbon moieties (Michaelis and Albrecht, 1979; Hoefs et al., 1997; King et al., 1998). In modern Black Sea seep carbonates and associated microbial mats, the C_{40} isoprenoids obtained by this method typically consist of strongly ^{13}C -depleted acyclic (Xa), mono- (Xb) and dicyclic (Xc) biphytanes ($\delta^{13}\text{C}$ as low as -96‰ , Thiel et al., 2001a; Michaelis et al., 2002). This indicates that methane-metabolizing archaea are the source of both acyclic and cyclic tetraether lipids at these sites.

Cyclic C_{40} isoprenoids characterize thermo- and acidophilic archaea and the widespread planktonic crenarchaeota rather than non-thermophilic methanogens (e.g. Koga et al., 1993). In the Black Sea seep deposits, the high abundance of the monocyclic compound (Xb) and the absence of the tricyclic derivative known as 'crenarchaeol' (Sinninghe Damsté et al., 2002; not shown in Fig. 4) differ from the distributions previously found in Black Sea sediments (Hoefs et al., 1997; King et al., 1998) and demonstrate the

phylogenetic distinctness of the seep-related taxa from the widespread planktonic crenarchaeota. The patterns observed agree well with recent results from Mediterranean seep deposits (Pancost et al., 2001a), and Black Sea particulates (Schouten et al., 2001; Wakeham et al., 2003). In these studies, low $\delta^{13}\text{C}$ -values were found for acyclic, mono- and dicyclic C_{40} isoprenoids (Xa-c), but not for crenarchaeol. Comparing Black Sea seep sites and water-column data, it seems that the distinctive methane-metabolizing taxa are not limited to localized sedimentary settings but may as well thrive in a planktonic state in methane-rich, anoxic water bodies. However, the specific biomarker signal of planktonic, methane-utilising archaea appears not to be transferred into the sediments, as no ^{13}C depleted biphytane moieties were found in Black Sea surface sediments (Schouten et al., 2001; Wakeham et al., 2003).

Possible early diagenetic products of archaeal tetraether lipids are the corresponding α,ω -diols and -diacids (Schouten et al., 1998) that were recently reported from modern methane-rich sediments (Pancost et al., 2000; Teske et al., 2002). Functionalized biphytanyl moieties may be readily incorporated into macromolecular fractions (Richnow et al., 1992; Schouten et al., 1998) which have the potential to produce the corresponding hydrocarbons upon thermal maturation. That process occurs at the expense of the cyclic derivatives, probably due to the lower stability of the five-membered ring structures. This may explain why *unbound* cyclic C_{40} isoprenoid hydrocarbons were, unlike acyclic biphytane (Xa), not observed in ancient sediments and oils (cf. Schouten et al., 1998). Accordingly, traces of free mono- (Xb) and dicyclic (Xc) hydrocarbons found associated with biphytane at some of the fossil seeps (Table 4) may be interpreted as remnants of what were once more abundant cyclic tetraether lipids.

4.3.2. Hopanoids

Hopanoids are widely distributed in bacteria (Rohmer et al., 1984) and their presence in sediments and oils is explained by contributions from bacterial sources (Ensminger et al., 1972; Mycke et al., 1987; Innes et al., 1997; Farrimond et al., 2000). However, the common occurrence of ^{13}C -depleted hopanoids in seep deposits (Table 3), needs to be discussed in some more detail. Recent microbiological work on methane-

rich environments, including gas hydrates, revealed a vast array of bacterial taxa (Lanoil et al., 2001; Orphan et al., 2001b; Teske et al., 2002), yet their capacity to biosynthesize hopanoids is unknown. Hopanoids have never been found in strictly anaerobic bacteria, including SRB (Ourisson and Rohmer, 1992). Two hypotheses for the origin of ^{13}C -depleted hopanoids have been proposed. One hypothesis explains the occurrence of sedimentary ^{13}C -depleted hopanoids, namely C_{30} compounds such as diplopterol (XIVa) and diploptene (XIVb), with contributions from aerobic methanotrophs (Spooner et al., 1994; Werne et al., 2002; Burhan et al., 2002), known producers of these compounds (Rohmer et al., 1984; Summons et al., 1994). Accordingly, Hinrichs (2001) used diplopterol as a molecular proxy for past gas hydrate destabilization events in the Santa Barbara Basin. Other studies indicated that ^{13}C -depleted hopanoids could also emerge from yet unknown anaerobic bacteria, probably linked with the AOM-performing population (Pancost et al., 2000; Thiel et al., 2003).

Fossil seep deposits generally show abundant ^{13}C -depleted hopanoid hydrocarbons which, in immature rocks, co-occur with hopanoic acids (XVI), alcohols, and ketones (Thiel et al., 1999; Burhan et al., 2002; Goedert et al., 2003). For the hydrocarbons, an apparent predominance of homologues with 30 C-atoms or less is consistent with a common origin from diploptene and/or diplopterol. Indeed, immature seep carbonates may still contain ^{13}C -depleted hopenes $\leq \text{C}_{30}$, in particular hop-17(21)-ene, a known diagenetic rearrangement product of diploptene (Table 2, sample F2; $\delta^{13}\text{C}$: -83‰ , Thiel et al., 1999).

Unlike hydrocarbons, oxygen-bearing hopanoids often maximize at C_{32} (hopanoic acids, XVI, and alcohols) in the fossil seep deposits. These structures widely occur in sediments and oils (Farrimond et al., 2002; Meredith et al., 2000 and references therein) and are considered as degradation products of C -32,33,34,35 tetrafunctionalized bacteriohopanoids (Innes et al., 1997). Among the fossil seep deposits, hopanoic acids and hopanols are less abundant in samples of higher maturity (Fig. 6). Where hopanoic acids and alcohols are present, appreciable ^{13}C -depletions indicate that at least a portion of their carbon derives from methane. However, as in modern seep environments, it is difficult to attribute the basal carbon skeletons to particular bacterial taxa.

Additional source information may arrive from hopanoids that show structural particularities restricted to only a few groups of bacteria. Such features may encompass an additional methyl group at the C-3 atom as found for 3β -methyl-17 β (H),21 β (H)-*bis*-homohopanol (XV) in the Miocene Marmorito limestone (Peckmann et al., 1999b), and for 3β -methyl-30-norhopanes and 3β -methyl-22,29,30-trisnorhopanes in the Pleistocene Be'eri seep deposit (Burhan et al., 2002). Hopanoids with ring-A methylation characterize aerobic Type I methylotrophs, for instance the genera *Methylococcus* and *Methylocaldum* sp. (Neunlist and Rohmer, 1985; Summons et al., 1994; Cvejic et al., 2000). Such a bacterial source agrees with the isotopic signatures found for the 3β -methyl-hopanoids from the fossil seeps ($\delta^{13}\text{C}$: -100‰ , Marmorito; $\sim -85\text{‰}$, Be'eri). These results indicate that aerobic methanotrophs may significantly contribute to the organic matter inventory of methane-seeps. They also highlight the potential of 3β -methylhopanoids as specific markers for aerobic methanotrophy in ancient environments, as it was previously suggested from the occurrence of 3β -methyl-norhopanes with δ -values as low as -90‰ in the Eocene Green River oil shale (Collister et al., 1992).

4.3.3. Non-isoprenoidal lipids

Fatty acids are lipid building blocks of the cell membranes in bacteria and eukaryotes. According to the lipid contents found in SRB and marine sediments, the common occurrence of ^{13}C -depleted C_{14} to C_{18} fatty acids and fatty alcohols at modern seeps has been explained by contributions from SRB associated with AOM (Table 3). In addition, non-isoprenoidal mono- and dialkylglycerolethers (MAGE, DAGE, e.g. XIII) have recently been reported from a number of modern environments (Sinninghe Damsté et al., 2000), including methane-rich deposits (Hinrichs et al., 1999, 2000; Pancost et al., 2001b; Michaelis et al., 2002). These structures are known from only a small number of bacteria, such as the phylogenetically deeply branching SRB *Aquifex pyrophilus* and *Thermodesulfobacterium commune* (cf. Hinrichs et al., 2000; Pancost et al., 2001b). Due to their strong ^{13}C depletions, MAGE and DAGE found in methane-seep deposits were attributed to yet unknown SRB linked with AOM (Hinrichs et al., 2000; Pancost et al., 2001b). Indeed, new results revealed the presence of MAGE phospho-

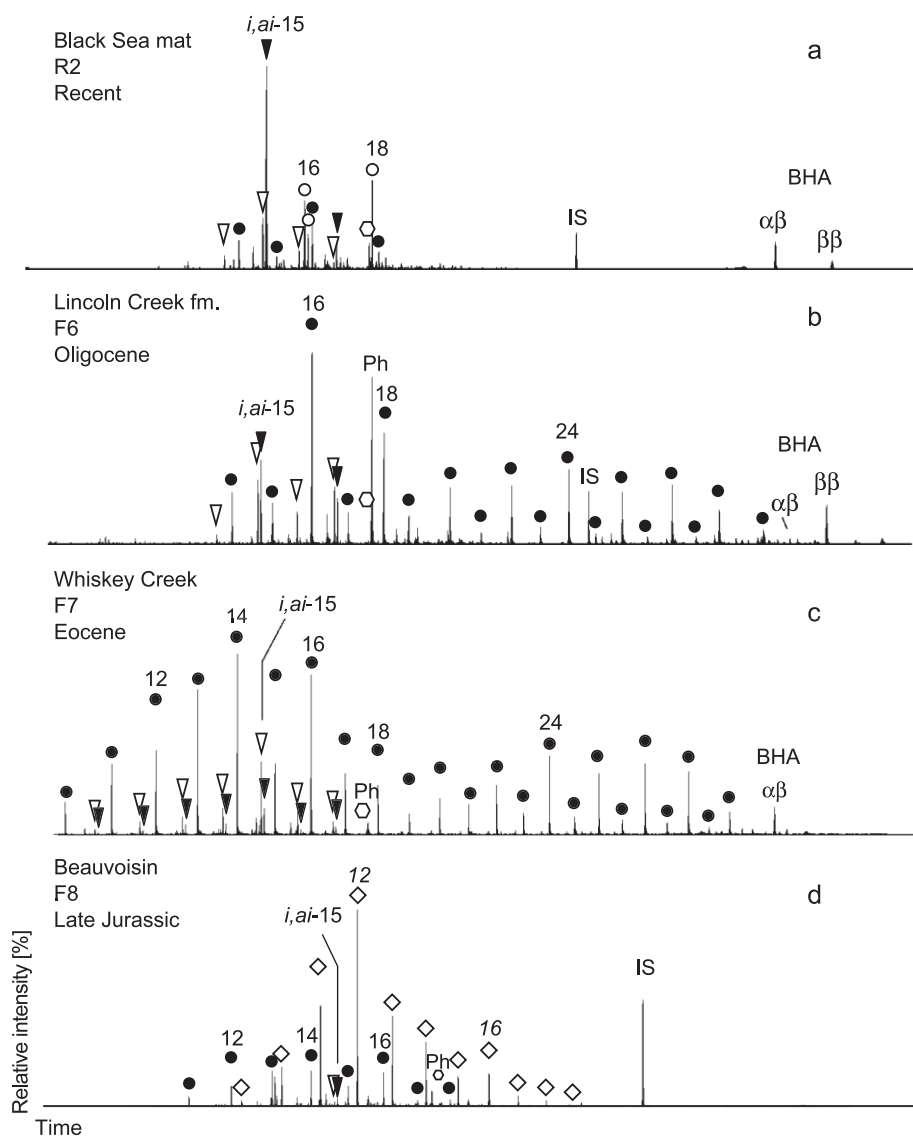


Fig. 6. Total ion current chromatograms (subtracted for background) of carboxylic acids (methyl esters) extracted from selected seep deposits. Age and thermal maturity increase from (a) to (d). Filled circles/numbers indicate *n*-alkanoic acids of the respective carbon chain length. Open circles = monoenoic C₁₆- and C₁₈-acids, respectively; open and filled triangles = ω 2- (*i*-) and ω 3- (*ai*-, XI) methylated alkanolic acids; Ph = phytanic acid (VII); hexagon = ω -cyclohexylundecanoic acid (XII, partly coeluting with Ph); BHA $\alpha\beta$, $\beta\beta$ = 17 α (H),21 β (H)-*bis*-homohopanoic acid (geological configuration) and 17 β (H),21 β (H)-*bis*-homohopanoic acid (biological configuration), respectively; open squares = α, ω -dicarboxylic acids of the respective carbon chain length; IS = internal standard.

lipids in *Desulfosarcina variabilis* (Rütters et al., 2001), a member of the mesophilic SRB genus which is commonly observed in AOM environments (Boettius et al., 2000; Orphan et al., 2001b; Thomsen et al., 2001; Michaelis et al., 2002).

Teske et al. (2002) pointed out that ¹³C-depleted neutral lipids and SRB-derived fatty acids rapidly degrade within the uppermost part of the sediment column in the Guaymas Basin. Therefore, it is indicated that these compounds are not preserved in

sediments with high microbial activity at elevated temperatures. However, ancient methane–seep deposits with pronounced carbonate formation apparently sustained the persistence of SRB-derived fatty acids and alcohols within the carbonate lattice (Thiel et al., 1999; Goedert et al., 2003). Their diagenetic fate can be deciphered in Fig. 6. Unsaturated carbon chains which are prominent at modern seeps (Elvert et al., 2000, 2003; Hinrichs et al., 2000; Zhang et al., 2002; Fig. 6a) are missing in even the most immature rocks, indicating that these lipids have been rapidly reduced and/or degraded upon early diagenesis. Fatty acids from the immature Tertiary seep-deposits encompass saturated, ^{13}C -depleted, even-numbered *n*-fatty acids, abundant *i*- and *ai*-branched (e.g., XI), and ω -cyclohexylundecanoic acids (XII), with similar carbon skeletons as found in modern settings (Fig. 6b; Table 3). In two Miocene carbonates, even intact DAGE were found (Table 4). Such patterns appear to get lost with increasing thermal stress, as inferred from the Eocene Whiskey Creek deposit (Goedert et al., 2003; Fig. 6c). Here, DAGE are missing and *n*-alkanoic acids show a much lower even-over-odd carbon number preference. Apparently, postdepositional alteration created saturated, short-chain homologues from biogenic compounds of higher molecular weight (i.e., C_{16} , C_{18} fatty acids). Likewise, the more specific bacterial *i*- and *ai*-isomers approach a random pattern with carbon chains shorter than in the putative precursor lipids. $\delta^{13}\text{C}$ values between -30‰ and -25‰ for the *n*-isomers indicate allochthonous sources, whereas the *ai*-acids show a significant ^{13}C depletion ($\sim -42\text{‰}$ for *ai*-14 and *ai*-15; Goedert et al., 2003), and may thus represent a fossil equivalent to the prominent occurrence of *ai*-carbon chains in modern seep deposits.

Low amounts of carboxylic acids were released upon hydrolysis from the thermally more mature seep carbonate from Beauvoisin (Late Jurassic). It shows only traces of monomethylated compounds, an unspecific pattern of *n*-alkanoic acids, and abundant α,ω -dicarboxylic acids (maximum at C_{12}) of unknown origin (Fig. 6d). $\delta^{13}\text{C}$ values from -22‰ to -29‰ for the latter gave no evidence for a contribution from methane carbon, whereas no reliable δ -values could be obtained for the branched acids. However, an indication for the occurrence of SRB linked to AOM was still found in the hydrocarbon

fraction (Fig. 5d), where *ai*-pentadecane is significantly depleted in ^{13}C ($\delta^{13}\text{C}$: -42‰) relative to the neighbouring *n*-alkanes (*n*- C_{16} : -30‰ , *n*- C_{15} : -31‰).

It has to be expected that the specific carbon skeletons of SRB lipids, due to their structure and low molecular weight, behave less refractory against biodegradation, thermal alteration, and weathering than isoprene-based archaeal biomarkers (Peters and Moldowan, 1993). Consequently, postdepositional processes may erase the source information on SRB more rapidly than the archaeal chemofossils. Tracking the distinctive methane-metabolizing consortia over extended geological periods will therefore require (i) to carefully combine biomarker and other evidence (e.g. sulphur isotopes) and (ii) to evaluate potential SRB biomarkers of greater diagenetic persistence. A possible candidate for such a lipid biomarker is ^{13}C -depleted *n*-tricosane. This compound most certainly derives from free *n*- C_{23} alkenes (XVII), which are abundant in modern Black Sea seep carbonates and associated microbial mats (Thiel et al., 2001b), and were also observed in a Black Sea sediment core (Simoneit, 1974). The microbial source of these straight-chain compounds is still unknown, but an origin from bacteria (SRB) rather than from archaea is more likely for biosynthetic reasons. The preference of the ^{13}C -depleted diagenetic product *n*-tricosane in ancient seep carbonates reveals its similar stability as PMI and its potential as a long-standing molecular fossil for AOM environments (Fig. 5, Table 4).

5. Conclusions

- (1) Numerous methane–seep deposits have been reported from Cenozoic strata. A much smaller number of Mesozoic deposits has been recognized and to date only two Palaeozoic deposits with high abundance but low diversity faunas have been shown to be related to methane seepage. Distinctive carbonate fabrics, stable isotope signatures, and biomarker patterns are diagnostic for biogeochemical processes at ancient seep sites.
- (2) When found in seep deposits, inverted stromatolite cavities indicate a downward direction of carbonate aggregation that is fuelled by the

oxidation of ascending methane. Likewise, upside-down stromatolites are related to a downward aggregation of the respective seep carbonate. Micritic nodules, which occur in the matrix of some ancient seep limestones, formed analogously to carbonate concretions. The genesis of pyritiferous nodules was probably linked not only to AOM, but also to iron reduction. A clotted microfabric of primary origin, common in many seep limestones is believed to reflect small-scale variations in the chemical environment due to microbial activity. The involvement of microbes in carbonate formation is further indicated by fossilised biofilms. As microbial activity is the prerequisite for carbonate formation at methane–seeps, seep limestones should be classified as ‘microbialites’, a term as yet mostly applied to shallow water carbonates related to phototrophic processes.

- (3) Some gas hydrate–sediment aggregates exhibit a globular texture. As hydrate-associated carbonates cast this globular texture, carbonate fabrics are a potential tool to track a relation of ancient seep sites with destabilising gas hydrates. Similarly, fracturing of semi-consolidated sediments may be caused by the growth of intercalated gas hydrates or by the release of hydrate chunks from the sediment into the water column. Up to now, however, early in situ brecciation in ancient seep limestones has not been shown to be linked to such processes. Unusually high $\delta^{18}\text{O}$ values of carbonate phases can be used to track the destabilisation of gas hydrates at modern seeps, but this approach has also not been successfully applied to ancient seep deposits.
- (4) Methane–seep carbonates are typified by low $\delta^{13}\text{C}$ values, as they inherit the stable isotope signature from their carbon source, ^{13}C -depleted methane. The $\delta^{13}\text{C}$ value of the methane source is usually significantly lower than $\delta^{13}\text{C}_{\text{carbonate}}$ values, indicating additional carbon sources involved in carbonate formation. Due to variable degrees of mixing, an evaluation of the carbon source based on $\delta^{13}\text{C}$ values alone is problematic. Apart from carbonate phases with low $\delta^{13}\text{C}$ values, ancient seep limestones often contain later diagenetic ^{13}C -enriched phases that apparently

formed in the zone of archaeal methanogenesis. This reveals that methane oxidation and formation may have successively occurred in the same deposit as a function of increasing burial.

- (5) Low but scattered $\delta^{34}\text{S}$ values of sedimentary pyrite enclosed in seep limestones indicate that bacterial sulphate reduction is the sulphide-generating process. Values as low as -41% cannot be explained with the known fractionation capacity of sulphate-reducing bacteria and may indicate an involvement of microbial disproportionation of sulphur. As sulphate reduction and methane oxidation are intimately associated processes in seep environments, future systematic studies on the sulphur isotopic composition of pyrite may reveal patterns typical for sulphate-dependent AOM.
- (6) Characteristic biomarkers in ancient seep environments are (i) ^{13}C -depleted archaeal isoprenoids, (ii) linear and methyl-branched carbon skeletons derived from SRB, and (iii) hopanoids of bacterial origin. Their close correlation with lipids from modern seep environments indicates that the relevant taxa and thus the mechanisms of carbon cycling at methane–seeps have persisted at least since the Mesozoic. Moreover, the consistent ^{13}C depletions of methane-related chemofossils allow tracking diagenetic alterations of the inferred precursor lipids. This knowledge is of paramount importance for further attempts to close the huge time gap between the first definite occurrence of AOM-chemofossils in the Jurassic (ca. 150 My) and the suggested prevalence of AOM in the Archaean (based on low $^{13}\text{C}_{\text{org}}$ in 2700-My-old sediments; Hinrichs, 2002). It has to be stressed, however, that many chemofossils still remain ‘orphan molecules’ with an uncertain biological origin. It will consequently improve our understanding of ancient settings if studies on modern seep microbes lead to a more precise assignment of particular lipids to their source organisms.

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