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Late Triassic mollusk-dominated hydrocarbon-seep deposits from Turkey

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ABSTRACT

Deep-sea hydrothermal vents and hydrocarbon seeps host unique ecosystems relying on geochemical energy rather than photosynthesis. Whereas the fossil and evolutionary history of these ecosystems is increasingly well known from the Cretaceous onward, their earlier history remains poorly understood and brachiopods are considered to have played a dominant role during the Paleozoic and Mesozoic. Here we report five new hydrocarbon-seep deposits from the Upper Triassic Kasımlar shales in southern Turkey. The pyritiferous seep limestones predominantly consist of ^{13}C-depleted micrite with δ^{13}C values as low as −10.4‰, and contain only sparse ^{13}C-depleted rim cement (δ^{13}C as low as −12.0‰), interpreted to result from the recrystallization of banded and botryoidal crystal aggregates of fibrous cement. The geologic ages of the studied seep deposits were determined as late Carnian and early Norian using conodonts. The associated fauna is dominated by modiomorphid and anomalodesmatan bivalves, and also includes a diversity of gastropods and the dimerelloid brachiopod *Halorella*. These faunal assemblages allow a comparison between seep faunas from the two major Triassic ocean basins—the present assemblages being from Tethys, and the only previously known examples being from eastern Panthalassa—and indicate that a cosmopolitan, seep-restricted fauna as in the present-day oceans has existed since the Late Triassic. With almost 20 species, the seep fauna of the Kasımlar shales approaches the diversity of Cretaceous to present-day seep faunas, further emphasizing the ecological similarity of seep faunas since the early Mesozoic. Our findings also highlight that brachiopods and bivalves had a more complex history of coexistence at seeps than currently appreciated.

INTRODUCTION

The discovery of hydrothermal vents and methane seeps on the deep-sea floor has significantly altered our understanding of the limits of life and the diversity of food webs on Earth. The majority of the macrofauna inhabiting these environments depend on symbiotic, chemotrophic bacteria from which they acquire most, if not all, of their nutrition. Hence these ecosystems differ radically from others in being based on chemosynthesis rather than photosynthesis (Sibuet and Olu, 1998). Their evolution may therefore be buffered from mass extinctions and other perturbations of photosynthetic primary production (Tunnicliffe, 1992; Kiel and Little, 2006) and may instead be driven by events affecting the discharge of the reduced chemicals that form the base of the chemosynthesis-based food web (Kiel, 2015).

The fossil record of vent communities, and in particular the much more complete record of seep communities, has provided important insights into the evolution of these ecosystems (Little et al., 1997; Kiel and Little, 2006) and indicates a turnover from brachiopod-dominated communities in the Paleozoic and Mesozoic to bivalve-dominated communities in the Late Cretaceous (Campbell and Bottjer, 1995a). Although the fossil history of seeps is increasingly well understood from the Cretaceous onward (Kiel, 2009), Triassic examples are known only from eastern Oregon, USA (Peckmann et al., 2011). Here we report five new hydrocarbon-seep deposits from the Upper Triassic Kasımlar shales of southern Turkey that are dominated by bivalves and also contain the dimerelloid brachiopod *Halorella*.

MATERIALS AND METHODS

Five limestone deposits from the Kasımlar Basin in the Anamas Akseki autochthon in the Taurus Mountains in southern Turkey (Ager et al., 1978) have been sampled (Fig. 1). This basin is interpreted as a small ocean basin separating large carbonate platforms to the east and west, interspersed with several rifted continental fragments capped by Mesozoic carbonate platforms (Roberson et al., 2003). Localized accumulations of isolated and reworked reef carbonates (so-called "cipit" blocks), which were interpreted as channel fills (Poisson, 1967), are embedded in marginal marine or deeper water (cf. Lukeneder et al., 2012), siliciclastic sediments known as

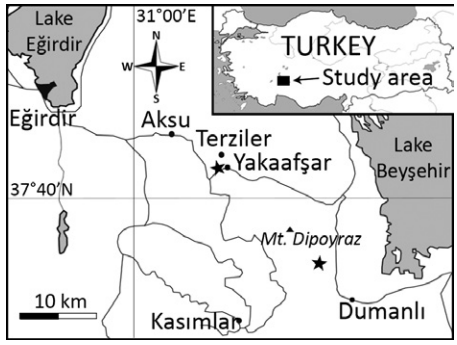


Figure 1. Map of study area (Turkey); two sample localities are indicated by stars.

Kasımlar shales or the Kasımlar Formation (Gutnic et al., 1979). The limestone deposits reported here were found among those accumulations. Two were found ~6 km northwest of the village of Dumanlı (37°36′0.2″N, 31°20′55.6″E, and 37°35′27.1″N, 31°20′58.2″E), each consisting of several loose boulders reaching 50 cm across, and three on a slope on the north side of the road just west of the village of Yakaafşar, at the turnoff to Terziler (37°44′33.5″N, 31°09′40.5″E). One of the Terziler deposits was *in situ* (Fig. DR1 in the GSA Data Repository[1]), measuring ~1.5 × 1 m, and the other two were loose boulders not more than 50 cm across.

Thin sections 150–100 mm in size were prepared from each deposit for petrographic analyses. Samples for carbon and oxygen stable isotope analyses were drilled from the rock slabs from which the thin sections were made. For stable isotope analyses, carbonate powders were reacted with 100% phosphoric acid at 75 °C using a Kiel III online carbonate preparation line connected to a ThermoFinnigan 252 mass spectrometer. All values are reported in per mil relative to the Vienna Peedee belemnite (VPDB) standard by assigning a δ^{13}C value of +1.95‰

[1]GSA Data Repository item 2017247: Figure DR1 (outcrop image), Figures DR2 and DR3 (photomicrographs of thin sections of the Dumanlı and Terziler seep deposits), and Figure DR4 (SEM images of age diagnostic conodonts), is available online at http://www.geosociety.org/datarepository/2017/ or on request from editing@geosociety.org.

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and a $\delta^{18}O$ value of –2.20‰ to NBS19 limestone reference material. Reproducibility was checked by replicate analysis of laboratory standards and was found to be better than ±0.05‰.

RESULTS

The two Dumanlı deposits (Dumanlı I and II) are petrographically similar and the abundant fossils of large bivalves are mostly articulated, as are the less-abundant fossils of *Halorella*. The matrix of the dark-gray limestones consists of homogenous, pyritiferous micrite to microspar that contains abundant detritus, mostly quartz grains, skeletal carbonate debris, wood fragments, and fecal pellets. The limestones reveal a nodular fabric (Fig. DR2), resembling the Jurassic seep deposits of Beauvoisin, France (cf. Peckmann et al., 1999). Nodules consist of homogenous micrite too, but contain far less detritus than the rock matrix (Fig. 2A). Dispersed framboidal pyrite is particularly common within the nodules. Seams of pyrite line some nodules (Fig. 2A) and corroded carbonate shells. Cavities are sparse and are mostly filled by late diagenetic equant calcite. The Dumanlı I deposit contains little early diagenetic rim cement in addition to the pore space occluding equant calcite. Ghost structures after fibrous crystals suggest that the rim cement was originally marine aragonite

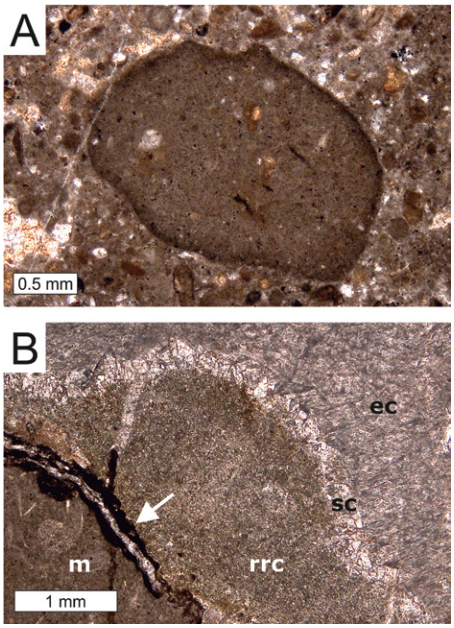


Figure 2. Photomicrographs of seep limestones; plane-polarized light. A: Nodule enclosed in detritus-rich micritic matrix; pyrite (dark) is enriched along the margin of the nodule. Dumanlı II deposit (Turkey) B: Terziler I deposit. Paragenetic sequence of matrix micrite (m), recrystallized rim cement (rrc) possibly representing former banded and botryoidal cement, scalenohedral calcite (sc), and equant calcite (ec). Transition from matrix micrite to recrystallized rim cement is affected by pressure solution and secondary mineralization (arrow).

or calcite cement that probably corresponds to banded and botryoidal cement, which is a common constituent of many Phanerozoic seep deposits (e.g., Savard et al., 1996).

The three Terziler deposits (Terziler I, II, and III) are gray limestones that contain abundant skeletal carbonate debris, significantly more than the Dumanlı deposits (Fig. DR3). Apart from unidentified debris, bivalve, brachiopod, gastropod, echinoderm, and ammonoid fragments have been recognized. The matrix of the rock is a homogeneous, pyritiferous micrite to microspar. It encloses detrital minerals, mostly quartz, nodules, fecal pellets, and wood fragments. Articulated specimens of *Halorella* are found in the Terziler I deposit, whereas articulated bivalves are common in the Terziler II and, particularly, Terziler III deposits. Abundant corrosion surfaces on skeletal carbonate and on carbonate clasts are partially lined by pyrite. Centimeter-sized cavities were found only in the Terziler I deposit. The cavity walls are lined by early diagenetic rim cements, which are largely recrystallized (Fig. 2B), but apparently also correspond to marine, banded and botryoidal cement as in the Dumanlı I deposit. Most of the cavity volume is filled by equant calcite cement. The presence of idiomorphic dolomite rhombs and stylolites reveals that the Terziler limestones have been affected by late-stage dolomitization and pressure solution.

All carbonate phases sampled from the Dumanlı and Terziler deposits revealed low $\delta^{18}O$ values (–10.7‰ to –6.8‰; Fig. 3), resulting from a resetting of the distribution of stable oxygen isotopes during late diagenesis (e.g., Tong et al., 2016). Carbon stable isotopes of carbonate minerals are much less affected by late diagenetic alteration processes (Tong et al., 2016). The $\delta^{13}C$ values of carbonate phases from the Dumanlı and Terziler deposits scatter widely, reflecting only insignificant resetting and, thus, close to primary isotope patterns. Micrite from the Dumanlı deposits yielded $\delta^{13}C$ values from –10.4‰ to –0.4‰, while values of micrite from the Terziler deposits fall between –9.5‰ and –1.2‰. Two samples of rim cement from the Dumanlı I deposit, apparently representing banded and botryoidal cement, yielded less-negative $\delta^{13}C$ values (–1.2‰ and –0.7‰), whereas its counterpart from the Terziler I deposit is more ^{13}C depleted (–12.0‰ to –7.0‰). The $\delta^{13}C$ values of three samples of equant calcite from the Dumanlı I and Terziler I deposits range from –2.6‰ to +0.6‰.

At Dumanlı, the conodont *Epigondolella triangularis* indicates a middle to late early Norian age; at the Terziler sites, the conodont *Quadralella polygnathiformis* indicates a late Carnian age (Fig. DR4) (Tekin, 1999; Chen et al., 2015). Four of the five deposits are dominated by bivalves with the brachiopod *Halorella amphitoma* (Figs. 4R and 4S) being a subordinate

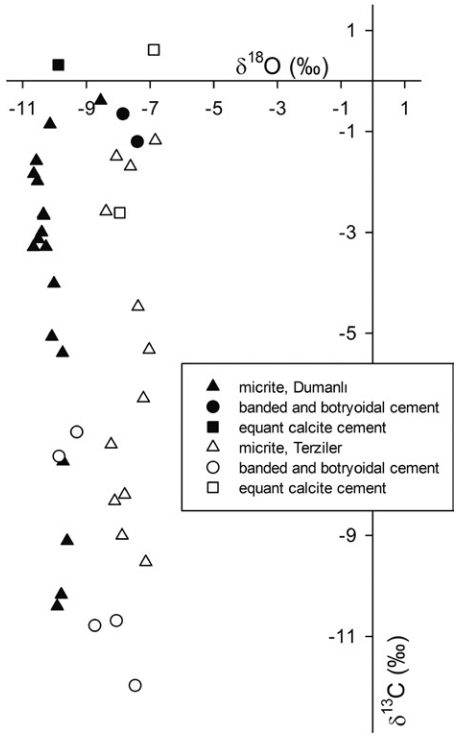


Figure 3. Carbon and oxygen stable isotope data for Late Triassic hydrocarbon-seep deposits in Kasımlar shales in southern Turkey. Black symbols represent the two Dumanlı deposits; white symbols represent the three Terziler deposits.

faunal element; only in the Terziler I deposit is *Halorella amphitoma* more common than the bivalves (Table 1). The dominant bivalves belong to three genera:

(1) A new genus of the Anomalodesmata that reaches 82 mm in length and dominates the two deposits near Dumanlı, and is smaller and less abundant in the Terziler deposits (Fig. 4A); the "nuculanid" from a Late Triassic seep deposit in Oregon (Peckmann et al., 2011) is very similar in shape and belongs to the same new genus.

(2) A modiomorphid resembling *Caspiconcha* and reaching 33 mm in length, which dominates the Terziler III deposit and is rare in the other deposits (Figs. 4B and 4C); the "permophorid" reported from a Late Triassic seep deposit in Oregon (Peckmann et al., 2011) is very similar in shape and belongs to the same genus.

(3) A new genus of the Modiomorphida that is strongly inflated and reaches 57 mm in length, which is present in the Terziler deposits (Fig. 4D).

Gastropods are diverse but poorly preserved (Figs. 4G–4Q); 12 different taxa were identified in the Terziler deposits, and one in the Dumanlı deposits. In addition, a small, unidentified rhynchonelloid brachiopod with a deep sulcus is common in the Terziler III deposit (Figs. 4T–4V), ammonoids (*Arcestes* sp.) were found in the Terziler I deposit, and a few small protobranch bivalves occur in both the Terziler and Dumanlı deposits (Figs. 4E and 4F).

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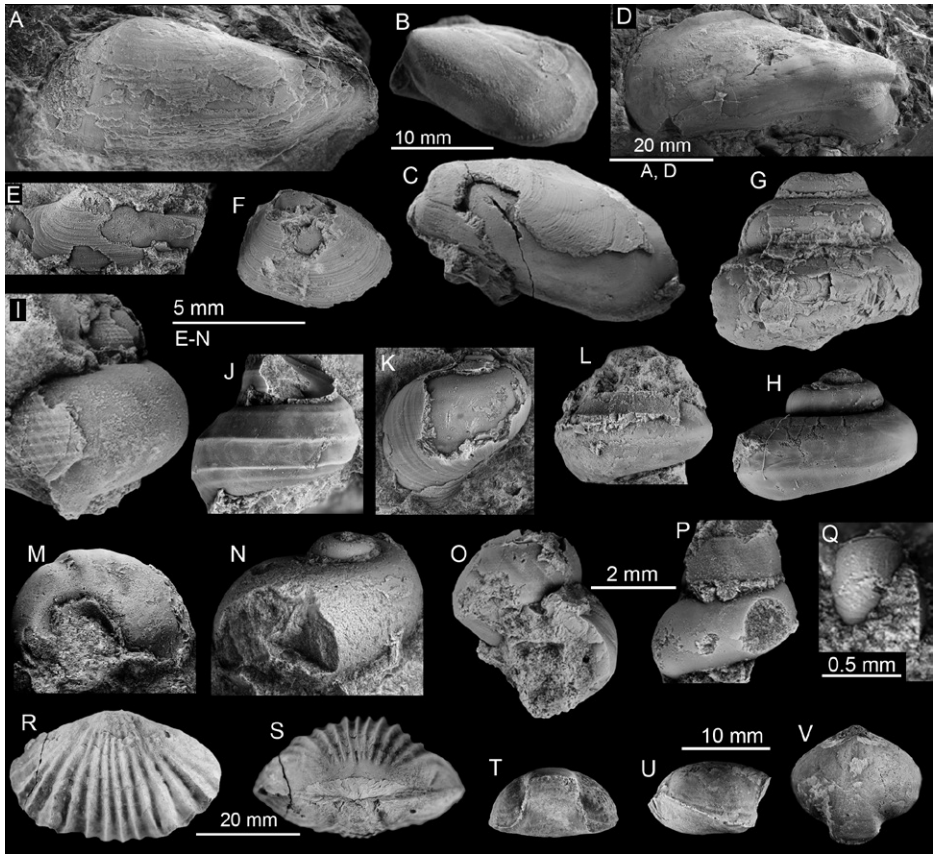


Figure 4. Fauna of Late Triassic hydrocarbon-seep deposits in Kasımlar shales in southern Turkey. A: New genus of bivalve clade Anomalodesmata. B,C: *Caspiconcha*-like bivalve. D: New genus of bivalve clade Modiomorphida. E: Nuculanid bivalve. F: Nuculid bivalve. G: Conical pleurotomariid. H: Low-spired pleurotomariid. I: *Paskentana*-like gastropod. J: Gastropod with three keels. K: Low-spired gastropod 1. L: Gastropod with one strong keel. M: Gastropod with oblique constriction. N: Low-spired gastropod 2. O: *Hikidea*-like gastropod. P: Tall gastropod. Q: Opisthobranch gastropod. R,S: *Halorella amphitoma*. T–V: Small brachiopod. A, E, and K are from Dumanlı deposits; all others from Terziler deposits.

DISCUSSION AND CONCLUSIONS

The Dumanlı and Terziler limestones reveal a number of characteristics that are typical of hydrocarbon-seep deposits. Most seep limestones reveal a matrix of pyritiferous micrite like in the studied deposits from the Kasımlar shales of southern Turkey (e.g., Peckmann et al., 1999; Campbell et al., 2002). Beyond that, the Dumanlı limestones share carbonate mesofabric with other seep deposits, including nodules made of pure authigenic micrite that are partially lined by an outer rim of pyrite (Peckmann et al., 1999). Similarly, pyrite rims lining corrosion surfaces are abundant in the Dumanlı and Terziler limestones, a feature shared with many seep limestones (Campbell et al., 2002). Although only a minor constituent of the limestones from the Kasımlar shales, banded and botryoidal aggregates of formerly fibrous marine cement are interpreted to be analogous to the characteristic banded and botryoidal cements typifying many Phanerozoic seep deposits (e.g., Savard et al., 1996; Peckmann et al., 2007). The listed carbonate fabrics are by no means restricted to seep deposits, but their co-occurrence with low-diversity but high-abundance faunal assemblages of bivalve taxa known from other Mesozoic seep deposits (Peckmann et al., 2011) and dimerelloid brachiopods (Sandy, 2010) is best explained by a paleoenvironmental setting shaped by hydrocarbon seepage. The great number of articulated bivalve and brachiopod specimens is in line with an autochthonous assemblage, allowing us to reconstruct the paleoenvironment on the basis of the associated authigenic carbonate phases of the Dumanlı and Terziler limestones. Moderately ^{13}C-depleted micrite and banded and botryoidal cement reflect the incorporation of organic carbon during mineral formation. The low $\delta^{13}C$ values of the Dumanlı and Terziler limestones are best explained by hydrocarbon seepage. Because the degree of mixing between marine carbonate and organic carbon is unknown, the composition of seepage fluids cannot be constrained without additional information. Attempts to extract biomarkers of chemotrophic prokaryotes from the limestones failed because of their high maturity and substantial late diagenetic alteration, reflected in low $\delta^{18}O$ values, local dolomitization, and pressure solution. Other seep limestones with lowest $\delta^{13}C$ values of −12‰ have been interpreted as oil-seep deposits, supported by the occurrence of pyrobitumen (i.e., metamorphosed crude oil; Peckmann et al., 2007) or a petroliferous odor (Kiel and Peckmann, 2007). No such additional evidence for oil seepage has been observed for the Dumanlı and Terziler limestones.

TABLE 1. FAUNA OF THE KASIMLAR SHALE SEEP DEPOSITS, SOUTHERN TURKEY

Taxon	Deposit				
	Dumanlı I	Dumanlı II	Terziler I	Terziler II	Terziler III
Brachiopoda					
Halorella	1	3	Abundant	1	50
Small, indet. rhynchonelloid	–	–	–	3	100
Bivalvia					
Anomalodesmata n. gen.	Abundant	Abundant	2	Abundant	2
Modiomorphid aff. *Caspiconcha*	–	–	–	2	Abundant
Modiomorphid 2	–	–	–	4	2
Nuculid	–	–	–	1	4
Nuculanid	–	1	–	–	–
Gastropoda					
Pleurotomariid, low-spired	–	–	–	–	2
Pleurotomariid, conical	–	–	–	–	1
Retiskenea-like	–	–	–	–	3
Low-spired sp. 1	2	2	7	–	–
Low-spired sp. 2	–	–	1	–	–
Hikidea-like	–	–	1	–	–
Sp. with three keels	–	–	6	–	–
Sp. with one strong keel	–	–	–	1	1
Sp. with oblique constrictions	–	–	–	–	2
Paskentana-like	–	–	2	–	–
Tall sp.	–	–	–	1	1
Opisthobranch	–	–	–	1	–

Note: All specimens are housed in the Swedish Museum of Natural History, Stockholm; dash (–) means not present.

The faunal assemblages associated with the Kasımlar shales seep deposits provide a wealth of new insights into the evolutionary history of seep faunas. For example, the new genus of the Anomalodesmata appears to be the first seep-restricted member of its clade, showing that the adaptation to this environment is widespread throughout the class Bivalvia and especially among the Heterodonta. This anomalodesmatan

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genus and the small, unidentified rhynchonelloid brachiopod open new windows in the "seep-search strategy" (Campbell and Bottjer, 1993) by extending the range of taxa that can be used to recognize ancient seep deposits, especially from the early Mesozoic and the more distant geologic past. The Kasımlar shales seep fauna allows, for the first time, a comparison of seep faunas from the two major Triassic ocean basins: Tethys and Panthalassa. Despite their paleogeographic separation and the far lower diversity of the Panthalassic seep fauna in Oregon, these faunas share their main taxa: the modiomorphid resembling *Caspiconcha*, the new anomalodesmatan, and the brachiopod *Halorella*. This is remarkable because despite their large size, these bivalves have, to the best of our knowledge, not been reported from other types of environments, implying that they most likely were restricted to seeps. A near-global distribution of a small number of seep-restricted clades is one of the characteristic features of the modern seep fauna (Sibuet and Olu, 1998), and this feature is well known from Cenozoic and Cretaceous seep faunas, too (Campbell and Bottjer, 1995b; Kiel, 2010). Thus the Kasımlar shales seep fauna and the coeval fauna from Oregon show that a cosmopolitan, seep-restricted fauna was already established in the early Mesozoic.

Whereas the Triassic seep faunas in Oregon consist of millions of specimens of the brachiopod *Halorella* and very few other species (four species represented by a total of 18 specimens; Peckmann et al., 2011), the Kasımlar shales seep fauna consists of 19 species, including 17 mollusks (Table 1). This approaches the diversity of modern, Cenozoic, and Cretaceous seep sites (Campbell, 2006) and further emphasizes the ecological similarity among seep faunas since the early Mesozoic. The abundance and diversity of bivalves at the Turkish seep sites also challenge the paradigm that Paleozoic and Mesozoic seeps were dominated by brachiopods that were replaced by the modern bivalve-dominated fauna in the Late Cretaceous (Campbell and Bottjer, 1995a). Indeed, bivalves with morphologies similar to those of extant vesicomyids and Mesozoic seep-inhabiting modiomorphids have been reported from Devonian seeps in Morocco (Hryniewicz et al., 2017), and seep deposits lacking brachiopods are known from the Carboniferous (Buggisch and Krumm, 2005; Himmler et al., 2008). Thus brachiopods and bivalves appear to have had a complex history of coexistence at seeps through the Phanerozoic that requires further investigation.

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