


Geochemical evidence (C and Sr isotopes) for methane seeps as ammonite habitats in the Late Cretaceous (Campanian) Western Interior Seaway

J. Kirk Cochran¹  · Neil H. Landman² · Neal L. Larson³ · Kimberly C. Meehan⁴ · Matthew Garb⁵ · Jamie Brezina⁶

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Abstract Methane seeps in the Upper Cretaceous Pierre Shale of the U.S. Western interior contain a rich fauna including ammonites (*Baculites*, *Hoploscaphites*, *Didymoceras*, *Placentoceras*, *Solenoceras*), bivalves (*Lucina*), gastropods, sponges, and crinoids. Occasionally, the shell material in the seeps is very well preserved, retaining the original mineralogy and microstructure. We explored two such seeps from the upper Campanian *Didymoceras cheyennense* and overlying *Baculites compressus* Zones (74.7–73.5 Ma) in southwestern South Dakota. Light values of $\delta^{13}\text{C}$ in the micritic limestones (–11 to –47 ‰) confirm the impact of anaerobic oxidation of methane on the isotopic composition of the dissolved inorganic carbon reservoir. At the seep from the *D. cheyennense* Zone, $\delta^{13}\text{C}$ values in well-preserved specimens of *Hoploscaphites* and *Baculites* are significantly lighter than those measured in specimens from approximately age-equivalent non-seep deposits. In addition, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is elevated in the authigenic carbonates and ammonite shells compared with

the coeval marine value. This suggests that seep fluids imprinted with a radiogenic Sr signature, perhaps derived from isotopic exchange with granitic deposits at depth associated with the Black Hills uplift, are transported through the surficial sediments into the overlying water. The persistence of these isotopic tracers of seep fluids in the ammonite shells suggests that these mobile animals were likely demersal and were living in close proximity to the seep. A more restricted data set on a single baculite and nautilid from the seep in the *B. compressus* Zone shows less divergence of $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ relative to non-seep values, suggesting that fluid transport was not as strong at that seep.

Keywords Carbon · Strontium · Isotopes · Ammonites · Cretaceous · Methane seeps

Introduction

Hydrocarbon or methane–seep deposits are known worldwide and testify to the importance of these systems in Earth history (e.g., Campbell 2006; Kiel and Tyler 2010). Methane-seep deposits (“Tepee Buttes”) ranging in age from the middle Campanian to early Maastrichtian (Metz 2010) have long been recognized in the Upper Cretaceous Pierre Shale of the United States Western Interior (Gilbert and Gulliver 1895). The seeps are characterized by authigenic carbonates occurring in a variety of morphologies, with unusually light $\delta^{13}\text{C}$ values (–35 to –50 ‰: Beauchamp and Savard 1992; –40 to –45 ‰: Kauffman et al. 1996) characteristic of methane-derived carbon. The geochemistry and geobiology of methane seeps in the Western Interior Seaway (WIS) have been explored only relatively recently (Kauffman et al. 1996). The realization that the

✉ J. Kirk Cochran
kirk.cochran@stonybrook.edu

¹ School of Marine and Atmospheric Sciences, Stony Brook University, Stony Brook, NY 11794, USA
² Division of Paleontology (Invertebrates), American Museum of Natural History, New York, NY 10024, USA
³ Larson Paleontology Unlimited, Hill City, SD 57745, USA
⁴ Department of Geography (Earth & Environmental Sciences), Hunter College, CUNY Graduate Center, New York, NY 10065, USA
⁵ Department of Geology, Brooklyn College, Brooklyn, NY 11210, USA
⁶ Department of Mining Engineering, South Dakota School of Mines and Technology, Rapid City, SD 57701, USA

WIS was peppered with methane seeps (Metz 2010) yields a new vision of the nature of the seaway and the biota that inhabited it (Landman et al. 2012). The methane seeps hosted a diverse fauna, including several species of ammonites. Documenting the role of these animals at the seeps, and their geochemical context, is critical in understanding the ecology of these unique geobiological systems. Here we present evidence from the stable isotopes of oxygen, carbon, and strontium in well-preserved shells of ammonites suggesting that the water column above the seep was affected by seep fluids and that seeps formed a persistent habitat for these mobile animals.

Setting

Seep distribution and exposure

Metz (2010) proposed that the distribution and duration of seeps in the WIS was related to tectonic activity associated with subduction of the Farallon Plate during the Late Cretaceous. The seeps cover a large area and locally can be quite numerous (Fig. 1). The classic “Tepee Butte” morphology is a topographic high, with a prominent carbonate capping the crest. Most seep deposits are extensively weathered, and the preservation of the molluscs is generally poor. However, recent field work by the American Museum of Natural History, in collaboration with Brooklyn College (City University of New York) and Stony Brook University (SUNY), has led to the discovery of several seeps from the *Didymoceras cheyennense* Zone (lower part of the upper Campanian, 74.67 ± 0.15 Ma) to the *Baculites compressus* Zone (upper part of the upper Campanian; ~ 73.2 Ma; Cobban et al. 2006) in southwestern South Dakota that contain well-preserved shell material from a diverse array of ammonites, nautilids, gastropods, and bivalves (Fig. 2). The seeps are exposed in cross section, often adjacent to creek or river banks, and display a complex “plumbing system.” Here we present results from two such seeps—AMNH loc. 3418 (Spring Creek, Custer County, SD) in the *D. cheyennense* Zone and AMNH loc. 3528 (Cheyenne River, Meade County, SD) in the *B. compressus* Zone.

Morphologies of seep-associated carbonates

The seeps in southwestern South Dakota are characterized by several distinct limestone morphologies (Figs. 3, 4):

1. Pipes or tubes (Figs. 3a, c, 4e)—These vary from large pipes as much 10 cm in diameter and 40 cm long to small tubes ~ 1 cm in diameter and 10 cm long. They often show vugs, suggesting that they were hollow. However, some of the smaller tubes (e.g., Fig. 4e) may originally represent the burrows of ghost shrimp that

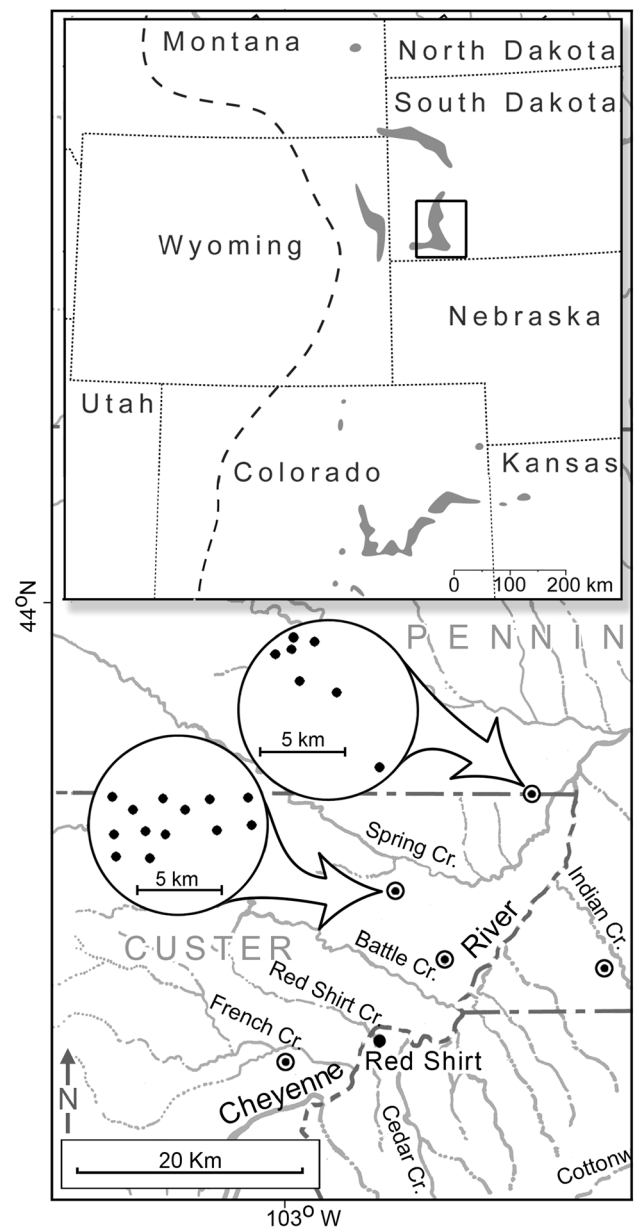


Fig. 1 Map showing locations of seeps within the Western Interior Seaway of North America. Shaded areas in upper map show broad distribution of seeps in South Dakota, Montana, Wyoming, and Colorado. The circles in the inset map indicate detailed locations of individual seeps in the *Didymoceras cheyennense* and *Baculites compressus* Zones (modified from Landman et al. 2012)

subsequently functioned as conduits for methane and were progressively cemented by carbonate precipitation as the methane was oxidized by cooperating Archaea—bacteria colonizing the tube perimeter. The morphologies of these carbonate tubes and pipes suggest advective transport of methane-rich fluids through the WIS sediment.

2. Platy, tabular pavements (Fig. 3d)—These frequently contain inoceramid shells that form the bulk of the platy carbonate, as well as other fossils, including

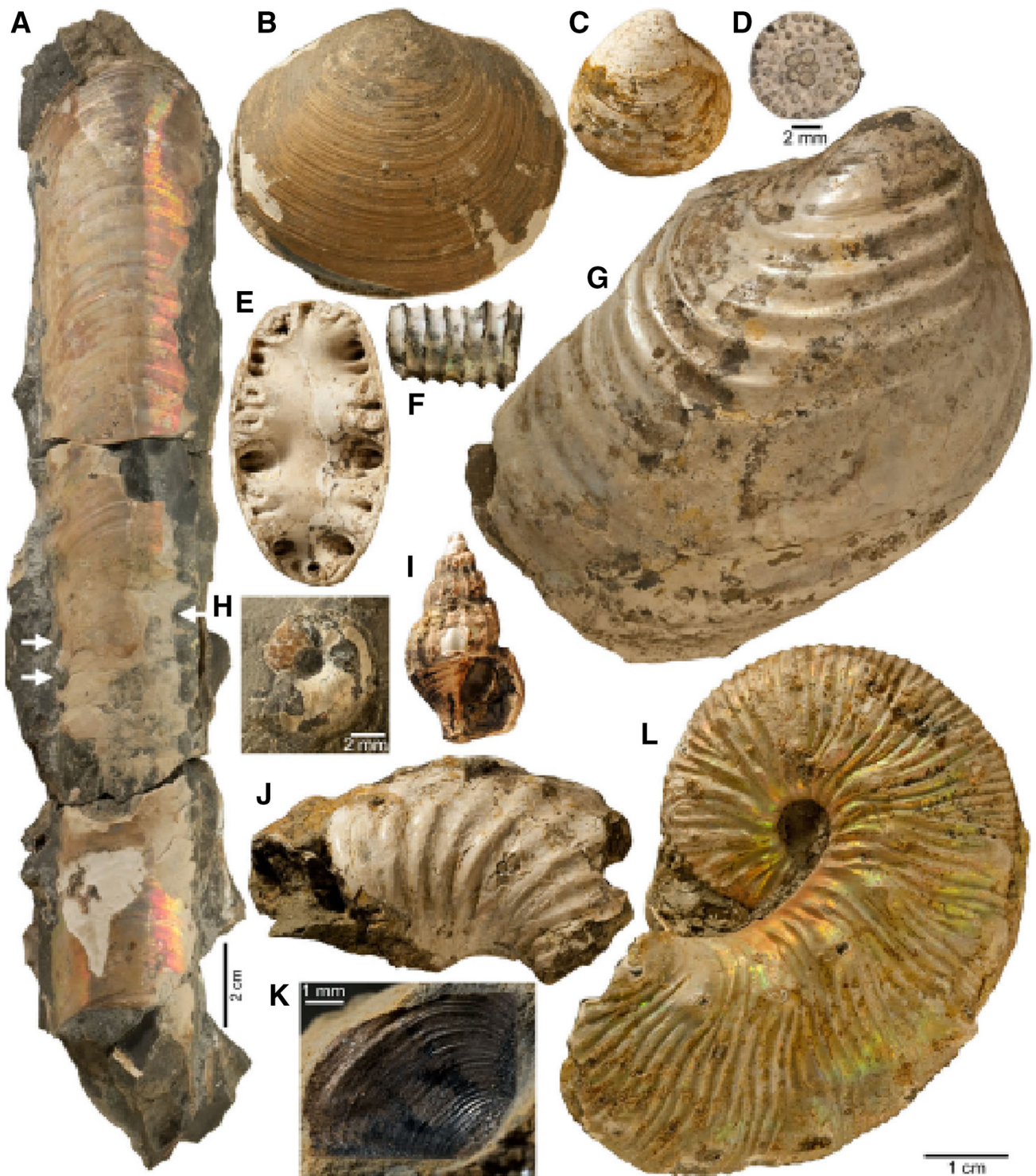


Fig. 2 Invertebrate fossils from the methane seep at AMNH loc. 3418, Custer County, South Dakota. **a** *Baculites corrugatus*, mature macroconch, showing a series of small scalloped edges along the entire length of the body chamber (arrows), probably reflecting predation. **b** *Nymphalucina occidentalis*. **c** *Crassatella evansi*. **d** Crinoid columnal showing canals. **e** *Baculites corrugatus*, whorl cross section showing septum. **f** *Spiroxybeloceras meekaanum*.

g “*Inoceramus*” *sagensis*. **h** *Hoploscaphites brevis*, juvenile. **i** *Drepanochilus trilirata*. **j** *Didymoceras cheyennense*. **k** Lower jaw attributed to *Hoploscaphites*. **l** *Hoploscaphites brevis*, mature microconch. Scale bar at bottom applies to all specimens except **a**, **d**, **h**, and **k** (modified from Landman et al. 2012; AMNH specimen numbers are given in Landman et al. 2012)

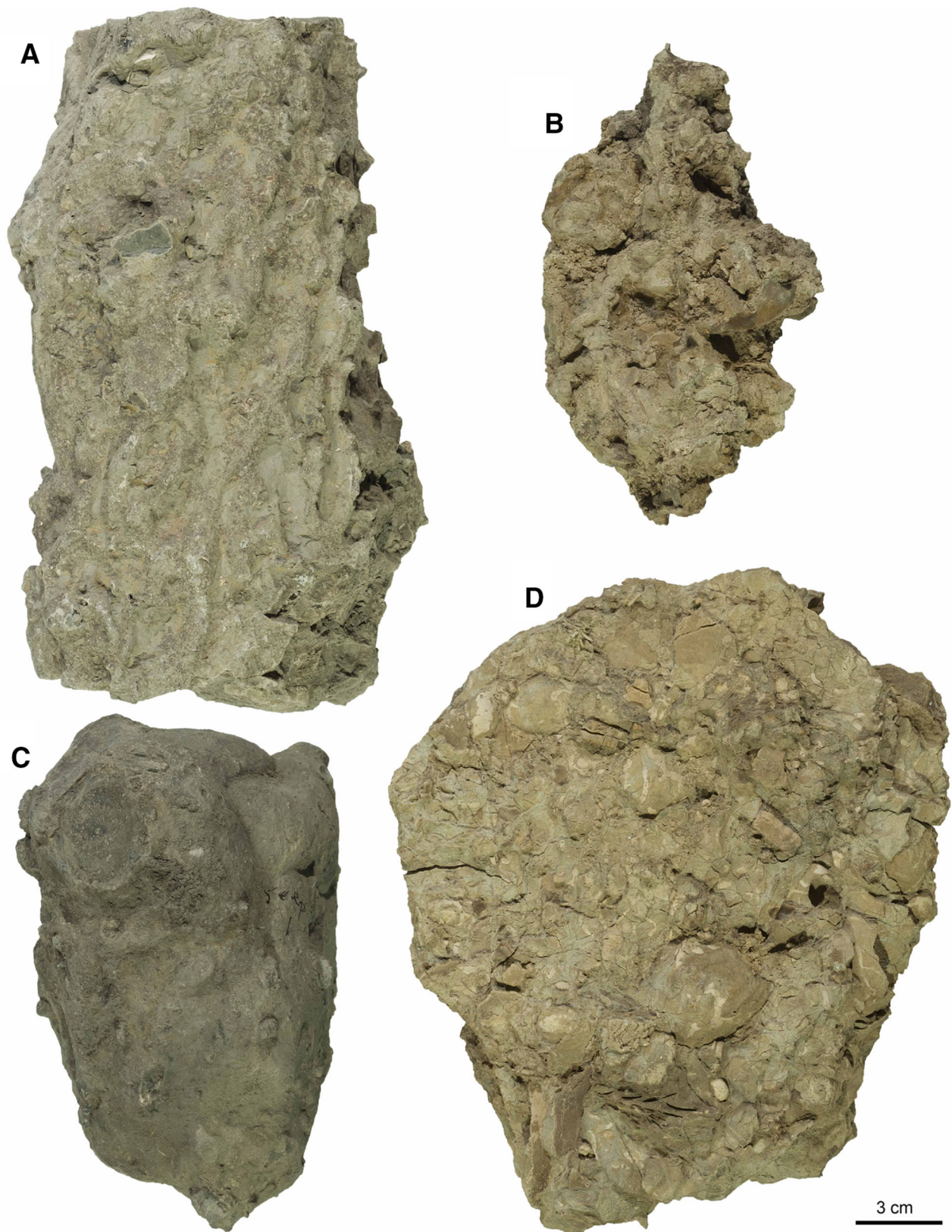


Fig. 3 Seep-associated carbonates. **a** Portion of large pipe ~30 cm long x ~10 cm diameter; composition is Mg-rich calcite with apatite and pyrite (AMNH 64594, loc. 3545); **b** angular concretion (AMNH

80770, loc. 3419); **c** massive, billowy concretion (AMNH 645611, loc. 3528); **d** platy carbonate (*top view*) with included shells of inoceramids and lucinids (AMNH loc. 3529)

crinoids, lucinids, baculites, and gastropods. This association suggests that these carbonates formed at the sediment–water interface as a hard substrate that served as a habitat for crinoids and other organisms. Indeed, the crinoid stems in these pavements are usually nearly complete.

3. Carbonate masses of irregular texture (Fig. 3b)—These have an irregular, angular surface and usually contain abundant fossils including crinoids, although the crinoids are commonly disarticulated columnals. They probably formed below the sediment–water interface surrounding accumulations of skeletal material.
4. Globular, billowing, bulbous micritic limestone masses—These can be as large as several meters in diameter and are often associated with other nearby structures such as pipes or tubes nearby (Figs. 3a, c, 4e). The mass is usually fossiliferous, but the fossils are not very abundant.
5. Sub-spherical or dumb-bell shaped concretions (Fig. 4a–d)—Many of these show vugs or vug ghosts and often include a fossil with well-preserved shell material (e.g., Fig. 4a–c). We hypothesize that these formed as methane diffused away from areas of high concentration and was oxidized.

Methods

Shell preservation

Molluscs occur in all of the carbonates described above, as well as loose in the adjacent Pierre Shale. Samples were screened for diagenetic alteration by high-magnification ($\sim 15,000\times$) scanning electron microscopy (SEM) of shell microstructure. The “Preservation Index” (PI) scale of Cochran et al. (2010), ranging from 1 (poor) to 5 (excellent), was used. Cochran et al. (2010) showed that, as WIS shell material became diagenetically altered, there was a shift in $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ toward lower values, even in samples that appeared to be unaltered aragonite according to X-ray diffraction analysis. Only material with a PI > 3.5 (good to excellent) was analyzed in this study, as Cochran et al. (2010) showed that such preservation retains the original isotopic signatures.

Seep sites with excellent shell preservation are currently known to occur only in the Campanian Pierre Shale of southwestern South Dakota, and the preservation at these sites (Fig. 5) offers, for the first time, the possibility of fully characterizing the geochemical and geobiological conditions at the seeps and the environment in which the animals were living.

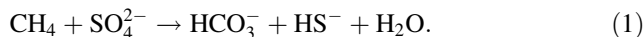
Isotope analyses

Following an assessment of preservation by SEM, samples were analyzed for Sr, O, and C isotopes, as described in Landman et al. (2012). Strontium was separated from ~ 1 mg of ground shell material dissolved in HNO_3 . Samples were loaded onto tungsten filaments and analyzed for $^{87}\text{Sr}/^{86}\text{Sr}$ on VG Sector 54 or IsotopX Phoenix thermal ionization mass spectrometers. Aliquots of NBS SRM 987 were analyzed with each batch of samples. Aliquots of shell material were dissolved in phosphoric acid, and oxygen and carbon isotope ratios were measured at the Keck Paleoenvironmental and Environmental Stable Isotope Laboratory (University of Kansas) using a Finnigan MAT 251 triple-collector isotope ratio mass spectrometer. Values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ are expressed relative to VPDB.

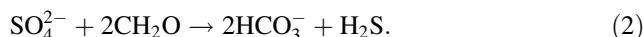
Results and discussion

Carbon isotope geochemistry of methane seeps

Fossil methane seeps of the WIS show many features that are typical of present-day methane seeps in which the anaerobic oxidation of thermogenically or biogenically produced methane (AOM) produces bicarbonate. Classically, AOM involves a consortium of methanotrophic Archaea and sulfate-reducing bacteria (Iversen and Jørgensen 1985; Boetius et al. 2000; Campbell 2006; Alperin and Hoehler 2009):

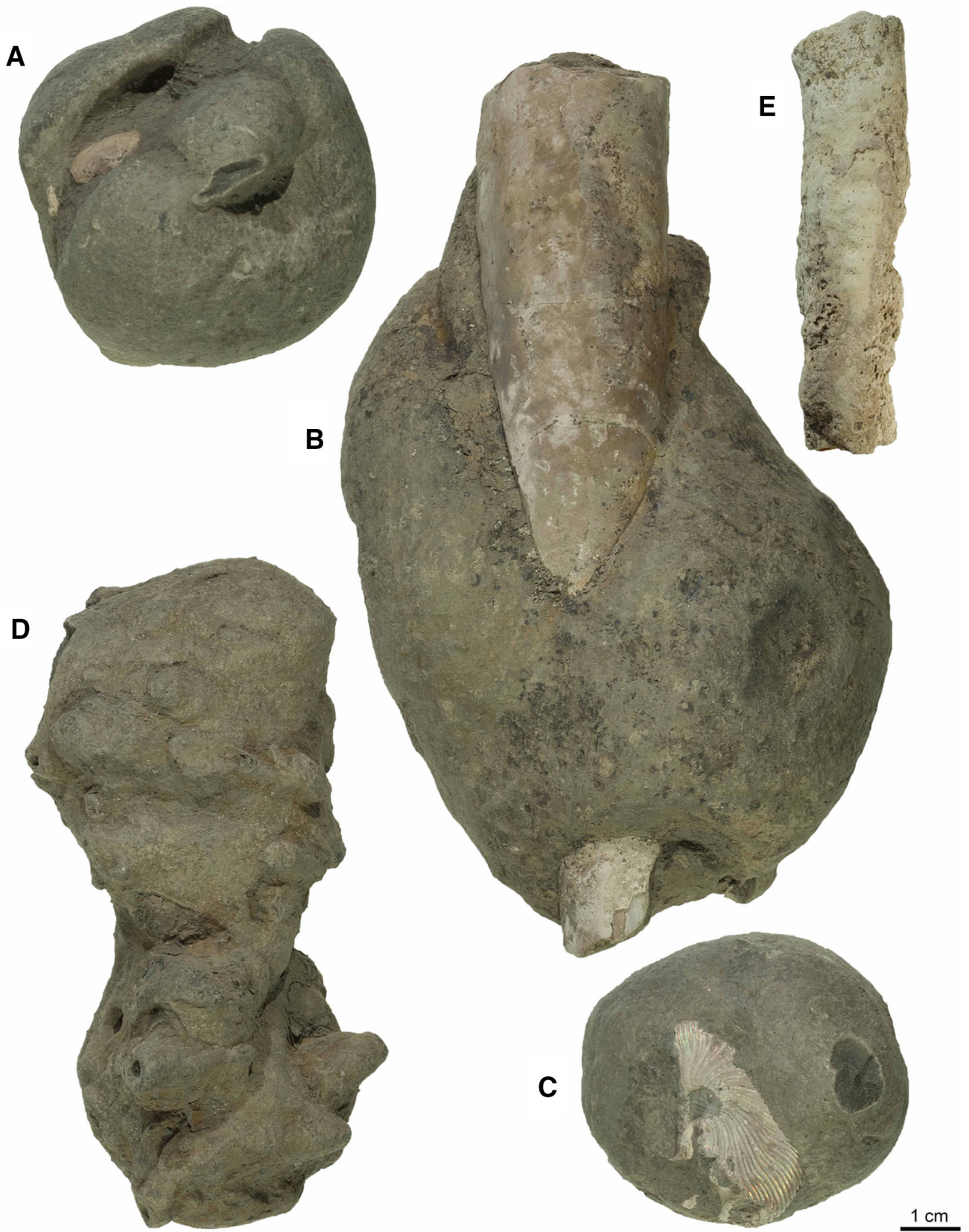


The carbon isotope composition of methane is light, and, as a consequence, the carbonates precipitated from the methane-derived carbon are light as well. In the seep from AMNH loc. 3418, this is evident in the light $\delta^{13}\text{C}$ values of the micritic limestones (-11 to -47 ‰; Landman et al. 2012). Sulfate is a necessary reactant for (1) to proceed, and the oxidation of organic matter (CH_2O) by sulfate-reducing bacteria reduces sulfate to sulfide in the pore water of marine sediments:



In organic-rich fine-grained sediment such as in the Cretaceous WIS, the Zone of sulfate reduction would likely have extended only to within a few meters (<10 m) below the sediment–water interface (Bowles et al. 2014). Thus, reaction (1) proceeds in the “sulfate–methane transition Zone,” in which both reactants are present.

Several alternative chemical pathways for AOM have been proposed: (1) cooperative microorganisms using the reduction of reactive metals such as Fe^{3+} or Mn^{4+} in place



◀ **Fig. 4** Seep-associated carbonates. **a–c** Sub-spheroidal concretions enclosing well-preserved shells of **a** lucinid, carbonate is Mg-rich calcite with minor amounts of apatite and pyrite (AMNH 64623, loc. 3528); **b** baculite (AMNH 64595, loc. 3545) and **c** scaphite (AMNH 64625, loc. 3528); **d** small pipe-like concretion (AMNH 64608, loc. 3528); **e** tube (AMNH 79109)

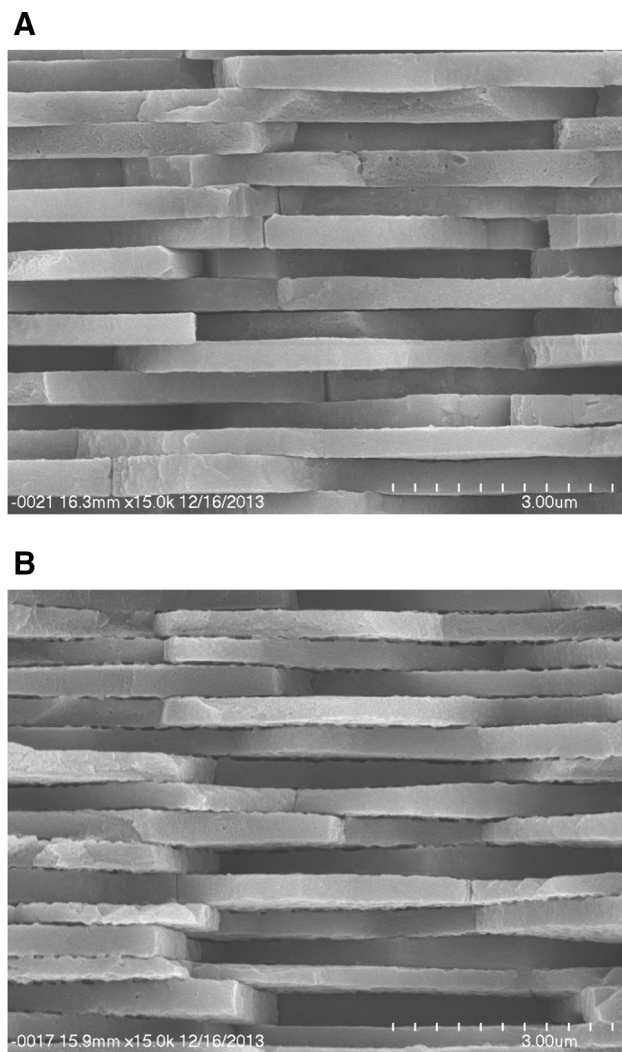


Fig. 5 SEM images showing examples of preservation in shell material in a specimens of **a** *Baculites compressus* (AMNH 64694) and **b** *Eutrephoceras dekeyi* (AMNH 64695) collected at a methane seep in the *B. compressus* Zone (AMNH loc. 3528). The SEM preservation index (Cochran et al. 2010) is 5 (excellent) in both

of sulfate (Beal et al. 2009), (2) production of oxygen through nitrite dismutation by the bacterium *Methoxymirabilis oxyfera* and use of the produced oxygen to oxidize methane (Ettwig et al. 2010), and (3) both sulfate reduction and methane oxidation undertaken by archaea of the ANME-2 clade (Milucka et al. 2012). If these alternate pathways were operating, they likely also took place close to the sediment–water interface. Methane transported advectively or diffusively through this Zone was subject to

AOM, and the bicarbonate produced allowed the solubility of calcium carbonate to be exceeded, resulting in precipitation of the various seep limestones (Figs. 3, 4). The presence of tabular carbonates with fossils of organisms such as crinoids that require a hard substrate suggests that the precipitation could occur at the sediment–water interface, as well as within the surficial sediments. In either case, the isotopically light carbon resulting from AOM was imprinted on the pore-water dissolved inorganic carbon (DIC) and subsequently incorporated into the limestone.

If the methane flux was sufficiently strong, the carbon isotopic signature characteristic of AOM may have been present in the water overlying the seep. As a consequence, both the DIC above the seep and marine organic matter formed from it would have been unusually light, in comparison with the $\delta^{13}\text{C}$ composition of these reservoirs away from the seep. If ammonites were spending extended time at the seeps, their shells should show lighter $\delta^{13}\text{C}$ in comparison with counterparts elsewhere in the WIS. A $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ cross-plot (Fig. 6) for the ammonite fauna at the seep at AMNH loc. 3418 shows that the seep ammonites, as a group, separate from coeval non-seep ammonites, with respect to both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. Values of $\delta^{13}\text{C}$ range to -14‰ and those of $\delta^{18}\text{O}$ range to -4‰ . If the $\delta^{18}\text{O}$ values are interpreted as reflecting the temperature of the water at which the aragonite precipitated, the calculated values range as high as $\sim 36\text{ °C}$, although the average for the seep ammonites is 26.9 °C . The upper limit is generally higher than temperatures assumed to have occurred in the WIS, and several factors may have influenced the calculated values. The seep fluids may have had either a slightly elevated temperature or a different $\delta^{18}\text{O}$ than that of the regional Late Cretaceous WIS ($\sim -1\text{‰}$), possibly as a result of fluid–rock interactions at depth. Indeed, the Sr isotope data for this seep (see below) imply equilibration of the seep fluids with a granitic host rock at depth.

The relatively light $\delta^{13}\text{C}$ signature of the seep ammonites suggests that they were impacted by methane-derived isotopically light carbon in the DIC or organic matter of the water column above the seep. However, the use of $\delta^{13}\text{C}$ in ammonite shells to constrain the habitat of these organisms is complicated by the fact that “vital” effects may produce non-equilibrium fractionation in the shell relative to the $\delta^{13}\text{C}$ of the DIC reservoir (e.g., He et al. 2005; Lukeneder et al. 2010; Stevens et al. 2015; Tobin and Ward 2015). In particular, molluscs can incorporate metabolic carbon as well as carbon derived from the DIC reservoir into their shells (Tanaka et al. 1986; McConnaughey 1989; McConnaughey et al. 1997; McConnaughey and Gillikin 2008). Studies of recent bivalves show amounts of metabolic carbon ranging from $<10\%$ in *Arctica islandica* (Butler et al. 2011; Beirne et al. 2012) to as much as $\sim 40\%$ in *Mercenaria mercenaria* (Gillikin et al. 2007).

However, the mobility of ammonites and nautilids may have resulted in different amounts of metabolic carbon incorporated into their shells compared with bivalves and gastropods (Tobin and Ward 2015).

The amount of metabolic carbon incorporated in the shell may have differed between nautilids and ammonites, as well as among different ammonite genera. Most of the isotope data presented in Fig. 6 are from ammonites in the Ancyloceratina, and we restrict ourselves to this suborder in comparing $\delta^{13}\text{C}$ data from seep and non-seep ammonites. Specifically, we compare the $\delta^{13}\text{C}$ values of baculites and scaphites from the seep at AMNH loc. 4318 with those

collected away from seeps (Table 1). In making this comparison, we assume that the fraction of metabolic carbon incorporated into the shell is approximately the same for seep and non-seep ammonites in the same genus. Non-seep data for these groups are limited in the *D. cheyennense* Zone, so we have tabulated results from samples collected in South Dakota from two additional ammonite Zones (*Baculites compressus* and *Hoploscaphites nebrascensis* Zones). We also include results from the *Discoscaphites iris* Zone on the Gulf Coastal Plain because of the large number of samples and the very high quality of preservation (Sessa et al. 2015). For the

Fig. 6 Cross-plot of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in seep (AMNH loc. 3418) and non-seep ammonites in the *D. cheyennense* Zone. Values are ‰ relative to VPDB. “Other heteromorphs” include samples of *Didymoceras* and *Spiroxybeloceras*. Circles are drawn to enclose the values in the two groups and have no statistical significance. See Table 1 for a detailed statistical comparison of the $\delta^{13}\text{C}$ data

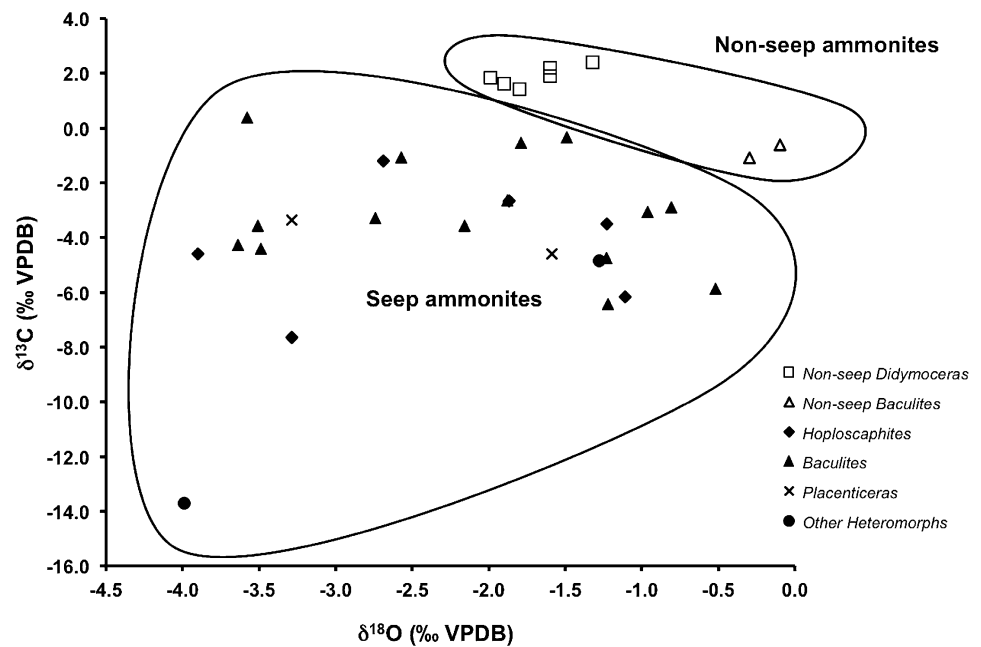


Table 1 Mean $\delta^{13}\text{C}$ (‰) of well-preserved ammonites from seep and non-seep environments

Organism	Seep (WIS) ^a	Non-seep (WIS) ^b	Non-seep (WIS) ^{b,c}	Non-seep (WIS) ^d	Non-seep (Gulf Coast) ^e
Ammonite Zone	<i>Didymoceras cheyennense</i>	<i>Didymoceras cheyennense</i>	<i>Baculites compressus</i>	<i>Hoploscaphites nebrascensis</i>	<i>Discoscaphites iris</i>
<i>Baculites</i>	-3.1 ± 2.0 (n = 15)	-0.85 (n = 2)	-1.6 ± 1.0** (n = 20) (P = 0.006)	-	-1.4 ± 1.3** (n = 87) (P < 0.0001)
<i>Hoploscaphites</i>	-4.3 ± 2.4 (n = 6)	-	-2.9 ± 2.4 (n = 3)	-1.3 ± 1.4** (n = 5) (P = 0.036)	0.4 ± 0.8** (n = 78) (P < 0.0001)

^a This study (AMNH loc. 3418); Landman et al. (2012)

^b He et al. (2005); samples from Pennington Co., South Dakota

^c Cochran et al. (2010) and Dennis et al. (2013)

^d Cochran et al. (2003) and Dennis et al. (2013); excludes brackish samples

^e Sessa et al. (2015)

** Indicates difference with seep ammonites is statistically significant (unpaired *t* test) at indicated *P* value

baculites, the mean $\delta^{13}\text{C}$ values of the non-seep specimens from the *B. compressus* and *D. iris* Zones are similar and are significantly different (unpaired *t* test) from the mean $\delta^{13}\text{C}$ of the *D. cheyennense* seep specimens (Table 1). (We cannot statistically compare the seep and non-seep specimens from the *D. cheyennense* Zone because of the lack of data in the latter group.) An additional comparison in the *B. compressus* Zone is possible using the results of Fatherree et al. (1998), who performed detailed $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ analyses of a single specimen of *B. compressus*. The outer shell sampled as an ontogenetic series (38 samples) yielded a mean value \pm 1SD of -1.63 ± 0.67 ‰ for $\delta^{18}\text{O}$ and -0.53 ± 0.42 ‰ for $\delta^{13}\text{C}$. This $\delta^{13}\text{C}$ value also differs from the mean value of -3.1 ± 2.1 ‰ for the seep baculites (Table 1).

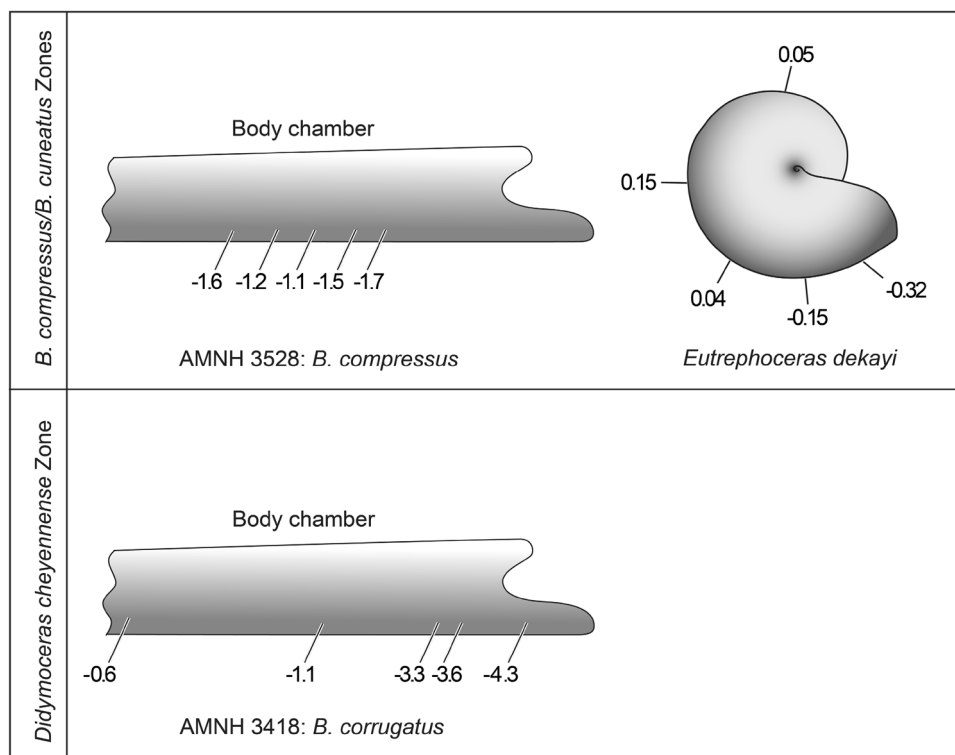
For the scaphites, the mean $\delta^{13}\text{C}$ values of the non-seep specimens vary across time and location. However, there is a statistically significant difference in $\delta^{13}\text{C}$ between scaphites from the *H. nebrascensis* Zone in the WIS and from the *D. iris* Zone on the Gulf Coastal Plain, on the one hand, and their seep counterparts from the *D. cheyennense* Zone, on the other. Based on the $\delta^{13}\text{C}$ offsets between ammonites collected at AMNH loc. 3418 and their non-seep counterparts, we conclude that the methane-derived carbon isotope signature was imprinted on the DIC in the overlying water column and probably on the organic matter generated in the food web, and was incorporated into the ammonite shells during growth.

Seeps as persistent ammonite habitats

If an active food web developed in the water column above the seep, it may have served as an important habitat for ammonites in the WIS. Indeed, evidence that ammonites lived, died, and were buried at the seeps includes the presence of juveniles (e.g., Fig. 2h) as well as adults (e.g., Fig. 2i) at seeps from the *Didymoceras cheyennense* and *Didymoceras nebrascensis* Zones in South Dakota and Colorado (Landman et al. 2013). Some of the specimens also exhibit lethal injuries, which were probably sustained at or near the site. Some seeps contain an abundance of ammonite jaws (Fig. 2k) as well as hook-like structures, both of which are attributed to *Hoploscaphites*, as described by Landman and Waage (1993). Because of the fragile nature of these structures, their presence suggests that they did not experience much transport after the animals died. As well, many of the body chambers are completely hollow or only partly filled with sediment, suggesting that they were rapidly buried and did not remain exposed on the sea floor for an extended period of time.

Sclerochronological sampling of baculite shells provides a way of assessing whether these ammonites were spending extended time at the seeps. Data from a baculite at the seep at AMNH loc. 3418 in the *D. cheyennense* Zone show variation in $\delta^{13}\text{C}$ over time (Fig. 7 bottom panel), with samples taken near the aperture displaying lower $\delta^{13}\text{C}$ than those sampled earlier in ontogeny: -3.3 to -4.3 ‰ vs.

Fig. 7 Values of $\delta^{13}\text{C}$ (‰ VPDB) in well-preserved shells of baculites (AMNH 64694—top left, and AMNH 63468—bottom) and a nautilid (AMNH 64695—top right) from two seeps (AMNH locs. 3528 and 3418) in the Western Interior Seaway. Preservation in the specimens of baculite and nautilid from AMNH loc. 3528 (top panel) is shown in Fig. 5



–0.55 to –1.1 ‰. The latter values are comparable to the $\delta^{13}\text{C}$ in non-seep baculites (Table 1) and suggest that this specimen moved to the seep environment as it matured. The $\delta^{18}\text{O}$ data from the same specimen (not shown, but available in Landman et al. 2012) also show a change from –1.79 ‰ earlier in ontogeny to –3.64 ‰ near the aperture. Interpreted as a temperature effect, this trend suggests variation from ~ 26 to ~ 34 °C, although, as described above, the light $\delta^{18}\text{O}$ recorded in some of the ammonite shells may be due to the effect of fluid–rock interactions on the $\delta^{18}\text{O}$ of the seep fluids. In either case, the ontogenetic trends in both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ reinforce the hypothesis that this baculite was exposed to an increasing seep influence as it grew.

In contrast to the seep at AMNH loc. 3418, a well-preserved baculite collected at the AMNH loc. 3528 in the *B. compressus* Zone shows $\delta^{13}\text{C}$ values that are comparable to those in non-seep baculites from the same Zone (Fig. 7 top panel, left; Table 1). The data from this site are limited to this single ammonite specimen, and it is difficult to characterize the seep environment from it. However, the methane flux may have been reduced at this seep such that the overlying water column DIC reservoir was imprinted to a lesser extent with methane-derived carbon. This possibility is supported by Sr isotope data for these specimens (see below).

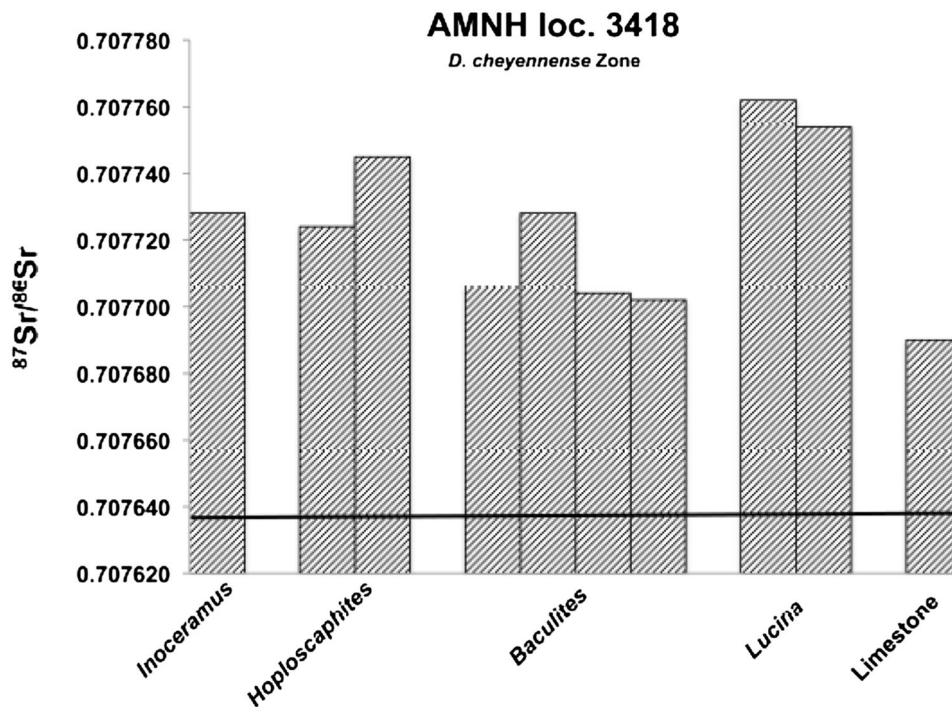
A nautilid (*Eutrephoceras dekeyi*) from the seep at AMNH loc. 3528 also was analyzed through ontogeny and showed higher $\delta^{13}\text{C}$ values than the co-occurring baculite (Fig. 7 top panel, right). As noted above, the $\delta^{13}\text{C}$ of

mollusc shells may reflect both the isotopic composition of the DIC reservoir and metabolic processes. Kruta et al. (2011) have shown that baculites likely fed on suspended particles, including small zooplankton. By analogy with their recent counterparts, nautilids were more likely to have been scavengers feeding on dead organic matter. These differences may have led the two groups to interact with the food web in different ways, with different proportions of metabolic and DIC-derived carbon incorporated into their shells. It is also possible that the ammonites were homing in on the community associated closely with the seep fluids and the nautilids were less strongly coupled with that community.

Strontium isotopes as tracers of intensity of fluid flow at seeps

Unlike carbon, which is intrinsically tied to the fate of methane in the seep environment, strontium is essentially a conservative element in seawater. In well-preserved ammonite shells, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio reflects the water in which the shell formed (McArthur et al. 1994; Cochran et al. 2003, 2010). At AMNH loc. 3418, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of shell material with excellent preservation (as well as the authigenic seep carbonates) show values that are significantly elevated relative to the coeval global seawater value (Fig. 8; McArthur et al. 1994). A radiogenic source of Sr is suggested, and the most likely possibility is equilibration of seep fluids with the nascent Black Hills granite at depth (Walker et al. 1986). Incorporation of this Sr into the

Fig. 8 $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios in well-preserved mollusc shells from methane seep at AMNH loc. 3418 (*D. cheyennense* Zone). Values are consistently elevated above the coeval seawater ratio (shown as solid horizontal line; McArthur et al. 1994)



limestone and ammonite shells is evidence of flow of seep fluids enriched in methane and perhaps other hydrocarbons through the surrounding Pierre Shale. The fact that the seep $^{87}\text{Sr}/^{86}\text{Sr}$ signature is recorded not only in the seep carbonates but also in the ammonite shells indicates that the fluids impacted the overlying water column, consistent with the $\delta^{13}\text{C}$ signatures of the seep ammonites from AMNH loc. 3418 (Fig. 5; Table 1). Differences between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seep carbonates and the coeval seawater value also have been observed by Joseph et al. (2012). They reported that the $^{87}\text{Sr}/^{86}\text{Sr}$ of carbonates precipitated at Oligocene seeps off the Cascadia margin (Vancouver Island) were lower than the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ and postulated that the source of the Sr was marine basalts at depth. After water–rock interaction, the fluid transported Sr toward the sediment–water interface.

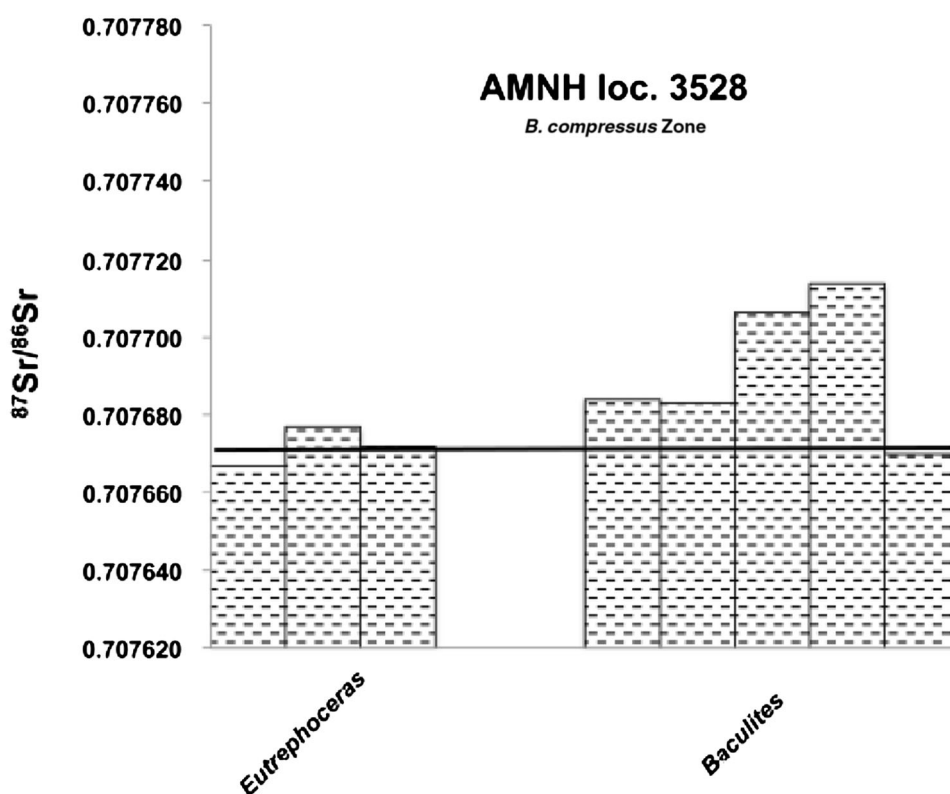
In contrast with AMNH loc. 3418, the seep from the *B. compressus* Zone (AMNH loc. 3528) shows less offset in $^{87}\text{Sr}/^{86}\text{Sr}$ values in a single shell of *B. compressus* and virtually no offset in a shell of *E. dekayi* (Fig. 9). These patterns are mirrored in the $\delta^{13}\text{C}$ values of the baculite, which are not as light as those typically seen in baculites from the seep in the *D. cheyennense* Zone (Fig. 7). This suggests that the flux of methane-rich fluids through the sediments was not as high at this site and had less of an impact on the dissolved Sr and DIC in the overlying water. The later age of the *B. compressus* seep may imply that the

flux of methane was decreasing with time, or the difference in the isotopic signatures may reflect regional variability in methane flux through the sediments. Additional analyses of well-preserved ammonite shells at AMNH loc. 3528 may help refine these possibilities.

Summary and conclusions

Carbon and strontium isotopes in limestone and well-preserved ammonite shells from methane seeps in the US Western Interior Seaway can help characterize the intensity of the methane flux through the sediments and its impact on the water overlying the seep. Samples of well-preserved ammonite shells from a seep in the *D. cheyennense* Zone examined in detail show significant offsets toward lower $\delta^{13}\text{C}$ values relative to those in non-seep environments, suggesting that methane-derived C has been incorporated into the shells. Sclerochronological sampling of a baculite from this seep shows that the ammonite spent extended periods in the vicinity of the seep. Ammonites and the limestone precipitates from this seep also display elevated $^{87}\text{Sr}/^{86}\text{Sr}$ relative to coeval seawater values, suggesting equilibration of seep fluids with a radiogenic Sr source (the nascent Black Hills granite) at depth and passage of the fluids through the muds of Pierre Shale and into the overlying water.

Fig. 9 $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios in well-preserved mollusc shells from methane seep at AMNH loc. 3528 (*B. compressus* Zone). Values are less elevated above the coeval seawater ratio (shown as solid horizontal line; McArthur et al. 1994) than at AMNH loc. 3418 (Fig. 8). Carbon isotope data for the same specimens are shown in Fig. 7 (top panel)



More limited $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ data from a baculite and nautilid from a seep in the *B. compressus* Zone show less difference from expected non-seep values, suggesting that fluid transport was reduced in this seep. We conclude that C and Sr isotopes are sensitive indicators that can help characterize the intensity of methane flux and the impact of seep fluids on the overlying water of methane seeps in the Late Cretaceous WIS. The excellent shell preservation at these WIS seeps also permits application of these isotopic tracers to understand better the relationship of the molluscan fauna, especially the mobile ammonites and nautilids, to the seep environment.

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